



# **Alternative Fuels Research Strategy**

## **Review Draft** (Do Not Cite or Quote)

### **NOTICE**

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Environmental Criteria and Assessment Office  
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Research Triangle Park, NC 27711

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## LIST OF ABBREVIATIONS

|                 |  |
|-----------------|--|
| ACGIH           | American Conference of Governmental Industrial Hygienists                |
| ADH             | alcohol dehydrogenase  |
| AMFA            | Alternative Motor Fuels Act of 1988                                      |
| ARB EMFAC       | (California) Air Resources Board (mobile source) emission factor (model) |
| BOD             | biological oxygen demand   |
| CAAAAs          | Clean Air Act Amendments of 1990   |
| CAFE            | corporate average fuel economy   |
| CARB            | California Air Resources Board   |
| CIIT            | Chemical Industry Institute of Toxicology                                |
| CNG             | compressed natural gas   |
| CO              | carbon monoxide  |
| CO <sub>2</sub> | carbon dioxide   |
| CRC             | Coordinating Research Council  |
| DMS             | dimethyl sulfate   |
| DNA             | deoxyribonucleic acid  |
| DNPH            | dinitrophenylhydrazine   |
| DOE             | Department of Energy   |
| DPX             | DNA-protein cross-links  |
| E85             | 85% ethanol, 15% gasoline  |
| E95             | 95% ethanol, 5% gasoline   |
| E100            | 100% ethanol   |
| EPA             | U.S. Environmental Protection Agency                                     |
| ETBE            | ethyl-tertiary-butyl ether   |
| FFV             | flexible-fuel vehicle  |
| FID             | flame-ionization detection   |
| FTIR            | Fourier transform infrared spectrometry/spectrometer                     |
| FTP             | federal test procedure   |
| g/bhp·hr        | grams per brake horsepower hour  |
| GC              | gas chromatography/chromatograph   |
| GCC             | gasification combined cycle  |
| GI              | gastrointestinal   |

## LIST OF ABBREVIATIONS (cont'd)

|                                |  |
|--------------------------------|--|
| GIS                            | Geographic Information System                |
| g/mi                           | grams per mile                               |
| GVW                            | gross vehicle weight                         |
| HC                             | hydrocarbon                                  |
| HOC                            | hydrophobic organic chemical                 |
| HONO                           | nitrous acid                                 |
| H <sub>2</sub> S               | hydrogen sulfide                             |
| H <sub>2</sub> SO <sub>4</sub> | sulfuric acid                                |
| I&M                            | Inspection and Maintenance                   |
| IARC                           | International Agency for Research on Cancer  |
| IC                             | internal combustion                          |
| IRIS                           | Integrated Risk Information System           |
| ip                             | intraperitoneal                              |
| iv                             | intravenous                                  |
| kg                             | kilogram                                     |
| km/h                           | kilometers per hour                          |
| LC <sub>50</sub>               | lethal concentration for 50% of the subjects |
| LNG                            | liquid natural gas                           |
| LOAEL                          | lowest observed adverse effect level         |
| M85                            | 85% methanol, 15% gasoline                   |
| M100                           | 100% methanol                                |
| μg/m <sup>3</sup>              | micrograms per cubic meter                   |
| mg/L                           | milligrams per liter                         |
| mg/m <sup>3</sup>              | milligrams per cubic meter                   |
| m/h                            | miles per hour                               |
| mL                             | milliliter                                   |
| MMS                            | monomethyl sulfate                           |
| MOBILE 4                       | mobile source emissions factor model         |
| mpg                            | miles per gallon                             |
| mph                            | miles per hour                               |

## LIST OF ABBREVIATIONS (cont'd)

|                  |  |
|------------------|--|
| MS               | mass spectroscopy/spectrometer                               |
| MTBE             | methyl-tertiary-butyl ether                                  |
| NAAQS            | National Ambient Air Quality Standard                        |
| NAPAP            | National Acid Precipitation Assessment Program               |
| NAPL             | nonaqueous-phase liquid                                      |
| NEDO             | New Energy Development Organization                          |
| NEM              | NAAQS (National Ambient Air Quality Standard) Exposure Model |
| NES              | National Energy Strategy                                     |
| NMHC             | nonmethane hydrocarbon                                       |
| NO               | nitric oxide   |
| NO <sub>2</sub>  | nitrogen dioxide   |
| N <sub>2</sub> O | nitrous oxide  |
| NO <sub>x</sub>  | oxides of nitrogen   |
| NOAEL            | no observed adverse effect level                             |
| NPDES            | National Point Discharge Elimination System                  |
| NSPS             | new source performance standard                              |
| O <sub>3</sub>   | ozone  |
| OH               | hydroxyl   |
| OMS              | Office of Mobile Sources                                     |
| ORD              | Office of Research and Development                           |
| PAH              | polycyclic aromatic hydrocarbon                              |
| PAN              | peroxyacetyl nitrate   |
| PBPK             | physiologically based pharmacokinetic                        |
| PM               | particulate matter   |
| PM <sub>10</sub> | particulate matter $\leq 10 \mu\text{m}$                     |
| PMOS             | partially miscible organic solvent                           |
| ppb              | parts per billion  |
| ppm              | parts per million  |
| psi              | pounds per square inch                                       |
| RBC              | red blood cell   |



## LIST OF ABBREVIATIONS (cont'd)

|                  |  |
|------------------|--|
| RD <sub>50</sub> | concentration associated with a 50% decrease in respiratory rate |
| RfC              | reference concentration  |
| RfD              | reference dose   |
| RIHRA            | Research to Improve Health Risk Assessments                      |
| RITG             | radiatively important trace gas                                  |
| RREL             | Risk Reduction Environmental Laboratory                          |
| RVP              | Reid vapor pressure  |
| SARA             | Superfund Amendments and Reauthorization Act                     |
| SMCM             | Spatial Multimedia Compartmental Model                           |
| SMR              | standard mortality ratio   |
| SO <sub>2</sub>  | sulfur dioxide   |
| SO <sub>x</sub>  | oxides of sulfur   |
| T <sub>90</sub>  | temperature at which 90% of fuel is distilled                    |
| THC              | total hydrocarbon  |
| TLV              | threshold limit value  |
| TSS              | total suspended solids   |
| UAREP            | Universities Associated for Research Education in Pathology      |
| UNAMAP           | Users Network for Applied Modeling of Air Pollution              |
| UST              | underground storage tank   |
| UV               | ultraviolet  |
| VMT              | vehicle-miles-traveled   |
| VOC              | volatile organic compound  |
| VOL              | volatile organic liquid  |
| wt               | weight   |

# **ORD ALTERNATIVE FUELS RESEARCH STRATEGY EXECUTIVE SUMMARY**

## **INTRODUCTION**

### **Goal and Purpose**

The primary purpose of this Research Strategy is to lay a foundation for developing the scientific information needed to compare the benefits and risks of alternative motor vehicle fuels to those of conventional gasoline and diesel. Although much information currently exists by which to make rough qualitative judgments about the relative impacts of various fuels, uncertainties in this information limit the ability to estimate benefits and risks in a quantitative manner. Such quantitative assessments are needed by policymakers to perform risk-benefit and cost-benefit analyses to identify optimal fuel and vehicular technology options.

No single organization is likely to have the resources to meet all of the research and assessment needs identified in this Strategy; rather, a complementary, multi-institutional approach will be necessary. This Strategy seeks to provide a risk-based framework for developing coordinated efforts among the various public and private organizations that may wish to conduct scientific research on issues related to the comparative benefits and risks of these fuels.

### **Regulatory Background**

In the United States, interest in the development of alternatives to conventional petroleum-based transportation fuels has grown in recent years because of concerns about declining worldwide petroleum reserves, national security interests, economic considerations, and deteriorating air quality. The latter concern has focused especially on difficulties in achieving air quality goals for reducing ozone and carbon monoxide levels in many U.S. cities and the potential for global climate changes owing to the combustion of fossil fuels and the resultant "greenhouse effect."

1           Tangible evidence of the interest in and movement toward the adoption of alternative  
2 fuels can be found in many places. The Alternative Motor Fuels Act of 1988 includes  
3 incentives to automobile manufacturers to encourage the development and widespread use of  
4 specified alternative fuels. This Act also requires that the U.S. Environmental Protection  
5 Agency (EPA) study the environmental and public health impacts associated with alternative  
6 fuels in comparison to conventional gasoline and diesel fuels and report to Congress every  
7 2 years on these impacts. The National Energy Strategy provides further incentives for  
8 increased use of alternative fuel vehicles. A rulemaking providing emissions certification  
9 procedures for methanol-fueled vehicles was issued by EPA in April 1989 "to remove the  
10 possibility that the absence of emissions standards could hinder development of methanol as a  
11 transportation fuel." The State of California and several other areas across the country  
12 already have taken steps to require or explore greater use of alternative fuels.

13           Major provisions in the 1990 Clean Air Act Amendments are also expected to result in  
14 significant increases in the use of alternative fuels. Key provisions include:

- 15           • more stringent tailpipe standards for nonmethane hydrocarbons and nitrogen oxides,  
16 both of which can form ozone, and carbon monoxide;  
17
- 18           • requirements for certain car and truck fleets to use clean fuels (e.g., within the next  
19 10 years in 22 metropolitan areas);  
20
- 21           • a California clean car pilot program that covers 150,000 cars and light trucks by  
22 1996 and more cars in later years (other states may opt into the program);  
23
- 24           • all gasoline sold in the nine worst ozone cities, beginning in 1995, must be  
25 reformulated gasoline (producing a 15% decrease in mass emissions of VOCs and air  
26 toxics and a 25% decrease by the year 2000);  
27
- 28           • beginning in 1992, during the winter months all gasoline in 41 carbon monoxide  
29 nonattainment areas must be oxygenated (i.e., must contain alcohols or ethers that  
30 increase the oxygen content of the fuel);  
31
- 32           • more stringent diesel particulate emission standards for urban buses;  
33
- 34           • authorization to control emissions from nonroad engines that contribute to urban air  
35 pollution (includes a mandate for a study of such engines);  
36
- 37           • additional requirements for controlling emissions during refueling, especially in  
38 ozone nonattainment areas;

- extension of auto emissions warranties;
- a requirement for a study of air toxics emissions of motor vehicles and fuels that addresses the need for and feasibility of controlling these emissions; and
- a ban on leaded gasoline, as of January 1, 1996.

These Clean Air Act Amendments can only be met with changes in fuels and vehicular technology. Such changes present a multitude of options to improve air quality and reduce the risks of fuel-related emissions to health and ecosystems. Identifying the optimal choice(s) among the various options available will require much investigation. For example, perhaps two fuel formulations would equally meet the required 15% reduction in mass emissions of VOCs and air toxics, but one of these formulations would result in a greater reduction in ozone or in cancer risk than the other due to differences in the chemical composition of the emissions. Further impetus for such scientific study is provided in the Clean Air Act Amendments, which mandate that EPA conduct a broad research program on alternative fuels compared to conventional fuels.

## **Content and Organization of the Strategy**

Several alternatives to conventional fuels exist. This Research Strategy focuses on: (1) methanol (either 100% methanol, M100; or 85% methanol and 15% gasoline, M85); (2) ethanol (either 100% ethanol, E100; or 85% ethanol and 15% gasoline, E85); (3) compressed natural gas (CNG); and (4) reformulated gasolines, the latter generally containing oxygenated organic compounds, such as ethanol or methyl- or ethyl-tertiary-butyl ethers (MTBE and ETBE, respectively), and reduced levels of other components of conventional gasoline formulations (such as aromatics and olefinic fractions). Other alternative vehicle power sources, such as solar, hydrogen, fuel cells, and electricity may be incorporated into the Strategy as their development progresses.

This Strategy is organized into four parts: (1) an introductory chapter that, among other things, identifies general issues common to all of the fuels under consideration; (2) five individual chapters for conventional fuels, methanol, ethanol, CNG, and reformulated

1 gasolines; (3) a chapter on the scientific assessments that will be needed to integrate, assess,  
2 and communicate information as it emerges; and (4) references.

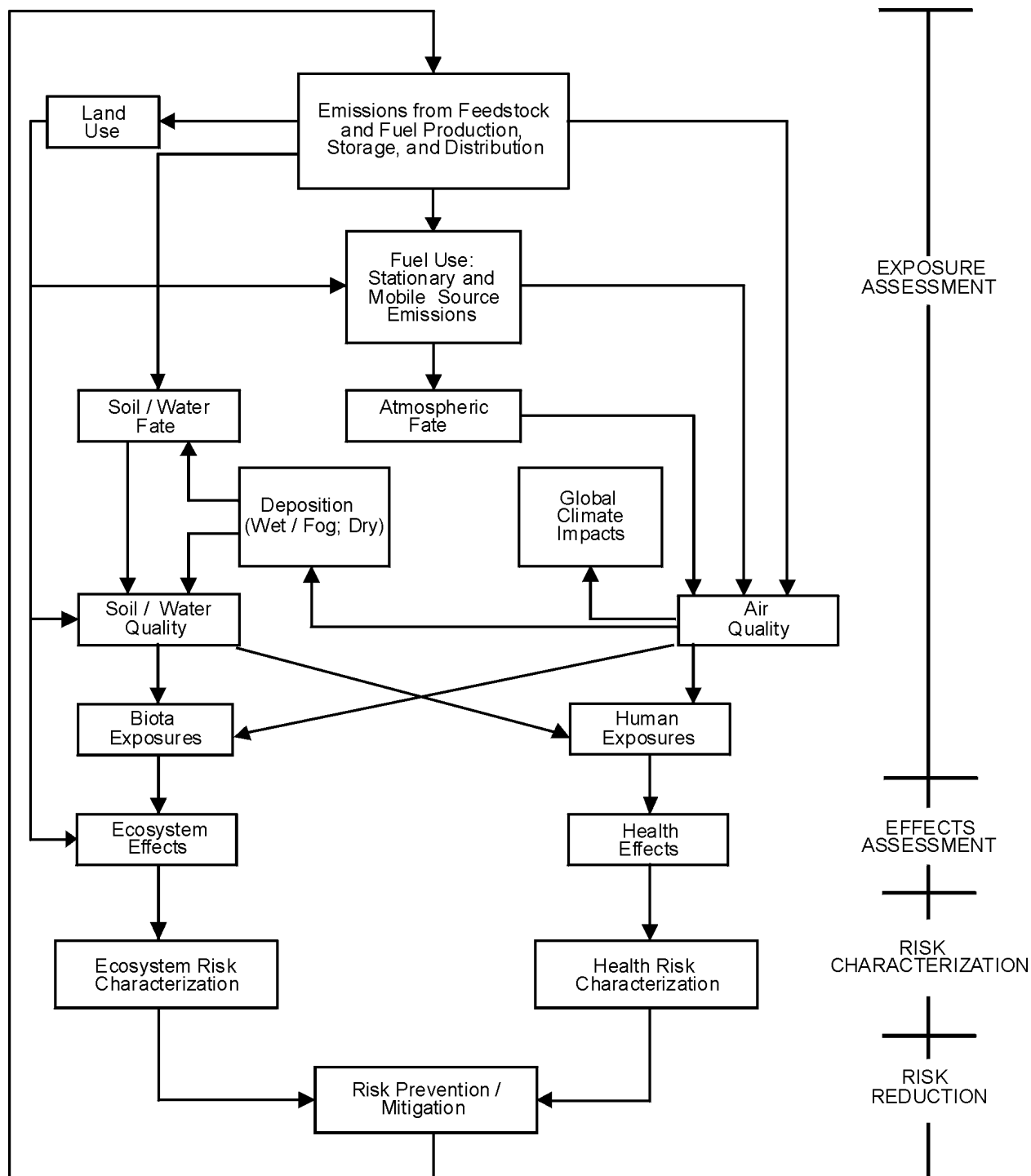
3 This document is not a risk assessment of alternative fuels; rather, it provides a risk  
4 assessment framework for identifying research priorities for achieving a quantitative  
5 assessment of the risks and benefits of specific alternative fuels relative to conventional fuels.  
6 The framework, consistent with that described by the National Academy of Science's  
7 National Research Council (1983), consists of a qualitative hazard identification stage, a  
8 quantitative dose-response assessment, an exposure assessment, and an overall risk  
9 characterization that integrates the first three steps. Technologies for the prevention, control,  
10 detection, and mitigation of environmental releases are also considered here because the  
11 availability and adoption of such technologies could alter the degree of certain risks related to  
12 the production, storage, and use of fuels. Figure E-1 illustrates some of the major  
13 environmental pathways of impacts associated with motor fuels and their relationship to  
14 components of a health and ecosystem risk assessment framework.

15 With this basic framework for risk assessment in mind, several issues common to the  
16 various alternative fuels are discussed below under "General Scientific Issues," which  
17 parallels Chapter 1 of the Strategy. This discussion makes little or no distinction as to the  
18 relative importance of these issues to the individual fuels under consideration because in  
19 many instances too little information exists to draw such distinctions. A subsequent section  
20 of this Executive Summary, "Fuel-Specific Scientific Issues," parallels the respective chapters  
21 on different fuel classes and summarizes the key scientific issues and uncertainties, based on  
22 current knowledge, that are likely to affect research program decisions regarding a given  
23 fuel. Thus, the latter discussion focuses only on those generic issues that are of particular  
24 relevance to a specific fuel. A final "Conclusions" section briefly notes the needs that are  
25 most basic to a comparative risk assessment of alternative and conventional fuels.

## 26 27 **GENERAL SCIENTIFIC ISSUES**

### 28 **Source Characterization**

29 Sources of emissions may be classified as stationary or mobile. Within these basic  
30 classifications, however, a multiplicity of specific sources exists, with a potentially large



**Figure E-1. Major environmental pathways of impacts associated with motor fuel production, distribution, storage, and use, and their relationship to components of a risk assessment framework.**

1 variety of emissions from each source being emitted into air, water, and soil. Facilities for  
2 processing feedstock into fuel generate liquid effluents, gaseous emissions, and solid waste,  
3 the nature and amount of which depend on factors such as the type of feedstock and  
4 production processes used. Petroleum feedstock is likely to produce volatile organic  
5 compounds and methane, which is a greenhouse gas. Biomass production could, depending  
6 on the scenario considered, increase or decrease emissions of carbon dioxide, another  
7 greenhouse gas. Natural gas recovery and production could result not only in increased  
8 methane releases, but in hydrogen sulfide releases as well. The magnitude of these and other  
9 potential impacts from the recovery and production of feedstocks will be primarily a function  
10 of the degree of growth in use of alternative fuels. Such impacts should be assessed based  
11 on available information to determine whether new empirical research is needed.

12       The storage and distribution of fuels and feedstocks also present many opportunities for  
13 acute and chronic emissions. Greatest interest currently centers on chronic emissions from  
14 storage tanks and on accidental spills from supertankers and barges. Recent EPA estimates  
15 indicate that more than 25% of the approximately 2.5 million underground storage tanks and  
16 associated piping in the United States may be leaking or expected to leak within the next 3 to  
17 5 years. Although newer technologies and regulations are intended to reduce the problem of  
18 leaking underground storage tank systems for conventional fuels, the widely different  
19 chemical properties of the various liquid alternative fuels raise questions about the adequacy  
20 of underground storage tank system designs, leak detection methods, and the need for  
21 developing guidance on investigating and cleaning up sites where leaks are suspected or  
22 known to exist. Major accidental releases from stationary sources and various options for  
23 preventing and controlling routine and accidental releases also must be factored into an  
24 evaluation.

25       Characterizing combustion and evaporative emissions from mobile sources is one of the  
26 highest priorities. Although much is already known about the emissions associated with  
27 conventional fuels, relatively little is known about emissions related to alternative fuels,  
28 especially under varied operating conditions. The limited data currently available for mobile  
29 sources have been obtained mostly under standard certification conditions (i.e., at about  
30 70 °F and 20 mph average speed). However, the composition and rates of emissions vary

1 greatly as a function of average vehicle speed and engine load, ambient temperature, age or  
2 degree of deterioration of emission control system, and altitude. It is also important to  
3 evaluate light-duty and heavy-duty vehicles representative of actual in-use fleets using fuels  
4 of varied composition representative of fuels already or projected to be in the marketplace.  
5 In addition, tailpipe emissions as well as evaporative losses while the vehicle is parked,  
6 running, and being refueled should be assessed.

## 8 **Environmental Fate**

9 The fate of emissions after they enter the environment is another key area of needed  
10 research. Transport and transformation processes in air, water, and soil can affect not only  
11 the emissions related to the fuels in question but, secondarily, produce other pollutants.  
12 Because of the number and complexity of these indirect impacts, this Strategy can consider  
13 only a few of the more significant environmental fate issues.

14 Of the four basic environmental media—air, water, soil, and food—air is of greatest  
15 importance to this Strategy. Because atmospheric fate processes are responsible for ozone  
16 formation from mobile source (and other) emissions, and since one of the major objectives of  
17 a shift to alternative fuels is to reduce ozone formation, research in this area needs to focus  
18 especially on the ozone-forming potential of emissions related to alternative fuel use. Such  
19 research needs to examine rural, as well as urban, conditions and second-day, as well as  
20 first-day, transformation products in order to assess quantitatively the potential impacts of  
21 alternative fuels on ozone formation. In addition, research is needed to determine if toxic  
22 compounds are formed in the atmosphere because of alternative fuel use. Among the  
23 transformation compounds already of interest because of their known toxicity are  
24 formaldehyde, acetaldehyde, dimethyl sulfate, and peroxyacetyl nitrate. Because a shift from  
25 conventional gasoline would presumably reduce atmospheric levels of some toxic compounds  
26 such as benzene, toluene, and xylenes, a comparative assessment of the net benefits and risks  
27 will clearly be needed.

28 The greatest concern for surface water contamination stems from accidental releases  
29 during transportation (e.g., from tankers, barges, and pipelines). The transport and fate of  
30 fuels in freshwater systems will need to be studied through modeling of mixing and



1 dispersion processes, which are likely to dominate in the near term, and chemical and  
2 biological processes, which are likely to dominate in the longer term. One of the issues to  
3 be addressed concerns the role of microbial degradation in transforming or reducing fuel  
4 residues. Investigating the differential fate of components of fuel mixtures such as M85 and  
5 reformulated gasolines will also be important. Similar concerns apply to marine systems,  
6 although sources, emissions releases, and transport processes (e.g., tidal and wind  
7 movements) are somewhat different. Soil and ground water are at potential risk from leaking  
8 underground storage tanks and large volume surface spills. The transport and fate of leaking  
9 fuels need to be modeled in order to estimate the possibility and magnitude of changes in  
10 groundwater quality. Contamination of food, either through deposition or uptake in the case  
11 of crops or through accumulation in the case of the food chain, does not appear to be a major  
12 issue at present.

## 14 **Exposure Assessment**

15 Exposure assessment uses source characterization and environmental fate information to  
16 identify exposure pathways of relevance to humans and ecosystems. Depending upon the  
17 findings from these initial steps, the primary fuels and their feedstocks (as well as  
18 combustion and transformation by-products) and complex mixtures of any or all fuel-related  
19 pollutants may need to be assessed. In addition, exposure assessment links information on  
20 pathways and sensitive populations or ecosystems with monitoring and modeling approaches.  
21 Particular attention needs to be given to human exposures in the ambient air and in  
22 microenvironments, such as private garages, public parking garages, vehicles during transit,  
23 and other situations that might afford relatively little dispersion of emissions. Research  
24 efforts should be focused on: developing and validating modeled estimates of maximum or  
25 "worst-case" exposures; obtaining basic data on human activity patterns and other factors  
26 likely to affect exposure; measuring ambient air quality before and after introduction of  
27 alternative fuels, including personal exposure monitoring, if feasible; and, in general,  
28 improving exposure models.

29 The primary focus of this Research Strategy is on exposure via air; however, to  
30 determine what further research may be necessary for other human exposure routes, such as

dermal absorption and accidental swallowing of fuels, existing information should first be evaluated. Because very little information is currently available on the potential for exposure via drinking contaminated ground water, research on this topic should be deferred until appropriate source characterization and fate information is available.

Ecosystem exposure assessment encompasses terrestrial and aquatic systems. Although very little information on such exposures currently exists, for terrestrial ecosystems primary attention clearly needs to be focused on atmospheric exposures, both direct (via ambient air) and indirect (via wet and dry deposition). Also, given the known phytotoxicity of ozone, nitrogen dioxide, and aldehydes, particular attention should be paid to these transformation products. Exposure assessments for aquatic ecosystems, including freshwater, estuarine, and marine, must await the results of source characterization and environmental fate determinations. Furthermore, aquatic populations at risk need to be identified and their microenvironments specified. Modeling efforts should be designed to be compatible with effects research, and vice versa, to facilitate the integration of such information into an overall risk assessment. As various fuels come into wider use, empirical data on environmental exposure levels resulting from chronic and accidental spills should be collected under field conditions.

## **Global Climate Change Impacts**

Several greenhouse gases (including methane, carbon dioxide and monoxide, tropospheric ozone, and nitrogen oxides) could be either increased or decreased as a result of a shift to alternative fuels. The direction of change is dependent on many factors that are not currently fixed, such as type of feedstock, production process, storage, distribution, and use. Although assessments of global climate change are outside the purview of this Research Strategy, data on emissions of greenhouse gases collected from source characterization and atmospheric fate research will be transferred to EPA's Global Climate Research Program.

## **Analytical Methodology**

Accurate and precise analytical methods are needed to characterize emissions from sources using alternative fuels (especially at mandated lower emission levels), to monitor the

1 atmospheric transport and transformation of such emissions, and to monitor human and  
2 ecosystem exposures to these and associated compounds. Although a few methods are  
3 available, others need to be developed; and some existing methods need to be improved to  
4 enable detection at lower emissions standards.

## 6 **Health Effects Assessment**

7 Health effects research covers both hazard identification and dose-response assessment.  
8 Such work should occur interactively with exposure assessment; that is, exposure findings  
9 should help guide effects research and vice versa. Various outcomes could result; for  
10 example, severe effects might appear to be limited to a small population, whereas less severe  
11 effects might apply to a much larger population. Either outcome would likely justify the  
12 need for further investigation and more precise quantification of the risks involved.

13 Table E-1 briefly summarizes the state of knowledge of the types of potential health  
14 effects associated with inhalation of the fuel-related pollutants under consideration here.  
15 Except for criteria pollutants such as ozone, carbon monoxide, and nitrogen dioxide, the  
16 existing health effects databases for combustion and transformation products, as well as the  
17 primary fuels themselves, are generally limited. In some cases, such as methanol and  
18 ethanol, a moderate to considerable body of oral toxicity data exists, but the relevance of this  
19 information to probably fuel-related inhalation exposures is uncertain at present. In other  
20 cases (e.g., ETBE, dimethyl sulfate, and complex mixtures of fuels and/or by-products), the  
21 available toxicity information is extremely limited. One of the highest priorities is to  
22 significantly increase knowledge of the cancer and noncancer health effects of evaporative  
23 and combustion emissions (with and without atmospheric transformation) of conventional  
24 unleaded gasoline. Such information is either sparse or nonexistent and is needed to serve as  
25 a baseline for future comparisons to alternative fuels.

26 Based on current and projected usage, present exposure estimates, and available toxicity  
27 data, methanol and MTBE/ETBE (used in reformulated gasolines) appear to warrant higher  
28 priority for health effects research than other primary fuels such as ethanol and CNG.  
29 Additionally, combustion and transformation products (mixtures and selected individual  
30 chemicals) of methanol and reformulated gasoline are of higher priority than ethanol and

**TABLE E-1. TYPES OF POTENTIAL INHALATION HEALTH EFFECTS  
OF INDIVIDUAL CHEMICALS OR COMPLEX MIXTURES RELATED  
TO CONVENTIONAL AND ALTERNATIVE FUELS USE<sup>a</sup>**

| Compound <sup>b</sup>   | Status of Data Base <sup>c</sup> | Types of Potential Effects <sup>d</sup>  | Susceptible or At-Risk Subpopulations                     |
|---|----------------------------------|--|---|
| <b>I. Alternative Fuels and Extenders</b>                     |                                  |  |   |
| Methanol  | ++                               | Neurobehavioral impairments; reproductive toxicity; developmental toxicity; other systemic effects | Children; folate-deficient people; adult males; fetuses   |
| Ethanol   | +                                | Neurobehavioral impairments; developmental toxicity; reproductive hormone decrements               | Children; adult males; fetuses                            |
| CNG   | +                                | Simple asphyxiant  | Not yet identified  |
| MTBE  | +                                | Neurotoxicity, other systemic effects  | Not yet identified  |
| ETBE  | 0                                |  |   |
| Gasoline-alcohol blends                                       | +                                | Developmental effects plus gasoline effects  | Not yet identified  |
| <b>II. Complex Mixtures of Conventional Fuels</b>             |                                  |  |   |
| Gasoline combustion emissions with or without UV irradiation  | +                                | Respiratory tract effects  | Not yet identified  |
| Gasoline evaporative emissions                                | +                                | Carcinogenic and noncarcinogenic effects   | Not yet identified  |
| Diesel combustion emissions                                   | +++                              | Class B2 carcinogen; respiratory tract effects   | Not yet identified  |
| <b>III. By-Products of Alternative and Conventional Fuels</b> |                                  |  |   |
| Formaldehyde  | ++                               | Class B1 carcinogen; lung irritation and hypersensitivity  | Asthmatics (for lung effects)                             |
| Other aldehydes   | ++                               | Some are carcinogens (e.g., acetaldehyde is B2 carcinogen); lung irritation and hypersensitivity   | Asthmatics (for lung effects)                             |
| NO <sub>x</sub>   | ++++                             | Lung function and structure changes; respiratory infections  | Children; exercising people; asthmatics                   |
| O <sub>3</sub>  | ++++                             | Lung function and structure changes; respiratory infections  | Exercising people; those with preexisting lung disease    |
| CO  | ++++                             | Cardiovascular effects   | People with preexisting heart or obstructive lung disease |
| PAN   | ++                               | Eye irritation; lung function decrements; potential carcinogenic effects                           | Not yet identified  |
| DMS (methanol fuel)   | +                                | Class B2 carcinogen; irritation; systemic toxicity   | Not yet identified  |
| Benzene   | +++                              | Class A carcinogen; hematopoietic changes  | Not yet identified  |
| 1,3-Butadiene   | ++                               | Class B2 carcinogen  | Not yet identified  |

<sup>a</sup> Note that the exposures to some of the compounds will increase, and exposures to others will decrease. See the section on mobile source characterization in fuel-specific chapters for a discussion of possible directional changes.

<sup>b</sup> Abbreviations: CNG = compressed natural gas; MTBE = methyl-tertiary-butyl ether; ETBE = ethyl-tertiary-butyl ether; UV = ultraviolet; NO<sub>x</sub> = nitrogen oxides; O<sub>3</sub> = ozone; CO = carbon monoxide; PAN = peroxyacetyl nitrate; DMS = dimethyl sulfate.

<sup>c</sup> ++++ = extensive information available; + = limited information; 0 = no information.

<sup>d</sup> See health effects discussion in fuel-specific chapters for a more detailed presentation and exposure scenarios that might cause these effects.

1 CNG. Prioritizing such research is problematic due to the number of possible pollutants  
2 (i.e., evaporative emissions, combustion products, and their transformation products),  
3 exposure scenarios (acute, subchronic, and chronic; ambient air and microenvironments),  
4 endpoints of interest, and subjects of concern (general populace and sensitive  
5 subpopulations). The need to understand the impacts of complex mixtures and the dynamics  
6 of fuel compositions further complicates matters.

7       The total matrix of research possibilities is so large that testing it, or even describing it  
8 in full, is infeasible. Instead, a sequential approach, wherein the results from one stage of  
9 research determine the priorities to be addressed in later stages of work, will be necessary.  
10 At present, only general priorities can be described, and these may change as new  
11 information becomes available. Given the current state of knowledge, it is not possible to  
12 make a general statement as to whether research on cancer or noncancer effects warrants a  
13 higher priority; the key issue is to evaluate whether encountered exposures are likely to cause  
14 adverse effects of any type.

15       For ambient air, noncancer impacts due to changes in ozone, carbon monoxide, and  
16 nitrogen dioxide can be assessed using existing health effects data coupled with exposure  
17 assessments developed through alternative fuels research. Potential cancer risks will require  
18 additional health effects research, however, with a focus on complex mixtures of combustion  
19 products, both with and without atmospheric transformation.

20       Compared to ambient air exposures, microenvironmental exposures to neat fuels and  
21 their combustion products are likely to have higher, briefer peaks of exposure, suggesting a  
22 focus of concern on noncancer health effects. Although understanding the effects of complex  
23 mixtures is an important goal, a program addressing these issues is costly and must be guided  
24 by initial work on key components such as methanol and aldehydes. Based on limited  
25 available evidence, developmental, reproductive, and neurotoxic effects should be given the  
26 highest priority with respect to evaporative emissions; these effects, plus pulmonary, hepatic,  
27 and immunologic effects, should be given the highest priority with respect to combustion  
28 products. Work on all of these endpoints requires pharmacokinetics research to provide  
29 essential information on the selection of appropriate animal models and on dosimetric  
30 adjustments in extrapolating animal dose-response data to humans.

## **Ecosystems Effects Assessment**

Ecosystem effects research, like human health effects research, encompasses both hazard identification and dose-response assessment, and should be conducted in an interactive manner with exposure assessment efforts. Terrestrial ecosystems are more likely to be impacted by air quality changes, and possibly by atmospheric deposition, than by accidental spills or leakage. Because plants and soils serve as sinks for pollutant deposition, the effects of fuels and associated combustion and transformation products on vegetation and soil organisms need to be investigated. The potential for bioaccumulation is expected to be minimal for the major neat fuels and their combustion products, but it could vary for each pollutant and should be quantified. A biomonitoring project that involves study of in situ natural terrestrial ecosystems before and after fuel switching would enable direct assessments. Feedstock production is also a concern, as mining, drilling, and agricultural operations will alter terrestrial ecosystems, but this topic may be assessed on the basis of existing information rather than new research.

Aquatic ecosystem effects could arise from releases at several stages of the process from feedstock production to fuel use; however, based on experiences with conventional fuels, spills from fuel storage and transportation systems appear to represent one of the more serious, albeit relatively rare, potential hazards that will require effects research. The greater corrosivity and water-solubility of many alternative fuels magnify this concern. The effects of fuel-related spills can be direct (e.g., acute lethality to organisms) as well as indirect (e.g., toxic effects from metabolic products of biodegradation or oxygen depletion due to biological assimilation).

## **Scientific Assessments**

As new data on exposures and effects are developed through research, they must be integrated into scientific assessments. These assessments will allow an overall evaluation and interpretation of benefits and risks to provide guidance for policy decisions, as well as decisions on future research directions. Such assessments need to be comprehensive, since the comparative benefits and risks to both human health and ecosystems are of interest. Because of the complexity and number of issues to be considered, a quantitative assessment

1 of the risks and benefits of alternative fuels in relation to conventional fuels will be an  
2 iterative process, requiring repeated assessments and reevaluations, and likely consequent  
3 adjustments in research priorities, as new information continues to be amassed. These  
4 ongoing assessments are expected to be of particular importance to EPA program offices as  
5 they fulfill various legislative mandates. For example, information will be needed by the  
6 Office of Mobile Sources (OMS) and the Office of Air Quality Planning and Standards in the  
7 formulation of rules and regulations mandated by the Clean Air Act Amendments, by the  
8 Office of Solid Waste in the development of regulations for underground storage tanks, and  
9 by the Office of Toxic Substances in relation to the requirements of the Toxic Substances  
10 Control Act (TSCA). In addition, ongoing assessments will contribute to the biennial  
11 Reports to Congress required under the Alternative Fuels Act of 1988.

12 Available information is sufficient for performing risk assessments on some issues, such  
13 as the health risks posed by accidental ingestion of fuels. However, assessments of other  
14 potential risks or benefits, as discussed above, are expected to require major research efforts.  
15 In some cases, newly generated information will only need to be integrated with other  
16 existing information (e.g., new data regarding the ozone-forming potential of various fuels  
17 can be related to well-documented evidence on the effects of ozone on humans and  
18 vegetation). In other cases, the results of certain research efforts will be necessary before  
19 other issues can even be adequately defined and framed for investigation.

## 21 **Risk Prevention/Mitigation**

22 As any potential risks to human health, ecosystems, or global climate are identified,  
23 prevention and mitigation strategies may be developed to reduce the risks posed by an  
24 otherwise attractive fuel option. For mobile sources, the development of emissions control  
25 systems with sufficient long-term durability is a high priority. For stationary sources related  
26 to fuel production, the key issues are (1) whether increases in ozone-forming emissions might  
27 offset the potential reductions in ozone-forming emissions from fuel combustion, and  
28 (2) whether net changes in methane and carbon dioxide emissions might exacerbate or  
29 mitigate global climate changes. Stationary source control technologies are important not  
30 only for reducing emissions, but for economic reasons as well. For example, improvements

1 in emissions control systems could determine whether a fuel with potential environmental  
2 benefits is economically viable. Another important area of stationary source risk reduction is  
3 the prevention and handling of leaks in underground fuel storage tanks. Finally, methods  
4 need to be developed or applied for preventing large accidental spills during fuel transport on  
5 surface waters.

## 8 **FUEL-SPECIFIC SCIENTIFIC ISSUES**

9 The following discussion summarizes key scientific issues and broad research priorities  
10 specific to each of the fuel types. Within each class of fuels, exposure and effect issues  
11 related to potential human health risk are presented first, followed by a presentation of key  
12 issues for potential ecosystem risks and, finally, a consideration of greenhouse gas emissions.  
13 Studies of stationary and mobile source emissions, transport, and environmental fate are  
14 essential to support the exposure and effects work highlighted in this section, and to varying  
15 degrees such studies are implicitly or explicitly noted as each fuel class is discussed.

### 17 **Conventional Gasoline and Diesel**

18 **Health Issues:** In 1989, 66.7 million people in the United States lived in areas where  
19 the ozone National Ambient Air Quality Standard (NAAQS) was exceeded, and it is  
20 estimated that mobile sources accounted for between 35 and 50% of the ozone nonattainment  
21 problem in U.S. urban areas. Also, in 1989, 34 million people in the United States lived in  
22 carbon monoxide nonattainment areas, and virtually all of the urban carbon monoxide  
23 NAAQS nonattainment problem is traced to vehicular carbon monoxide.

24 Cancer risks posed by conventional fuels relative to alternative fuels are a major issue.  
25 Diesel exhaust has been classified by EPA's Office of Research and Development (ORD) as  
26 a B2 carcinogen, but in a recent draft update, the classification was changed to a  
27 B1 carcinogen based on newer epidemiological evidence. The OMS estimates that the U.S.  
28 cancer incidence associated with diesel exhaust ranges from 178 to 860 cases/year  
29 nationwide, but this estimate may change following development of an updated unit risk



1 estimate (in progress). Exposure to high levels of diesel exhaust also has the potential for  
2 causing various types of lung disease and neurotoxic effects.

3 The evaporation and combustion of conventional gasoline release various carcinogens,  
4 such as benzene, 1,3-butadiene, formaldehyde, gasoline combustion particles, and gasoline  
5 vapors. The OMS estimates that the U.S. cancer incidence associated with gasoline,  
6 calculated by combining cancer rates for individual gasoline-related compounds, ranges from  
7 approximately 400 to 754 cases/year nationwide. The Office of Air and Radiation estimates  
8 that the cancer incidence from both gasoline and diesel exposures represents approximately  
9 50% of the carcinogenic air toxics problem. Little is known of the cancer implications of the  
10 atmospheric transformation products of motor vehicle emissions. However, atmospheric  
11 transformation can increase the mutagenicity of combustion products.

12 The noncancer health effects associated with the inhalation of gasoline combustion  
13 emissions have not been adequately studied, because most of the research in this area was  
14 conducted prior to the removal of lead. Also, unleaded and leaded gasoline can differ in  
15 composition in other ways (e.g., more aromatics in unleaded gasoline), which may result in  
16 differing health effects. The primary expected outcomes include adverse pulmonary effects,  
17 but effects on other systems also are likely. Adverse effects such as vertigo are associated  
18 with the inhalation of high levels of gasoline vapors, but are of minimal concern. Exposure  
19 and health studies on complex combustion emissions, with and without atmospheric  
20 transformation, are needed to provide data for risk assessments.

21 Highest priority health risk needs for conventional fuels include:

- 22 • preliminary risk characterization of conventional gasoline based on currently  
23 available data to better focus research targets;
- 24
- 25 • quantitative human exposure assessment for unleaded conventional gasoline and  
26 diesel fuel emissions;
- 27
- 28 • dose-response (cancer and noncancer) research on combustion emissions (with and  
29 without atmospheric transformation) of unleaded conventional gasoline; and
- 30
- 31 • reevaluation of the cancer unit risks for diesel emissions (nearing completion),  
32 formaldehyde (nearing completion), benzene, 1,3-butadiene, and gasoline vapors.
- 33
- 34

**Ecosystem Issues:** Spills and leaks of conventional fuels are well-known concerns. Gasoline is only sparingly soluble in water. Much information is available on the transport of gasoline and diesel in soils, surface/groundwater threats to drinking water, and the adverse effects of conventional fuel spills on aquatic ecosystems. Historically, spills of gasoline and diesel fuels from storage facilities and surface water transport activities have resulted in acute toxicity to aquatic life in the immediate spill area. Few laboratory toxicity studies have been conducted with whole fuels; test results have varied with the method of preparing a water-soluble fraction intended to simulate aquatic exposure. Although spills and leaks have been known to cause fish and wildlife kills, there are few data from controlled laboratory exposures measuring whole ecosystem responses or from contaminated sediment exposures. The lack of these studies makes it difficult to estimate overall ecological impacts.

Ecological perturbations caused by conventional-fuel pollutant deposition (fuel plus combustion and transformation products) on terrestrial ecosystems may have ramifications through all levels of biological organization, depending on the duration and severity of pollutant exposure and organism sensitivity. Effects may range from disruption of biochemical or physiological processes and reduction in growth, reproduction and abundance of sensitive individuals or populations, to changes in the composition, structure, and function of communities and ecosystems. Research has shown that the criteria air pollutants (e.g., O<sub>3</sub>, NO<sub>2</sub>) associated with conventional fuels (as well as other sources) can impact crop yields, causing an estimated economic loss between 2 and 4 billion dollars annually within the United States.

Highest priority ecosystem studies for conventional fuels include:

- terrestrial exposure assessment for ozone, peroxide, and formaldehyde; and
- targeted research on exposure to and effects of large spills of conventional gasoline and diesel fuels into surface waters (fresh and marine waters plus their sediments).

**Greenhouse Gas Issues:** The production and combustion of conventional fuels release significant amounts of carbon dioxide (about 3% of world emissions) as well as methane, nitrous oxide, and other gases having potential for contributing to global warming. Although vehicular carbon dioxide and methane emissions have been well characterized, nitrous oxide

emissions have been less studied. Further research efforts on greenhouse gas emissions associated with fuel production and distribution are also indicated.

## **Methanol**

**Health Issues:** The combustion of methanol can result in fewer and slower reacting organic emissions than does conventional gasoline, thus providing the potential for reducing overall tropospheric ozone levels. For example, OMS reports that M100-fueled and M85-fueled vehicles will reduce gasoline-equivalent (reactivity adjusted) volatile organic compounds reactive in ozone formation by 80 and 44%, respectively. The State of California has recently estimated the relative ozone potential of M85-fueled vehicle emissions (not adjusted for oxygen mass) at 36% of that of conventional unleaded gasoline-fueled vehicles. This estimate was based on comparison of the ozone formation potential of emissions with gasoline and M85 using procedures developed by Carter and colleagues at the University of California (maximum incremental reactivities). The amount of actual ozone reduction that methanol fuels will provide depends on a number of site-specific variables, including the local nonmethane hydrocarbon/nitrogen oxides ratio, the emission contribution of stationary sources, and local atmospheric chemistry and meteorology. For example, in some cities the use of M100 may have a negligible effect on ozone. Although additional research is needed to determine the ozone reduction benefits with greater certainty, some recent scientific literature indicates that M100 may provide less than a 10% reduction of ozone for a number of reasonable scenarios in actual nonattainment cities, depending on assumed formaldehyde emissions. Also, flexible-fuel vehicles (i.e., vehicles capable of using mixtures of gasoline and methanol ranging from 100% gasoline to M85) will have elevated evaporative emissions (relative to conventional gasoline) with fuel blends between approximately 0 and 70% methanol and will have a negligible effect on ozone reduction.

The release of methanol in the atmosphere can potentially result in the increased formation of dimethyl sulfate under certain atmospheric conditions. Dimethyl sulfate is a carcinogen, is acutely toxic to the nervous system, and is highly irritating to the eyes, respiratory system, and skin. The compound has been observed in ambient air downwind of power plants, presumably as a product of the reaction of hydrocarbons with sulfur dioxide on

1 particles. Research is needed to determine whether dimethyl sulfate is also formed to any  
2 significant degree with methanol as the hydrocarbon and, if so, to assess its potential for  
3 increasing human cancer incidence in areas using methanol fuels.

4 The combustion of methanol, as does the combustion of conventional gasoline, results  
5 in the formation of formaldehyde directly, as well as indirectly in the atmosphere through  
6 atmospheric transformation of hydrocarbons. Formaldehyde is a carcinogen and can cause  
7 various acute and chronic noncancer effects. Available data suggest that combusting  
8 methanol results in increased "direct" formaldehyde levels relative to those of gasoline, and  
9 in decreased "secondarily-formed" formaldehyde levels. An analysis of the overall trade-offs  
10 needs to be undertaken to determine what a switch to methanol would mean for total human  
11 exposure to formaldehyde in terms of carcinogenic risk. For noncancer risks, a primary  
12 issue is microenvironmental exposures, which would increase, making acute effects on  
13 pulmonary function a concern. The Office of Toxic Substances is revising the formaldehyde  
14 cancer risk assessment, which will assist in estimating impacts of ambient lifetime exposures.

15 Another key issue is the potential for health effects to be induced by direct exposure to  
16 methanol resulting from the evaporation or combustion of M100 and M85. The OMS has  
17 estimated levels of potential human exposure to methanol in various microenvironments  
18 (e.g., personal garages, public parking garages, tunnels, street canyons). However, more  
19 research is needed to address the many uncertainties in these exposure estimates, including  
20 (1) limited emissions data, (2) uncertainty as to the representativeness of the assumed vehicle  
21 driving conditions, and (3) dispersion modeling uncertainties. Independent laboratory studies  
22 using two species of rodents have indicated that inhalation of high concentrations of methanol  
23 vapors (relative to estimated microenvironmental levels) can cause birth defects in rodents.  
24 Thus, qualitatively, methanol could be called a developmental toxicant. The implications of  
25 these findings for humans, however, must await the results of further pharmacokinetics and  
26 health effects research. Pregnant women are of special concern because many have folate  
27 deficiency, which can increase susceptibility to methanol. Preliminary research suggests that  
28 inhalation of methanol vapor also may result in adverse reproductive, neurotoxic,  
29 immunotoxic, and hepatotoxic effects. Additional health research is needed to confirm these  
30 preliminary results and to further characterize exposure-response relationships.

1       Ingestion of methanol fuel in small amounts (as little as two teaspoons for children) can  
2 result in blindness and death; M85 can also be quite toxic and introduces a potential problem  
3 of diagnosis for appropriate treatment (the likely odor of gasoline on the breath after  
4 ingesting M85 may lead to treatment for gasoline rather than methanol exposure). There are  
5 an estimated 35,000 accidental gasoline ingestions each year in the U.S., a third of which are  
6 children under 6 years old. Although the potential risk could be reduced through the  
7 addition of a nontoxic denaturant, unsophisticated users may try to neutralize the denaturant;  
8 and, therefore, some baseline level of accidents is likely inevitable. However, because  
9 methanol fuels are not good solvents for grease and likely will be unusable with lawn  
10 mowers, these fuels are not expected to be stored around the home as in the case of gasoline.  
11 Also, because auto storage tanks will be equipped with spark/flame arresters, siphoning from  
12 cars would be impossible. Therefore, while the incidence of ingestion, especially by young  
13 children, likely would be reduced relative to that suggested by gasoline history, a quantitative  
14 assessment based on existing data is needed.

15       The combustion of methanol will result in a complex mixture of pollutants. While  
16 there is limited understanding of the health effects associated with exposures to several of the  
17 individual chemicals, the effects resulting from exposures to the combinations of these  
18 pollutants are unknown. The individual effects of exposures to methanol and formaldehyde  
19 are discussed elsewhere in this section. The mixture is of concern because, for example,  
20 exposures to CO alone, like methanol, can cause fetal effects, as well as adversely affect the  
21 cardiovascular system. Also, exposures to nitrogen dioxide, like formaldehyde, can cause  
22 pulmonary effects. Synergistic and/or additive effects of the mixtures are, therefore, possible  
23 and require research if they are to be understood and quantified.

24       The health effects of M85 evaporative and combustion emissions will be some  
25 combination of those associated with both methanol and gasoline. Because the noncancer  
26 health effects of neither unleaded gasoline nor methanol are adequately understood for  
27 advanced risk assessments, more information on M85 must await further research.

28       The impact of methanol on underground storage tank leaks is uncertain. The  
29 probability of leakage with methanol may be higher than with gasoline and diesel fuel due to  
30

methanol's higher corrosivity. Shallow urban aquifers and certain underground structures may therefore be at increased risk.

Highest priority health risk studies for methanol fuels include:

- quantitative human exposure assessment for emissions with M85 fuel (focus on ozone and air toxics);
- dose-response relationships for effects of evaporative emissions of M100 and M85, especially effects on development, reproduction, and the nervous system;
- dose-response relationships for effects of acute exposure to formaldehyde, especially for respiratory tract effects;
- characterization of sensitive subpopulations;
- hazard identification (cancer and noncancer) for combustion emissions of M85, with and without atmospheric transformation;
- risk characterization of accidental oral exposure to M85; and
- determination of potential for leaks from underground storage tanks for methanol and of consequent potential for urban aquifer contamination.

**Ecosystem Issues:** It is uncertain whether the effects from M100 and M85 fuel spills on freshwater and marine systems would be greater or less compared to those for gasoline. Although the effects are uncertain, M85 is likely to exhibit the environmental problems associated with both gasoline and methanol. Because methanol is more water soluble than gasoline, spills of methanol in open turbulent water might decrease the potential hazard, because rapid dilution would occur. By contrast, methanol spills in restrictive waterways, such as rivers and lakes, could result in potentially significant impacts caused by acute methanol toxicity followed by rapid depletion of oxygen in the water. Methanol releases to restricted waters could also influence the bioavailability of sediment-bound contaminants, such as polynuclear aromatic hydrocarbons, thereby indirectly affecting aquatic systems.

Methanol combustion products (formaldehyde and formic acid) have been shown to affect plant growth and development in controlled greenhouse and field experiments. However, because ambient air concentrations of formaldehyde are predicted to decrease with

the use of methanol fuel, a benefit may result, which needs to be quantified through research.

Highest priority ecosystem studies for methanol fuels include:

- quantitative terrestrial exposure assessment for ozone, peroxide, formaldehyde, and formic acid;
- freshwater and marine exposure estimates for major spills;
- hazard identification for M100 and M85 spills into freshwater and marine ecosystems; and
- hazard identification for formaldehyde, alone and in combination with ozone (and peroxide and formic acid), to vegetation.

**Greenhouse Gas Issues:** The net effect on greenhouse gas releases relative to conventional fuels will depend primarily on the feedstock chosen for producing methanol. (The vehicular emissions of carbon dioxide from methanol-fueled vehicles are estimated to be similar to those from gasoline-fueled vehicles.) However, methanol derived from coal could significantly increase both carbon dioxide and methane releases and, thereby, double the motor vehicle contribution to greenhouse gas emissions. Alternatively, methanol derived from natural gas could have a negligible effect on net releases, whereas methanol derived from cellulosic biomass might have a beneficial effect due to the recycling of combustion carbon dioxide through the biomass growth process.

## Ethanol

**Health Issues:** As with methanol, the combustion of ethanol can result in fewer and slower reacting organic emissions than does conventional gasoline, thus providing the potential for reducing ambient ozone levels. Limited evidence shows that ethanol's potential for ozone reduction, although dependent on the same site-specific factors as methanol, may be equal to or exceed that of methanol's if significant levels of formaldehyde are emitted by methanol-powered vehicles. The reason for this is that formaldehyde is more reactive photochemically than acetaldehyde. Emissions data, however, are sparse, and no quantitative modeling studies of potential ozone reductions from E100-fueled or E85-fueled vehicles in

1 any U.S. cities have been undertaken. The Office of Technology Assessment has concluded  
2 that E85 is believed to have negligible impacts on urban ozone levels and that although total  
3 hydrocarbons would be reduced, increases in certain reactive compounds such as  
4 peroxyacetyl nitrate (PAN) and acetaldehyde would offset some of the benefit. Air quality  
5 research is needed to evaluate ozone impacts quantitatively.

6       Evaporation and combustion of ethanol fuel also generates ethanol vapor. Although it  
7 is unknown whether inhalation of ethanol vapors can result in a toxic dose to the fetus,  
8 extensive evidence links ingestion of ethanol to the serious, permanent effect known as Fetal  
9 Alcohol Syndrome in the offspring of mothers who ingest above-average amounts of ethanol  
10 during pregnancy. This suggests the need for pharmacokinetics and health effects research to  
11 determine to what extent inhalation of ethanol vapors can affect the fetus and, if so, at what  
12 levels of exposure. If adverse health effects are suggested, human exposure assessment  
13 research (especially in microenvironments) will be crucial for evaluating potential health  
14 risks.

15       The combustion of ethanol results in the formation of acetaldehyde (and acetic acid).  
16 Acetaldehyde is a carcinogen (although weaker than formaldehyde). Also, it has acute  
17 effects, such as respiratory irritation (for which limited data exist), and chronic noncancer  
18 effects that include growth retardation, decreased body weight, anemia, and increased blood  
19 pressure. The EPA has verified an Inhalation Reference Concentration (RfC) for this  
20 chemical, but acute risk has not been assessed, and exposure studies in the United States  
21 have not been undertaken. Acetaldehyde can also serve as a precursor to PAN in the  
22 presence of nitrogen oxides and sunlight. Exposure to low levels of PAN can cause eye  
23 irritation, and higher levels can affect lung function in adults. Peroxacetyl nitrate is also  
24 mutagenic in several test systems and is considered a potential carcinogen.

25       Although health effects associated with complex mixtures of pollutants resulting from  
26 the evaporation and combustion of E100 and E85 are of concern, virtually no information  
27 exists in this area, making such research important.

28       The corrosive effect of ethanol fuels on underground storage tanks has not been  
29 investigated, preventing quantitative estimates of risks to urban aquifers serving as drinking  
30 water supplies or to subsurface structures (e.g., utility lines, steel supports).



Highest priority health risk studies for ethanol fuels include:

- quantitative human exposure assessment for emissions with E85 fuel (focus on ozone, PAN, and acetaldehyde);
- pharmacokinetics of inhaled ethanol, compared to oral exposure; and
- hazard identification (cancer and noncancer) for combustion emissions of E85, with and without atmospheric transformation.

**Ecosystem Issues:** The ecological effects of accidental spills and storage tank leaks of ethanol fuels on fresh water, soil, groundwater, and marine systems are uncertain in comparison to gasoline and require investigation. Like methanol, ethanol is more water soluble than gasoline. This property in some instances, such as spills in restrictive waterways, could increase the potential hazard for aquatic biota (e.g., by rapidly depleting dissolved oxygen), whereas in other cases, such as spills in open waters, it could decrease the potential hazard (e.g., through rapid dilution resulting in short, relatively mild exposures).

Ethanol's combustion products (acetaldehyde and acetic acid) and their atmospheric transformation products (ozone and PAN) can injure or destroy various types of plants and, therefore, adversely affect crop yields and forest-tree production. Although ethanol may cause less ozone to be formed than gasoline, more PAN and acetic acid may be formed, so that the net effect relative to conventional fuels is uncertain. Peroxyacetyl nitrate is more phytotoxic than ozone.

Ethanol from biomass could lead to a more intensive use (on existing and new acreage) of pesticides and fertilizers, because these crops are destined for nonfood uses and are likely to be grown on marginal land. Pesticides applied to corn or other biomass crops have potentially acute and chronic adverse affects on both aquatic and terrestrial ecosystems. Fertilizers can contaminate groundwater, base-flow surface waters, reservoirs, and estuaries, resulting in toxicity and accelerated eutrophication. This Strategy proposes assessments of these issues based on available information and predicted increases in relevant activities before undertaking new empirical research.

Highest priority ecosystem studies for ethanol fuels include:

- quantitative terrestrial exposure assessments for ozone and peroxyacetyl nitrate;
- freshwater and marine exposure estimates for major spills;
- hazard identification for E100 and E85 spills into freshwater and marine ecosystems; and
- hazard identification for effects of acetaldehyde (alone and in combination with acetic acid and ozone) on vegetation.

**Greenhouse Gas Issues:** As with methanol, the choice of production feedstock will influence the type and amounts of net greenhouse gas emissions. An ethanol-fueled system derived from coal could double the motor vehicle contribution to the greenhouse gas inventory (by increasing methane and doubling carbon dioxide emissions). An ethanol-fueled system derived from biomass (e.g., corn) could have greatly different effects depending on the land-use substitution. In the absence of sensitive substituted land uses, such as rain forests, it can be expected that such a system will have a negligible effect on, or even decrease, net greenhouse gas emissions (due to off-setting removal of carbon dioxide by the biomass growth.)

## **Compressed Natural Gas**

**Health Issues:** The combustion of CNG will result in fewer and slower-reacting organic emissions than combustion of conventional gasoline, thus providing the potential for reducing ambient ozone levels. Hydrocarbon emissions are typically 90 to 95% methane, which reacts too slowly to contribute significantly to ozone. Thus, only 5 to 10% of the hydrocarbon emissions are composed of ozone-forming compounds (compared to 65 to 95% in conventional gasoline-fueled vehicles.) Most of the existing emissions data, however, for CNG vehicles are for older technology dual-fuel designs. New designs for dedicated CNG-fueled vehicles may have substantially different emissions. No site-specific modeling studies (e.g., for nonattainment cities) of the impacts of CNG use on ozone levels have been conducted. Therefore, the amount of ozone reduction potentially possible with the use of CNG is unknown and investigation is needed.

1       Also, the use of CNG is expected to reduce the likelihood of carbon monoxide health  
2 effects from exposures to fuels. The limited available data indicate that its use results in  
3 approximately half the tailpipe carbon monoxide emissions of a gasoline-fueled vehicle (cold  
4 start carbon monoxide emissions are minimal). Even though the possibility of increases in  
5 nitrogen oxide emissions associated with CNG use may necessitate adjustments that could  
6 cause some additional carbon monoxide, the overall reductions are expected to be significant.

7       The combustion of CNG results in the formation of formaldehyde, at approximately the  
8 same levels as gasoline-fueled vehicles. As discussed in other sections, the inhalation of  
9 formaldehyde can cause cancer, as well as result in acute and chronic noncancer effects. The  
10 combustion of CNG can also result in the formation of benzene and 1,3-butadiene in amounts  
11 that, although significantly lower than those associated with conventional gasoline, could  
12 pose concerns. More knowledge of CNG emissions is needed for exposure assessment.

13       The effects of inhaling CNG in its combustion phase are unknown. Potential exposures  
14 have also not been adequately characterized. Inhalation of very high levels of methane, an  
15 odorless and tasteless gas comprising 85 to 90% of CNG, can cause asphyxiation, a potential  
16 problem in catastrophic accidents but not in normal fuel-use conditions. Inhaling methane is  
17 not likely to produce general systemic effects and, therefore, poses a lower potential for  
18 health effects than do conventional fuels.

19       Highest priority health risk study for CNG is:

- 20       • quantitative human exposure assessment for emissions with CNG fuel (focus on  
21       ozone and air toxics).

22  
23  
24       **Ecosystem Issues:** Because CNG disperses very rapidly after accidental or fugitive  
25 releases, it should not pose a significant threat to soil, water pathways, or vegetation. Also,  
26 because CNG use should reduce ozone levels, it would have less severe effects than gasoline  
27 on terrestrial ecosystems, and its effects should be adequately covered by terrestrial studies  
28 conducted for gasoline and other fuels.

Highest priority ecosystem study for CNG is:

- quantitative terrestrial exposure assessment (focus on ozone and air toxics).

**Greenhouse Gas Issues:** The production and accidental release of CNG may increase the atmospheric load of methane. Methane is a greenhouse gas, the heat retention potency of which is 20 to 30 times greater than that of carbon dioxide. However, the use of methane that is at present simply released or flared (such as that emitted from landfills, coal mines and oil fields) could reduce the greenhouse gas inventory. Overall, vehicle-related greenhouse gas emissions from CNG vehicles will probably be reduced. That is, although they are likely to release more methane than conventionally fueled vehicles, they will emit significantly less carbon dioxide.

## **Reformulated Gasolines**

**Health Issues:** A proposed EPA rulemaking requires that reformulated gasoline emit 15% less ozone-forming VOCs by 1995. This requirement is expected to reduce VOC emissions. Depending on the relative reactivity of the emissions from conventional and reformulated gasolines, the reduced VOC emissions could result in an associated reduction in ozone levels. Carbon monoxide emissions are also expected to decrease. The actual extent of such reductions is unknown currently, but studies of reformulated gasolines through the ongoing Auto/Oil Air Quality Improvement Research Program will significantly elucidate these issues. The preliminary results from this effort suggest that for the reformulated gasolines studied, the contribution of light-duty vehicles to peak ozone levels can be reduced by as much as 26%, primarily as the result of reducing fuel olefin content.

Reducing the aromatic content of gasoline will likely reduce the cancer incidence associated with inhalation exposure to gasoline vapor and combustion emissions. For example, reformulated gasolines will have significantly less benzene. However, the net potential cancer risk is the result of the entire complex mixture, rather than only benzene and a few selected individual substances. To determine whether reformulated gasolines reduce overall cancer risk will require research on the complex mixtures of both combustion emissions and atmospheric transformation products. Inhalation of the evaporative and

1 combustion emissions of reformulated gasolines is likely to result in some noncancer effects  
2 that are different from those associated with conventional gasoline. No complex mixture  
3 studies have been reported and, thus, the nature of these comparative effects cannot be  
4 determined without exposure and health research.

5 Sparse health effects information exists for MTBE, and none exists for ETBE.  
6 A chronic inhalation study underway pursuant to TSCA Section 4 is investigating possible  
7 effects on different target organs, including the nervous system, liver, kidney, immune  
8 system, and hematopoietic system. The ORD currently is developing an RfC for MTBE.  
9 However, exposure levels to MTBE or ETBE have not been characterized. Additional  
10 oxygenates, most with sparse or no information on health risk potential, are under  
11 consideration for use in reformulated gasoline.

12 Highest priority health risk studies for reformulated gasolines include:

- 13 • quantitative human exposure assessment for emissions with reformulated gasoline  
14 fuels (focus on ozone, carbon monoxide, and air toxics);
- 15
- 16 • hazard identification (cancer and noncancer) of high-use oxygenates; and
- 17
- 18 • hazard identification (cancer and noncancer) for evaporative and combustion  
19 emissions, with and without atmospheric transformation.
- 20
- 21

22 **Ecosystem Issues:** The effects of MTBE, ETBE, and reformulated gasolines on  
23 terrestrial and aquatic ecosystems are unknown. It is unknown whether the ecological effects  
24 resulting from either the spills of reformulated gasoline or leaks from storage tanks will be  
25 greater or less than for conventional gasoline. There is little information on the aquatic fate  
26 and effects of oxygenates in reformulated gasoline. The problem is additionally complex  
27 because of the many formulations under consideration. The available aquatic toxicity data  
28 for MTBE indicates that it is the same order of magnitude as that of the alcohols. However,  
29 the lack of fate and response data do not allow comparative evaluation. Although MTBE and  
30 ETBE are more soluble in water than gasoline and, thus, would likely leach more rapidly  
31 through soil and groundwater, this same property could result in diluted concentrations and  
32 milder exposures for some spill or leak scenarios. The atmospheric fate properties of  
33 MTBE, ETBE, and their combustion products are not well characterized, and their effects on

crop yields and forest-tree production are not known. However, expected ozone reductions would have a benefit.

Highest priority ecosystem studies for reformulated gasolines include:

- quantitative terrestrial exposure assessment (focus on ozone and oxygenate combustion and transformation products);
- freshwater and marine exposure estimates for major spills; and
- hazard identification for freshwater and marine biota.

**Greenhouse Gas Issues:** Reformulated gasolines are not expected to differ greatly from conventional gasolines in their impact on greenhouse gases.

## CONCLUSIONS

In spite of major uncertainties regarding the potential risks and benefits of alternative fuels and their comparisons to those of conventional fuels, several prominent issues have been highlighted. Because of these uncertainties, however, it can be expected that future knowledge will challenge certain assumptions and support others underlying the issues discussed above. It must be emphasized that until research on both alternative and conventional fuels significantly expands, most key issues and conclusions will rely heavily on hypotheses and assumptions, rather than on quantitative risk assessments.

Although generic and fuel-specific research priorities have been identified here, priorities between fuels are more difficult to state because they are dependent on EPA's regulatory information needs as well as the missions of various research funding organizations. Nevertheless, one fundamental priority is clear. It is essential to obtain information for the quantitative health and ecosystem risk assessment of conventional fuels so that this can serve as a baseline against which to measure the changes in benefits and risks of alternative fuels. For example, currently available information does not permit quantitative assessment of the cancer and noncancer risks of conventional gasoline combustion emissions, with and without atmospheric transformation.

1       Two other basic priorities exist. One is to improve the hazard identification data base  
2       for all the alternative fuels to help direct future research. This priority includes elements of  
3       both exposure and effects (health as well as ecosystems). Although some possible hazards  
4       have been identified and are current research targets, others that may cause greater risks may  
5       be currently unrecognized. The same is true of benefits. Another basic priority of equal  
6       importance is to determine the impact of some key provisions of the Clean Air Act  
7       Amendments on the goal of this law. For example, we need to know to what degree a fixed  
8       percentage reduction in mass emissions of VOCs and air toxics will reduce the health and  
9       ecosystem risks of ozone and air toxics. Although a reduction in mass of complex mixtures  
10      of emissions is certainly a positive direction, a unit of mass reduction is not necessarily  
11      equivalent to a unit of risk reduction. In general, more precise quantitative data are needed  
12      if the net impacts of efforts to improve air quality are to be adequately evaluated.

## 1.0 INTRODUCTION

### 1.1 PURPOSE OF THE RESEARCH STRATEGY

Many scientific questions must be answered through research to provide a basis for quantitative assessments of the health and ecosystem risks or benefits of alternative motor fuels compared to conventional fuels. The purpose of this Strategy is to define these research goals and their interdependencies. Alternative fuels discussed in this strategy include methanol (M100, 100% methanol; M85, 85% methanol and 15% gasoline), ethanol (E100, E85), compressed natural gas (CNG), and reformulated gasolines (with oxygenates and altered organic composition). Electric vehicles and more advanced technologies also come under the heading of alternative fuels, but are not discussed here. It should be noted that other definitions of alternative fuels exist, but for simplicity here, vehicular energy sources other than conventional gasoline and diesel fuel are termed alternative fuels.

Although various estimates exist, approximately 50% of air pollution problems are thought to be directly or indirectly related to conventional vehicular fuels. Additionally, some drinking water and surface water contamination can be traced to conventional fuel sources. Congress has enacted legislation and EPA and States have taken actions to reduce these problems by encouraging the use of alternative fuels. Thus, the United States and some other countries are embarking on changes that are expected to have major air quality impacts as well as water quality impacts. It is therefore prudent to understand both the risks and benefits of such changes before they are fully implemented and to allow scientific knowledge to guide the selection of options that will be most beneficial. The only way to achieve such understanding is through research directed at developing risk assessments that compare alternative to conventional fuels.

As will be discussed in Section 1.4, research needs to assess motor fuels are broad in scope and complexity (i.e., multidisciplinary and multimedia) and extensive in depth. A complete listing of all conceivable research needs would be massive; performing all of this research would be virtually impossible, even with full public and private support. Thus, to



1 develop an achievable and useful research program, it is essential to narrow a listing of  
2 research needs to high priorities based on defined risk assessment and risk reduction goals.  
3 This Strategy is intended to serve as a basis for communicating these priorities to interested  
4 parties.

5 Many of the research goals identified here are relevant to the missions of numerous  
6 organizations. Indeed, much of the discussion is derived from work already performed by  
7 several institutions, including not only EPA but also the oil, vehicle, fuel, and chemical  
8 industries, other Federal agencies, and various public and private institutions. The intent of  
9 this Research Strategy is to be broadly inclusive, describing needs that as a whole can be  
10 fully addressed only through the collective efforts of EPA and other interested institutions.  
11 Thus, the risk assessment and risk reduction/control technology goals described here can be  
12 achieved only with appropriate levels of communication and coordination among these  
13 institutions. The EPA's Office of Research and Development (ORD) own research program  
14 on conventional and alternative fuels is described separately, as part of ORD's research  
15 program planning activities.

## 16 17 18 **1.2 ORGANIZATION OF THE RESEARCH STRATEGY**

19 This Research Strategy is organized into four parts: (1) this Introduction; (2) five fuel-  
20 specific chapters (comprising conventional fuels, to serve as the basis for comparisons, and  
21 the fuel types being recommended for near-term examination: methanol, ethanol, CNG, and  
22 reformulated gasolines), which summarize currently available information and identify  
23 specific research needs; (3) a scientific assessment chapter describing programs necessary to  
24 assess and communicate the dynamic state of knowledge related to alternative fuels to assist  
25 policy makers and to better guide future research; and (4) references. In addition, an  
26 Executive Summary provides an overview of the Research Strategy.

27 This Introduction explains the goals and purposes of the Strategy (Section 1.1) and the  
28 regulatory background that drives the research (Section 1.3). Section 1.4 describes the  
29 general issues common to all alternative fuels in a risk assessment framework. It also  
30 portrays the interdependencies between fuels and the linkages of the various scientific

1 disciplines involved, and provides a template for the specific fuel chapters to follow. Due to  
2 the multiplicity and complexity of the issues, an approach to prioritization is needed and is  
3 discussed in Section 1.5. Accomplishing such a program requires a significant planning  
4 effort, which is described broadly in Section 1.6.

5 Each fuel-specific chapter is divided into three sections, beginning with an overview of  
6 the key research issues presented in a risk assessment format, using the risk framework of  
7 the Introduction (Section 1.4) as a point of departure. Essentially, the frameworks  
8 summarize the issues and research needs. The second major section of each chapter provides  
9 a background and rationale for the research needs. It is not a comprehensive review of the  
10 literature; rather, it highlights findings and areas of uncertainty that guide the research  
11 program. It is important to note that, although a risk assessment format is used, neither the  
12 framework nor the background and rationale section constitutes a scientific assessment. The  
13 final section in each chapter describes the research needs for each fuel in terms sufficiently  
14 broad to allow for flexibility in planning and merging with the different missions of the wide  
15 range of institutions that are likely to be interested in alternative fuels issues. Research  
16 objectives are also described and prioritized.

17 Those readers interested in a general overview should focus their attention on the  
18 Introduction (Chapter 1). For readers desiring an overview of issues specific to each fuel of  
19 interest, the first section of each fuel-specific chapter (Sections 2.1, 3.1, etc.) should be  
20 consulted. For those seeking information on the broad research directions for each fuel, the  
21 background and rationale (Sections 2.2, 3.2, etc.) and research needs (Sections 2.3, 3.3,  
22 etc.) sections should be reviewed. Although the Strategy does not provide a level of detail  
23 appropriate for developing, designing, or conducting specific research projects, it will  
24 provide a framework to begin such project development. To further assist the reader, two  
25 tables of contents are provided. The first follows the organization of the Strategy directly.  
26 The second is indexed by scientific discipline.

### 1.3 REGULATORY BACKGROUND

A widespread shift to alternative motor vehicle fuels represents a major societal, economic, and technical break with the past. This shift began during the 1980s with growing use of oxygenate-gasoline blends, as suggested in Table 1-1.

**TABLE 1-1. MARKET PENETRATION OF GASOLINE BLENDED WITH OXYGENATED ORGANICS<sup>a</sup>**

| Year | Percent of Gasoline that Contains the Oxygenates: |                   |          |
|------|---|-------------------|----------|
|      | Ethanol   | MTBE <sup>b</sup> | Methanol |
| 1984 | 4   | 8                 | 2        |
| 1985 | 7   | 12                | 3        |
| 1986 | 7   | 14                | 1        |
| 1987 | 7   | 20                | 0        |
| 1988 | 7   | 22                | 0        |

<sup>a</sup>Ethanol blended at 10% v/v; MTBE blended at 2 to 15% v/v; methanol blended at 3 to 5% v/v.

<sup>b</sup>MTBE = methyl-tertiary-butyl ether.

Source: Wilson (1989).

The movement to alternative fuels is seen in various recent governmental actions, especially the 1988 Alternative Motor Fuels Act (AMFA) (Statutes-at-Large, 1988), the Clean Air Act Amendments of 1990 (CAAAAs), and the National Energy Strategy (NES). The AMFA is intended to: improve national energy security by displacement of energy derived from imported oil; improve air quality by development and widespread use of methanol, ethanol, and CNG as transportation fuels; and increase the production of methanol, ethanol, electric, and CNG motor vehicles. The AMFA encourages the introduction of methanol-, ethanol-, and CNG-fueled vehicles by (1) increases in corporate average fuel economy (CAFE) benefits from fuel economy calculations based only on petroleum components of the fuel and (2) procurement of government fleets of "flexibly fueled vehicles." It also provides for heavy-duty truck and bus demonstration programs and establishes an Interagency Commission on Alternative Fuels to coordinate federal agency

1 efforts to develop and implement a national alternative motor fuels policy. The AMFA also  
2 requires EPA to report to Congress in December 1990 (and every 2 years thereafter) on  
3 environmental impacts associated with alternative fuels. Specifically, Section 400EE (b)  
4 requires:

- 5  
6 • "a comprehensive analysis of the air quality, global climate change, and other  
7 positive and negative environmental impacts, if any, including fuel displacement  
8 effects, associated with the production, storage, distribution, and use of all  
9 alternative motor vehicle fuels under the Alternative Motor Fuels Act of 1988, as  
10 compared to gasoline and diesel fuels; and  
11
- 12 • an extended reasonable forecast of the change, if any, in air quality, global climate  
13 change, and other environmental effects of producing, storing, distributing, and  
14 using alternative motor vehicle fuels, utilizing such reasonable energy security,  
15 policy, economic, and other scenarios as may be appropriate" (Statutes-At-Large,  
16 1988).  
17

18 In April 1989, EPA issued a rulemaking that provides standards and certification  
19 procedures for methanol-fueled vehicles, the purpose of which was "... to remove the  
20 possibility that the absence of emissions standards could hinder development of methanol as a  
21 transportation fuel." At the state level, California plans to introduce several thousand  
22 alternative-fueled vehicles over the next few years. Moreover, the South Coast Air Quality  
23 Management District has mandated the use of clean-fuel vehicles by operators of fleets of  
24 15 or more vehicles in the Los Angeles area by 1992.

25 The 1990 CAAAs include important provisions for alternative fuels. The Director of  
26 EPA's Office of Mobile Sources (Wilson, 1991) recently summarized the strategy for dealing  
27 with motor vehicle emissions under the new CAAAs as follows:  
28

29 "A new car today emits about 95% less pollutants from the tailpipe than does an  
30 uncontrolled car. The device most responsible for this cleanup is the catalytic  
31 convertor, which has been installed on almost all cars built since 1975. Other  
32 improvements include the widespread use of electronic feedback controls and fuel-  
33 injection systems in place of carburetors. They allow a car's microcomputer to send  
34 into the engine the precise amount of fuel needed, thereby making combustion more  
35 efficient and less polluting.  
36

1 Under the new law, new cars sold in 1994 and later will emit about 30% less  
2 hydrocarbons and 60% less nitrogen-oxide pollutants from the tailpipe than cars do  
3 today. The law also extends the durability requirements of emission-control equipment  
4 from 50,000 miles to 100,000 miles.

5  
6 New trucks must also meet more stringent tailpipe requirements. In particular, large  
7 diesel trucks will have to cut emissions of particulate matter by 90% compared to  
8 uncontrolled levels; this should eliminate the visible black smoke that regrettably is so  
9 common with these vehicles. Buses used in urban areas must do even better than  
10 trucks in controlling harmful emissions.

11  
12 Currently, on a cold day, most carbon-monoxide emissions occur during the first few  
13 minutes after vehicle start-up. But the current carbon-monoxide emission standard  
14 applies at 75° F. Under the new law, for the first time, new cars, minivans, and small  
15 trucks must meet an emission limit for carbon monoxide under cold temperature  
16 conditions; specifically, 20°.

17  
18 Starting in a few years, new cars nationwide will be equipped with 'on-board'  
19 diagnostic systems. These systems, made up of under-hood computers coupled with a  
20 dashboard display, must be capable of alerting drivers and mechanics to malfunctioning  
21 emission-control equipment.

22  
23 Environmental Protection Agency is given new authority to regulate any category of  
24 non-road mobile engines that contribute to urban air pollution. The Agency is directed  
25 to control, at a minimum, locomotive emissions and to consider emission limits for  
26 construction and farm equipment, lawn and garden equipment, boats, and other  
27 machines driven by internal combustion engines.

28  
29 Gasoline vapors that escape from the fuel tank of a car as it is refueled will be  
30 controlled. The vapors will be recycled and used as fuel, instead of contributing to  
31 pollution.

32  
33 As a complement to the control of vapor during refueling, improvements will be made  
34 in the systems which prevent the evaporation of gasoline from vehicles both when they  
35 are operating and when they are parked on hot summer days.

36  
37 The new law requires EPA to review the procedures used to test vehicle compliance  
38 with emission standards and to make any revision needed to reflect actual driving  
39 conditions.

40  
41 Environmental Protection Agency's ability to enforce all existing and new requirements  
42 on vehicle and fuel manufacturers is strengthened under the amendments. For example,  
43 the Agency is now able to collect fees from auto makers to recover the cost of EPA  
44 compliance monitoring.

1 Compared to cleaning up the emissions from cars, less has been done on cleaning up  
2 the fuels they use. It is not difficult to understand how the quality of fuel burned in an  
3 engine affects its emissions. The most environmentally successful fuel-related program,  
4 to date, has been the virtual elimination of lead in gasoline. Another EPA program,  
5 which took effect across the country in the summer of 1989, reduced the volatility of  
6 gasoline. Reducing volatility means that less fumes evaporate into the atmosphere on  
7 hot weather days which, in turn, means significantly reduced smog levels. The new  
8 amendments require that additional steps be taken by fuel producers to improve fuel  
9 quality.

10  
11 During summer months, beginning in 1992, all gasoline in the country will evaporate  
12 less rapidly, as required by a second step in the volatility-reduction program.

13  
14 Beginning in the winter of 1992-1993, the amendments mandate the addition of oxygen to  
15 all gasoline sold during winter months in any city with carbon monoxide problems.  
16 Adding oxygen, in the form of alcohols or ethers, greatly reduces carbon monoxide  
17 emissions from all cars, new and old.

18  
19 Oil refiners will be required to reduce the amount of sulfur in diesel fuel as of  
20 October 1, 1993.

21  
22 Beginning in 1995, all gasoline sold year-round in the nine cities with the worst air  
23 pollution must be reformulated to reduce smog-forming and toxic pollutants. For  
24 example, the amount of benzene, a component of gasoline known to cause cancer, will  
25 be lowered. Other cities may choose to have this 'clean' gasoline sold within their  
26 boundaries as well.

27  
28 The law establishes a California Pilot Program to encourage and demonstrate the  
29 production of even cleaner fuels and vehicles. Beginning in 1996, auto companies must  
30 sell 150,000 cars in California that have emission levels one-half that allowed for other  
31 new cars. The number of cars increases to 300,000 a year in 1999; in 2001 emission  
32 levels are reduced by half again.

33  
34 As early as 1998, a percentage of new vehicles purchased in centrally fueled fleets in  
35 22 polluted cities must meet tailpipe standards that are about one-third of those in place  
36 for general passenger cars. This program is intended to stimulate development of new,  
37 low-polluting fuel/vehicle combinations."

38  
39  
40 Title IX of the CAAAs requires EPA to provide a research program on alternative  
41 fuels. In amending Section 104(c) of the Clean Air Act, the CAAAs state:

42 "The Administrator shall conduct a research program to identify, characterize, and  
43 predict air emissions related to the production, distribution, storage, and use of

1 clean alternative fuels to determine the risks and benefits to human health and the  
2 environment relative to those from using conventional gasoline and diesel fuels.  
3 The Administrator shall consult with other Federal agencies to ensure coordination  
4 and to avoid duplication of activities authorized under this subsection."  
5

6 The National Energy Strategy seeks to reduce oil use in the transportation sector by  
7 increasing the overall efficiency of the transportation system and expanding the use of  
8 alternative fuels. Unlike the CAAAs definition of "clean alternative fuel," it does not  
9 include reformulated gasolines or diesel fuels. The NES accelerates federal fleet vehicle  
10 purchases, proposes eliminating the cap on CAFE credits that manufacturers can earn by  
11 producing dual-fuel and flexible fuel vehicles, and proposes that fleets in all urban areas be  
12 required to purchase alternative-fueled vehicles.

13 As policy decisions are made in the course of implementing such governmental actions,  
14 the selection of particular options concerning expanded use of specific alternative fuel(s) will  
15 have major implications with regard to potential impacts on human health, ecosystems, and  
16 global climate. A comprehensive integrated research program on alternative fuels is needed  
17 to supplement the available information and advance the quantitative scientific foundation for  
18 future decision-making. Given the complexity of the scientific issues involved, research must  
19 be carefully targeted. The 1990 CAAAs mandate such a program. For all these reasons,  
20 ORD developed this Research Strategy. As a strategy for future research, it provides an  
21 overview of the present understanding of alternative fuels issues (as related to the  
22 development of a research strategy) and identifies needed information for assessing changes  
23 in the benefits and risks to public health, ecosystems, and global climate that may result from  
24 changes in transportation fuel usage.

25 Options for replacing and/or supplementing conventional gasoline and diesel  
26 transportation fuels are numerous, and all have positive and negative attributes. Political,  
27 economic, and scientific considerations will drive the development and introduction of new  
28 fuels. As fuel options emerge and technology becomes available for evaluation, assessments  
29 of their impacts on the environment and the public health and welfare will be needed. The  
30 initial Strategy focuses on "replacement" fuels, namely methanol, ethanol, and CNG  
31 (as specified in the AMFA) and on reformulated gasolines (as specified in the CAAAs),

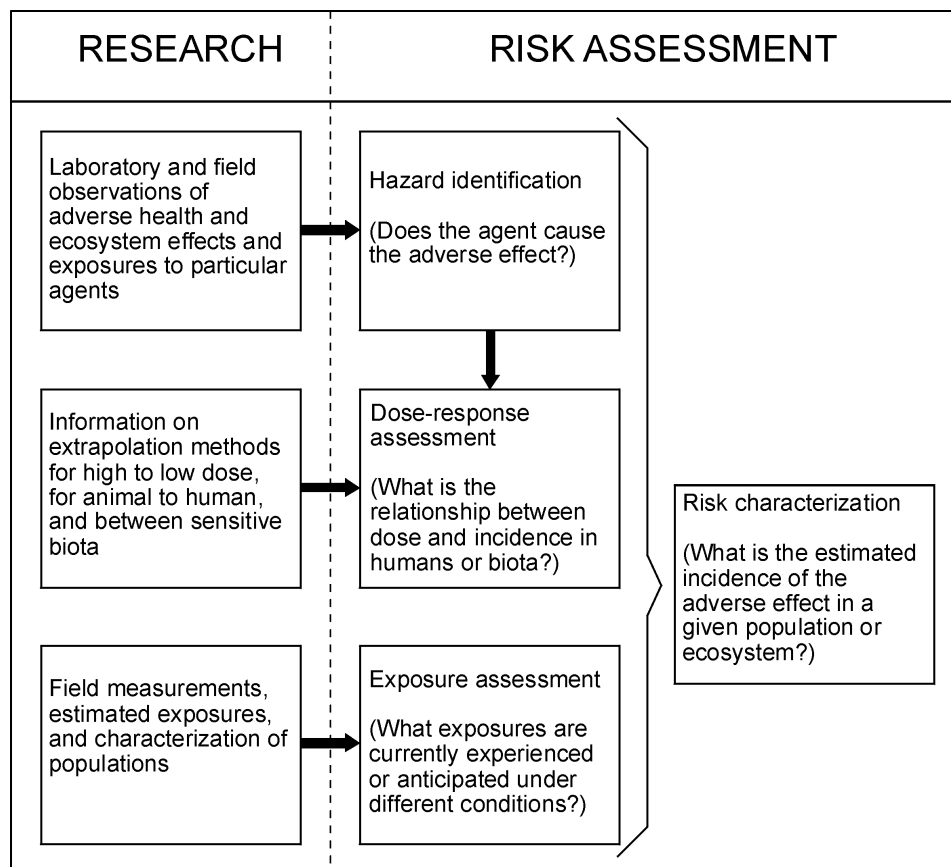
1 which generally include oxygenated organics such as ethanol, methyl-tertiary-butyl ether  
2 (MTBE), ethyl-tertiary-butyl ether (ETBE), and reduced aromatic and olefinic hydrocarbon  
3 fractions, with reduced volatility. Both replacement fuels and reformulated gasolines must be  
4 compared to conventional gasoline and diesel fuels to meet the mandate of the AMFA and to  
5 permit comparisons of health, ecosystem, and global climate impacts.

#### 6 7 **1.4 INTRODUCTION TO RISK ASSESSMENT FRAMEWORK FOR** 8 **FUELS**

9 The ultimate goal of the research proposed in this Strategy is to provide information  
10 comparing the quantitative health and ecosystem risks of alternative fuels to those of  
11 conventional fuels. This will include information on the emissions of radiatively important  
12 trace gases (RITGs) that may be used in EPA's Global Climate Research Program to evaluate  
13 the influence of alternative fuels on global warming. Figure 1-1 displays the four general  
14 key elements of risk assessment, which need to be applied to develop comparative  
15 assessments of fuels. The major steps are hazard identification, dose-response assessment,  
16 and exposure assessment, with their linkage constituting risk characterization, the final or  
17 ultimate objective of risk assessment.

18 The initial hazard identification step entails determining whether a pollutant of interest  
19 can cause an adverse health or ecological effect. Some degree of knowledge of potential  
20 exposures is also required to enable identification of a pollutant of interest. This is especially  
21 important for fuel-related pollutants because so many are involved and some have not yet  
22 been chemically characterized. Once a pollutant is identified as having hazardous potential,  
23 that potential needs to be characterized further in a human or ecological dose-response  
24 assessment. For health effects, much of the research will, of necessity, utilize animals;  
25 however, because the subjects of interest are humans, extrapolation research is also required.  
26 Ecological effects research should focus initially on plants and aquatic biota. The  
27 dose-response assessment must be characterized in terms of an exposure-response relationship  
28 because (1) the dose delivered to a target site at a given duration and rate ultimately results  
29 from exposure, and (2) the exposure will be the metric of interest to regulatory strategies.  
30 A given exposure-response assessment must be linked to an exposure assessment to



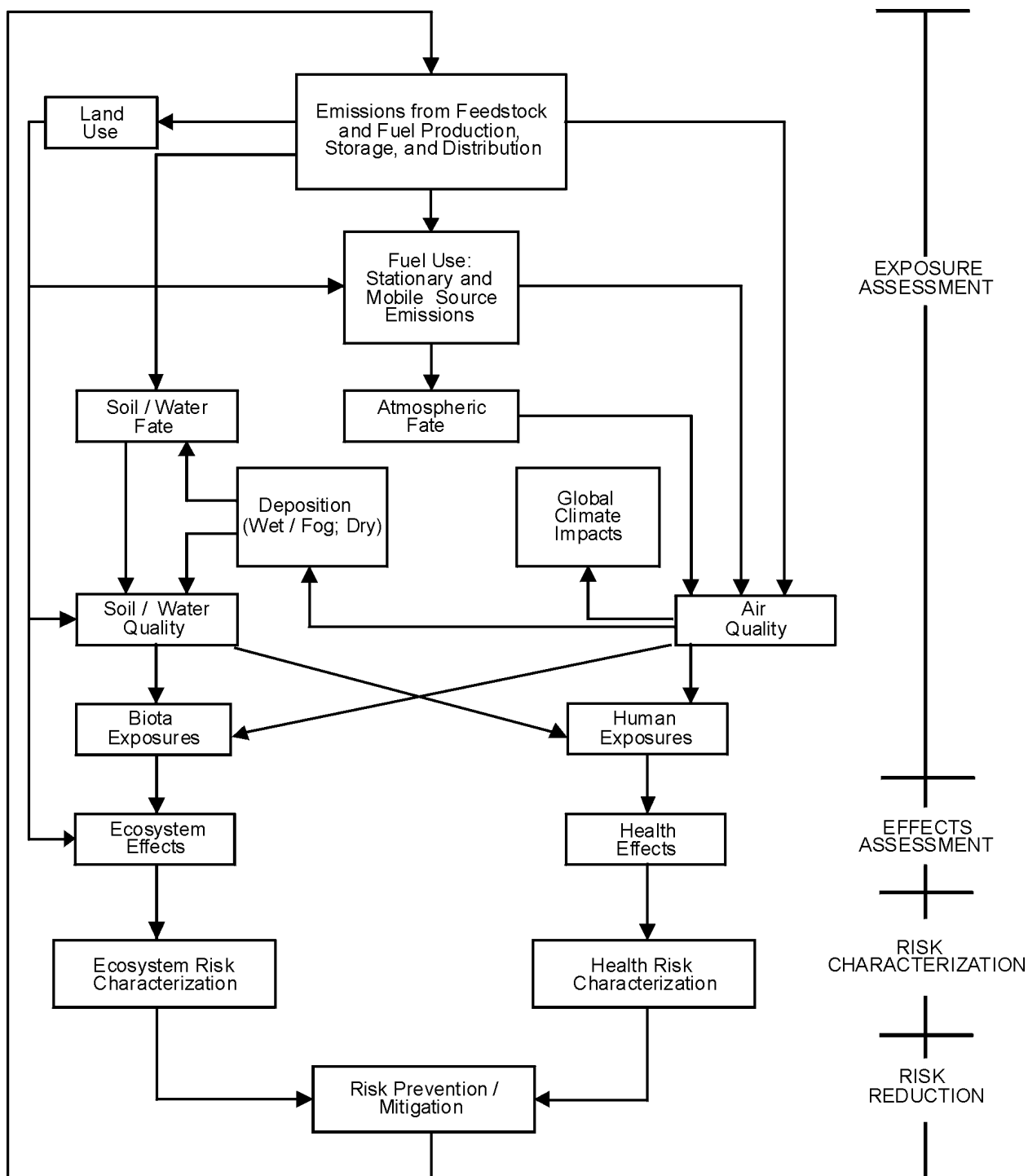


**Figure 1-1. Key elements of risk assessment.**

Source: Adapted from National Research Council (1983).

characterize risk. For example, if a 1-h exposure to a certain level of a pollutant causes effects, what is the likelihood that susceptible people will experience that pollutant level for 1 h? Thus, a key step is to develop an exposure assessment which involves monitoring and/or modeling the intensity, frequency, and duration of exposures to a pollutant actually encountered by a population of a particular size and composition (e.g., the number of asthmatics, children, healthy adults).

These basic features of risk assessment are incorporated into Figure 1-2, which is a schematic representation of the major pathways involved in assessing and mitigating the risks



**Figure 1-2. Generic major risk assessment pathways of motor fuel production, distribution, storage, and use.**

1 associated with fuels. Categories of activities are denoted by the headings along the vertical  
2 line on the right side of the figure: exposure assessment, effects assessment, risk  
3 characterization, and risk reduction. Exposure assessment occupies the largest area of the  
4 schematic because so many exposure-related issues pertaining to fuels need to be answered  
5 before other components of the assessment can commence. As answers to these and other  
6 questions become available, other parts of the figure will need to be expanded. Also, for the  
7 sake of visual simplicity, the single boxes for effects assessment represent both the  
8 identification of the qualitative nature of the hazard posed by a pollutant and the assessment  
9 of its dose-response characteristics. Both of these facets of effects research encompass many  
10 scientific issues and specialized areas of inquiry. Similarly, risk characterization is a  
11 complex product of all the pathways that lead into it and is obviously oversimplified as  
12 depicted in the figure.

13 Beginning with the characterization of emissions and impacts associated with fuel and  
14 fuel-feedstock production, storage, and distribution, Figure 1-2 shows pathways leading  
15 through different environmental media to human and biota exposures. As suggested by the  
16 number and cross-linkages of arrows in the figure, the stages in this process are quite  
17 complex. For example, ecosystem effects could be mediated through any of several  
18 pathways, including direct impacts via land use and water quality changes as well as various  
19 indirect impacts through changes in air quality. Notwithstanding its apparent complexity,  
20 this schematic greatly understates the number of potential linkages and pathways by omitting  
21 the multiplicity of exposure conditions (e.g., chronic versus acute, ambient versus  
22 microenvironmental), receptors potentially exposed (e.g., freshwater versus marine versus  
23 terrestrial flora and fauna, as well as the varieties of human subpopulations), and types of  
24 effects resulting from exposures (e.g., population changes within ecosystems, various health  
25 endpoints in humans). If integration of all of this information indicates a potential for  
26 adverse risk, appropriate risk prevention and reduction steps may be sought to reduce the  
27 emissions and impacts identified at the top of the chart.

28 These issues will be elaborated in greater detail in the remaining sections of this  
29 chapter. For now, it is important to note that such complexity requires that, to be effective,  
30 a research program must coordinate and appropriately link key risk assessment issues and

1 that these issues must be considered in a rational priority order. Thus, the results of one  
2 project must be evaluated for the guidance they may provide to other projects. The fuel-  
3 specific chapters that follow attempt to construct such an interactive program. The Risk  
4 Assessment Research Framework section for each fuel briefly characterizes the potential risk  
5 pathways and the information needs for risk assessment. It also discusses the present state of  
6 knowledge and describes those pathways that appear to be of greatest interest at this time,  
7 further identifying which steps of those pathways must be the subject of research or  
8 assessments before proceeding to later steps.

9 To avoid excess duplication later, this introductory section uses a risk assessment  
10 format to describe issues that are generic to most of the fuels (e.g., coal can be used as a  
11 feedstock for methanol and petroleum-like liquids; human exposure assessment requires  
12 knowledge of activity patterns, independent of the fuel of interest; pharmacokinetics is basic  
13 to all health research). The presentation is categorized according to exposure assessment  
14 (source characterization, pollutant fate, human and biota exposures, global climate impacts,  
15 and analytical methods), effects assessment (health effects and ecosystem effects), risk  
16 assessment, and risk prevention/reduction. Although essential for presentation purposes, this  
17 categorization fragments the risk assessment process; all facets of the risk assessment  
18 framework must be considered as a particular pathway is being addressed.

19 In this generic presentation, issues are prioritized based on currently available  
20 information, which is presented in more detail in the fuel-specific sections. The ranking of  
21 risk assessment pathways is based on judgments of potential magnitude of risk. Severe  
22 effects on small populations are considered to be of equivalent concern to moderate effects  
23 on large populations. The state of knowledge about conventional fuels largely drives this  
24 prioritization. For example, combustion of conventional fuels is a major contributor to the  
25 problem of tropospheric ozone ( $O_3$ ). Because alternative fuels may result in lower  $O_3$  levels,  
26 it is important to verify and quantify this potential impact of alternative fuels. However, this  
27 prioritization must be considered preliminary and subject to change as more information  
28 becomes available. As will be noted in subsequent text, numerous full literature evaluations  
29 and/or assessments should be undertaken to determine whether an issue should be the subject  
30 of laboratory or field research.

### 1.4.1 Exposure Assessment

Exposure assessment identifies sources of exposure, microenvironments with potentially high concentrations, and other factors that may result in increased risks to exposed human populations and ecosystems. The relative degree of risk associated with each alternative fuel will depend on the route of exposure, the concentration of the chemical in a given medium, and the frequency and duration of exposure. The major elements of an exposure assessment are:

- identifying and quantifying source emissions and transformation products (source characterization);
- characterizing important physical and chemical fate processes using validated models;
- understanding the movement of pollutants to exposed populations (both humans and ecosystems) and identifying exposure pathways;
- determining the concentration of the substance in various media and microenvironments;
- assessing exposure from all sources;
- determining the magnitude, duration, frequency, and probability of exposure and the percent of a population exposed above specified levels of health or ecosystem concern; and
- determining the amount of a pollutant that actually enters an exposed subject.

Exposure assessments must be closely linked with both health and ecosystem effects research. Some basic information on exposure is important in designing initial hazard identification research. If the effects research identifies a potential hazard from such first-tier exposure data, then the exposure research proceeds to higher tiers to achieve quantitative exposure assessments and the effects research proceeds to dose-response research. This continual interaction will enable the research to focus on the issues of greatest concern and will result in an ability to link exposures and effects more directly and quantitatively in the final risk assessments.

1       The exposure assessment process outlined above requires information in a more or less  
2 sequential manner, starting with characterizing the emissions, determining through  
3 measurements the concentrations within microenvironments that will lead to maximum  
4 exposures and the extent of the exposure (e.g., the number of people who experience these  
5 exposures), and developing/evaluating/validating exposure models for predicting exposures to  
6 the emissions. The discussion that follows is categorized according to source  
7 characterization, fate, and integrated exposures. To a degree, both human and ecosystem  
8 exposures have common sources, and air, soil, and water quality will influence both.  
9 Human and biota exposures are separated only in the integrated exposure section.  
10 Radiatively important trace gas emissions related to global climate impacts are also discussed  
11 here, since many of the results of the source characterization and atmospheric fate research  
12 are applicable to global climate information needs.

#### 14 **1.4.1.1 Source Characterization**

15       Source emissions characterization is very complex due to the multiplicity of sources,  
16 the large number of potential emissions from each source that vary by mass per unit time and  
17 by physicochemical properties, and the different media that may be impacted. All emissions  
18 contribute eventually to air, soil, and water quality, but to differing degrees. Research  
19 should focus on those pathways of greatest potential risk, which are discussed generically  
20 below and are categorized as (1) emissions from feedstock and fuel production, storage, and  
21 distribution, which are predominantly from stationary sources; and (2) emissions from fuel  
22 use, which are predominately from mobile sources and can be quite varied because  
23 combustion transformation products are included.

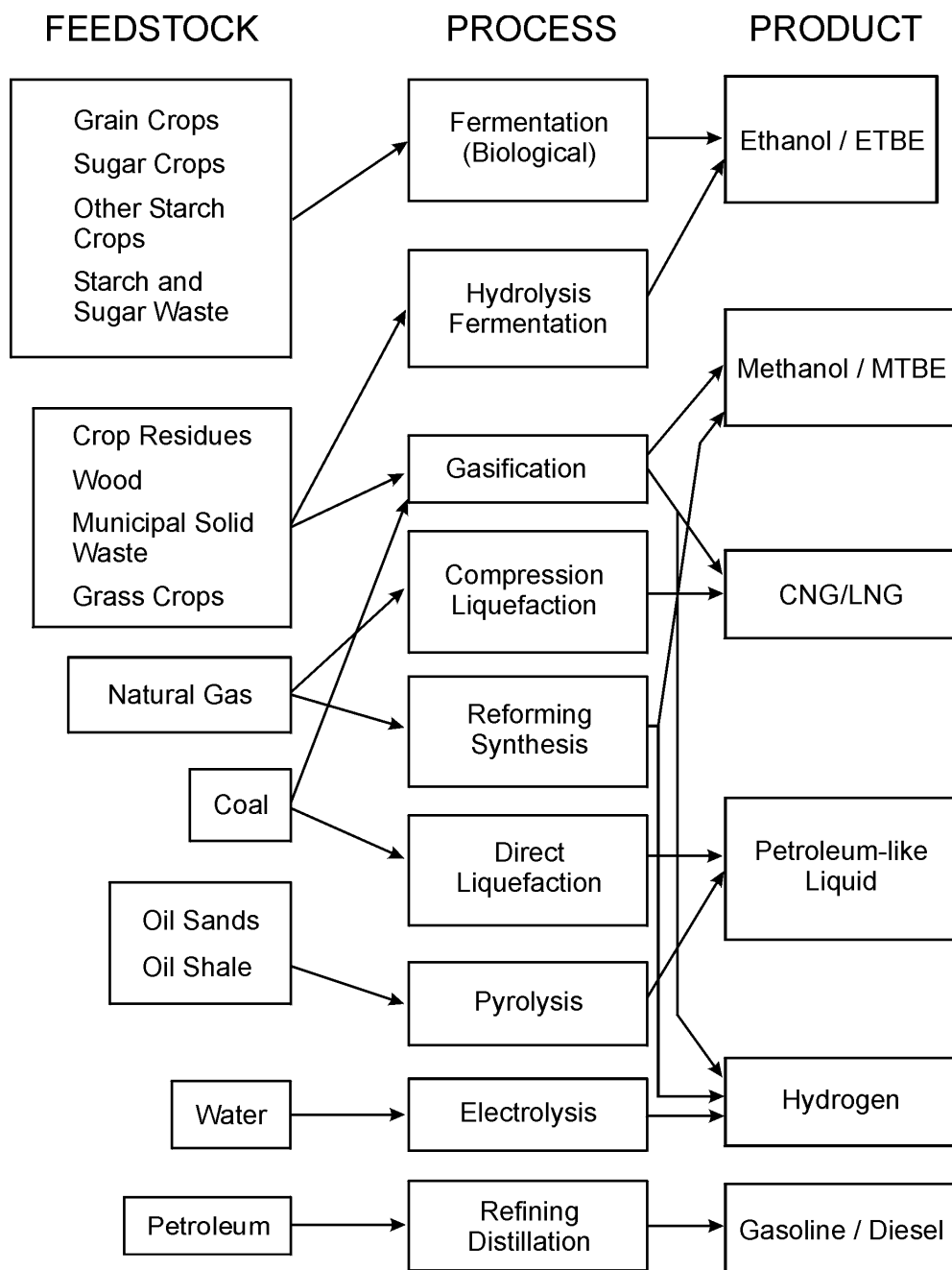
##### 25 ***1.4.1.1.1 Emissions from Feedstock and Fuel Production, Storage, and Distribution***

26       The combined contribution of area sources and point sources of RITGs, volatile organic  
27 compounds (VOCs), and toxic compounds from the use of petroleum-based transportation  
28 fuels pose a serious problem for health and the environment. Although alternative fuels may  
29 offer opportunities to reduce some of these problems, they may also present problems of  
30 their own. To assess fully the potential health, ecological, and global climate risks from the

1 production and use of these fuels, the potential emissions/discharges into air, water, and land  
2 must be quantified. This characterization must address the emissions/discharges from  
3 recovery of feedstocks that could be used to produce the specific fuel, as well as the fuel's  
4 production technology, and its transportation, storage, and distribution.

5 The energy processing steps, energy efficiencies, and emissions/discharges (including  
6 continuous, transient, and major accidental) must be defined; and differences from  
7 conventional fuels in relation to feedstocks, production techniques, and other factors must be  
8 quantified. In the case of large accidental releases, the conditions potentially causing such  
9 releases and the probability of their occurrence must be determined in relation to prevention  
10 measures. The emissions resulting from such releases will depend on source strength and  
11 control technology effectiveness. The major uncertainties in assessing this issue pertain to  
12 the quantification of emissions and discharges as a function of the prevention and control  
13 options that are either available now or could be developed in the future.

14  
15 ***Feedstocks.*** Many feedstocks can be used to produce fuels (Figure 1-3). Petroleum,  
16 biomass, and natural gas are currently considered primary near-term feedstocks for  
17 alternative fuels, with coal of secondary near-term importance. The use of oil shale as a  
18 feedstock for the production of alternative fuels is uncertain because of unproven technology,  
19 potentially unacceptable environmental risks, and economic considerations; therefore,  
20 although it will be considered, it will not be a primary near-term research focus. As listed in  
21 Table 1-2, these feedstocks have several emissions of interest and can impact land-use via  
22 mining, drilling, or biomass production used to obtain the feedstock. Although the focus of  
23 this Research Strategy will be emissions, land use impacts can be quite important. Natural  
24 gas and petroleum exploration, extraction, and pipeline systems will disturb wildlife habitat,  
25 soil resources, and land surfaces. Coal extraction will result in land, habitat, geological, and  
26 hydrological alterations. The mining process also can affect regional air and water quality  
27 through toxic chemical and particulate matter releases. Biomass production will alter use of  
28 fertilizers, pesticides, and herbicides, with consequent impacts on human health and  
29 ecosystems. Rather than initiating new research into these topics, the extent of changes in



**Figure 1-3. Vehicular fuel feedstocks and production processes. Key: CNG = compressed natural gas; ETBE = ethyl-tertiary-butyl ether; LNG = liquified natural gas; MTBE = methyl-tertiary-butyl ether.**

Source: Adapted from Sperling (1988).



**TABLE 1-2. EMISSIONS AND OTHER POTENTIAL  
IMPACTS FROM FEEDSTOCKS**

| Feedstock   | Potential Environmental Impacts   |
|-------------|---|
| Coal        | RITGs (methane), mining <sup>a</sup>  |
| Natural gas | RITGs (methane), hydrogen sulfide, drilling <sup>a</sup>  |
| Biomass     | Land use shift; <sup>a</sup> fertilizer, pesticide, herbicide use; <sup>a</sup> CO <sub>2</sub> recycling |
| Oil shale   | RITGs, VOCs, mining <sup>a</sup>  |
| Petroleum   | RITGs, VOCs, drilling <sup>a</sup>  |

Key: RITG = radiatively important trace gas; VOC = volatile organic compound.

<sup>a</sup>Key issues to be considered in an assessment, but not part of this Research Strategy.

feedstocks and land use will need to be estimated in relation to developments in alternative fuels and incorporated into risk assessments based on existing information on these impacts.

**Production.** Facilities for processing feedstock into fuel will generate liquid effluents, gaseous emissions, and solid waste, all of which may contribute toxic substances to environmental media. Although current regulations to protect air, water, and soil quality should limit potential impacts, the character and magnitude of these emissions must be more fully quantified to determine the nature of potential problems and the level of prevention or control that may be needed to satisfy existing regulations.

Processing steps must be defined, particularly in terms of variations as a function of feedstocks and other factors. First, the energy efficiencies and emission/discharge factors for these steps must be better understood, with a focus on all types of pollutant releases, including continuous, transient, and major accidental releases. The estimated resulting emissions will be a function of existing source strength and control technology effectiveness. Second, energy trajectories linking the individual steps for predefined levels of fuel production must be determined. In this case, an energy trajectory refers to a sequential

1 series of energy processing steps, (e.g., natural gas extraction, separation and cleanup of the  
2 production gas, pipelining, processing of methane to liquified natural gas [LNG], LNG  
3 terminal transfer, etc.). A multitude of different possible trajectories exists, depending on  
4 the choices of feedstock (fuel) types, processing options, and handling/utilization options.  
5 Finally, the resulting overall emissions/discharges must be determined by aggregating the  
6 linked emissions/discharges. As discussed in the fuel-specific chapters to follow, some of  
7 this information exists and can be used to target research. In the case of major accidental  
8 releases, the factors leading to releases must be identified, and the probability for maximum  
9 credible releases should be determined as a function of the range of operations and  
10 application of potential prevention measures.

11 Since the use of alternative fuels will be changing and will need to be assessed relative  
12 to conventional fuels, the baseline condition must be considered, and factors that will  
13 influence future emissions must be understood. To determine the baseline case, the emission  
14 levels of conventional-gasoline VOCs and RITGs occurring in actual practice for stationary  
15 sources and the variation of these emissions as a function of prevention and control options  
16 must be more quantitatively understood. Sources should include storage/transportation/  
17 marketing, non-highway vehicles (e.g., stationary engines, construction equipment, small  
18 engines), use as a solvent, and waste disposal. Emission factors must also be determined,  
19 taking into account future fuel strategies that will be necessary within the United States and  
20 globally to deal with the refractory, growing problem of O<sub>3</sub> nonattainment and concern for  
21 global warming.

22  
23 ***Storage and Distribution.*** Feedstocks and fuels will be widely stored and distributed,  
24 presenting many points at which acute or chronic emissions could occur. Possible sources  
25 include underground storage tanks (USTs), above-ground storage tanks, marine super  
26 tankers, freshwater barges, pipelines, rail tanker cars, and tanker trucks. All of these  
27 systems are designed to prevent releases, but accidents do occur. Existing information on  
28 the frequency and magnitude of accidents needs to be reviewed in detail to identify clearly  
29 which elements of storage and distribution are more likely to generate emissions that may be  
30 of potential concern.

1       At present, the greatest interest centers on chronic emissions from under- and above-  
2 ground storage tanks and on accidental spills from supertankers and barges. Although  
3 natural gas has an explosive potential if released in a confined space, and hence its storage  
4 and distribution present matters of safety risk, it will not be further explored in this Research  
5 Strategy because the focus is on emissions, rather than on safety issues, which can be  
6 assessed based on available information.

7       Chronic emissions from above-ground storage tanks can alter the burden of atmospheric  
8 VOCs, which have the potential to contribute to O<sub>3</sub> and air toxics formation, and of RITGs,  
9 which influence global warming and, therefore, are of high priority. In addition, such  
10 sources could experience acute, high-level releases with potential impacts on human health  
11 and ecosystems.

12       Underground storage tanks are also of high interest. The United States has  
13 approximately 2.5 million USTs, and EPA has estimated that more than 25% of existing tank  
14 systems (i.e., tanks and their associated piping) may be leaking or are expected to leak  
15 within the next 3 to 5 years. Most of these systems contain conventional fuels. Newer  
16 technologies, coupled with federal regulations, are intended to substantially prevent or limit  
17 such problems in the future with either alternative or conventional fuels. Conventional and  
18 alternative fuels, however, are sufficiently different to necessitate research to determine  
19 whether the engineering solutions for conventional-fuel USTs are as effective as those for  
20 alternative-fuel USTs. Key issues include (1) research on adequacy of UST system designs,  
21 (2) research on adequacy of leak detectors, and (3) development of guidance documents for  
22 on-site investigations (where leaks are suspected) and site cleanup technologies based on  
23 improved knowledge from soil fate research and risk prevention/reduction research.

24       Accidental large spills of fuel (except natural gas) in terrestrial or aquatic ecosystems  
25 could be very deleterious to biota and could have a direct or indirect effect on human health  
26 through food-chain exposures or contamination of drinking water. Transport on water also  
27 results in low-level releases of fuels that are assumed to be of lesser risk, pending analysis of  
28 such releases of petroleum products. The potential risks from spills should vary markedly  
29 among alternative fuels, due to widely different chemical properties that affect fate and  
30 toxicity. Preliminary, conservative risk assessments based on simple fate calculations and

1 available effects information should be conducted to determine whether a potential exists for  
2 significant damage from spills and leakages of fuels.

#### 4 ***1.4.1.1.2 Emissions Related to Fuel Use***

5 For the purposes of this Strategy, emissions related to fuel use are defined as those  
6 emitted from motor vehicles and stationary combustors. Both must be considered when  
7 evaluating air quality impacts; their respective importance will vary locally with the  
8 emissions of interest.

10 ***Stationary Source Emissions.*** For stationary sources, the most important emission  
11 sources are likely to be those involved in feedstock and fuel production, storage, and  
12 distribution, rather than in fuel combustion itself. In most cases, use of the alternative fuels  
13 is expected to provide emission reductions, as most of the fuel alternatives are relatively  
14 "clean" and the continuous combustion processes generally involved are highly efficient.  
15 Such changes in emissions, however, must be quantified to aid the health and ecosystem risk  
16 assessments. On the other hand, some types of stationary sources could have emissions of  
17 concern similar to or more troublesome than mobile source emissions. Examples include  
18 internal combustion engines such as stationary engines, construction equipment, and small  
19 engines, as well as the use of alternative fuels as solvents.

21 ***Mobile Source Emissions.*** Assessment of the impact of motor vehicle fuels on air  
22 quality problems, such as O<sub>3</sub>, carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), particulate  
23 matter (PM), and other air toxic compounds, or on global climate change requires  
24 comprehensive examination of emissions from several vehicle categories under the widely  
25 variant operating conditions typical of motor vehicle fleets. The limited emissions speciation  
26 data available in the literature for motor vehicles are dominated by those obtained under  
27 certification driving conditions (i.e., about 70 °F and 20 mph average speed). The  
28 compositional character and rates of emissions are sensitive to variations in average speed  
29 and ambient temperature, however, necessitating an understanding of a fuller array of  
30 operating conditions. Based on experience with conventional gasoline vehicles, hydrocarbon

1 and CO emission rates (grams of emissions per vehicle mile traveled) typically are minimal  
2 at 70 °F and increase as temperature is elevated or reduced. These emission rates also  
3 increase as average speed is decreased. Oxides of nitrogen (NO<sub>x</sub>) emission rates, although  
4 not as sensitive to temperature and speed as hydrocarbons and CO, increase as temperature is  
5 decreased and as average speed is increased or decreased from 20 mph. Carbon monoxide  
6 air quality violations often occur at temperatures well below 70 °F, and O<sub>3</sub> air quality  
7 violations often occur at temperatures well above 70 °F. The emission rates and composition  
8 are also very sensitive to fuel characteristics such as volatility and composition.

9       The relative importance of the various categories of motor vehicles depends on the  
10 target air-quality problem. The mobile source emissions model MOBILE 4 can be used to  
11 examine the sensitivity of emissions to ambient temperature. At 100 °F, light-duty gasoline  
12 vehicles were responsible for about 90% of O<sub>3</sub>-precursor hydrocarbons from vehicles in  
13 1990; and at 25 °F, they were responsible for about 85% of CO emissions from vehicles in  
14 1990. Motor vehicle NO<sub>x</sub> and particulate emissions are distributed about 2/3 and 1/3  
15 between light-duty cars/trucks and heavy-duty trucks/buses, respectively. Priorities for study  
16 of the air quality impact of alternative transportation fuels, therefore, should be directed to  
17 the category of vehicles most responsible for the air quality problem being addressed: light-  
18 duty passenger cars and trucks for O<sub>3</sub> and CO air quality, and all categories of vehicles if  
19 NO<sub>2</sub> and particulate air quality are of interest.

20       Throughout this Strategy, reference is made to motor vehicle emission estimates based  
21 on the model MOBILE 4. A revised version of this model, MOBILE 4.1, was published in  
22 July, 1991 (U.S. Environmental Protection Agency, 1991a). For calendar year 1990, the  
23 speed-weighted nonmethane hydrocarbon (NMHC) emissions at 90 °F estimated by MOBILE  
24 4.1 are similar to those estimated by MOBILE 4.0; the speed-weighted NO<sub>x</sub> emissions at  
25 90 °F estimated by MOBILE 4.1 are about 38% greater than those estimated by MOBILE  
26 4.0; and the speed-weighted CO emissions at 30 °F estimated by MOBILE 4.1 are about  
27 21% greater than those estimated by MOBILE 4.0.

Efforts to characterize emissions from motor vehicles to assess their impact on risks to human health and ecosystems need to encompass three general categories of variables:

- (1) Vehicle-fuel technology: (a) light-duty passenger cars and trucks and heavy-duty trucks and buses representative of in-use fleets, (b) varied fuel compositions representative of marketplace fuels or projected future fuels.
- (2) Operating conditions: (a) varied average vehicle speeds and engine loads, (b) varied ambient temperatures, (c) varied ages (control system deterioration), and (d) varied altitudes.
- (3) Emission sources: (a) tailpipe emissions, (b) evaporative emissions (e.g., diurnal, hot soak, and running-loss), and (c) refueling.

Laboratory simulations of roadway conditions and actual roadway studies should be used in a complementary fashion to examine the complex array of variables that influence the characteristics of motor vehicle emissions.

Assessment of the potential impact of fuels on O<sub>3</sub> air quality will require determination of organic emission rates and detailed composition (hydrocarbons, oxygenates, etc.), as well as determination of CO and NO<sub>x</sub> emission rates. Knowledge of detailed organic compound compositions will also be necessary for assessing the impact of these fuels on air concentrations of, and exposure to, toxics such as benzene, formaldehyde, and 1,3-butadiene. Operating conditions should be varied to provide data representative of the motor vehicle microenvironments (parking garages, congested freeways, urban street canyons, etc.) dominating human exposure to the primary emissions. Data representative of overall urban use are also needed to permit estimation of impacts on O<sub>3</sub>, CO, NO<sub>2</sub>, and PM air quality and assessment of exposure to atmospheric transformation products of the emissions. The emission rates of RITGs important to climate change, such as carbon dioxide (CO<sub>2</sub>), methane, nitrous oxide (N<sub>2</sub>O), and other radiatively significant species, also need to be examined.

The focus of the CAAA effort to achieve and maintain acceptable air quality is regulation of emissions from on-highway, area, and stationary sources. The focus of this Research Strategy is examination of the impact of alternative fuels on emissions from these

1 sources, and on the health and welfare implications of the emissions. The EPA has recently  
2 published a study examining the relative significance of nonroad engine emissions (U.S.  
3 EPA, 1991b). This category of emissions includes those from lawn and garden equipment,  
4 recreation equipment, construction equipment, agricultural equipment, commercial marine  
5 vessels, and others. The study concludes that the median nonroad engine contribution is  
6 about 7.3 to 12.6% of the total VOC emissions inventory, 14.5 to 17.3% of the NO<sub>x</sub>  
7 inventory, 5.2 to 9.4% of the CO inventory, and 1.0 to 1.8% of the PM inventory. There  
8 exists substantial uncertainty in these estimates because of the lack of emissions data. There  
9 are essentially no data for nonroad engines using alternative fuels, and currently there is little  
10 interest in developing this technology for use of alternative fuels. Therefore, no further  
11 discussion of nonroad engines is included in this Research Strategy.

#### 13 **1.4.1.2 Environmental Fate**

14 When emissions enter the environment, they can be transported and transformed,  
15 resulting in what is termed environmental fate. Thus, exposure will be a combination of  
16 exposures to the initial emissions plus emissions as they are altered, often profoundly, by  
17 environmental fate. This Research Strategy focuses on environmental fate directly related to  
18 fuels, but in a few key instances, it considers the indirect impacts of these fate processes on  
19 alteration or release of other pollutants unrelated to fuels. The discussion below is  
20 categorized according to fate in air, aquatic systems, and soil, including ground water.

21 Although knowledge of fate within all media is critical to understanding the totality of  
22 potential risks, atmospheric fate is of greatest interest. Fuel-related pollutants are major  
23 contributors to air pollutant problems, and in many air sheds, the combustion of fuels  
24 represents half or more of the problem. Atmospheric fate processes are responsible for  
25 O<sub>3</sub> formation, and hence are a matter of great interest with respect to both health and  
26 ecosystem effects. Atmospheric transformations also result in exposures to other secondary  
27 air toxics (e.g., formaldehyde), increasing the interest in these processes.

#### 1.4.1.2.1 *Air Fate*

A number of toxic compounds produced by atmospheric transformations of evaporative and combustion emissions of alternative fuels are of interest with regard to human health and ecosystem exposures. Such transformation products include, but are not necessarily limited to, formaldehyde, acetaldehyde, dimethyl sulfate (DMS), peroxyacetyl nitrate (PAN), and O<sub>3</sub>. Because of the severity of the tropospheric O<sub>3</sub> problem, the primary focus of atmospheric studies needs to be characterizing the impact of alternative fuel use on O<sub>3</sub> formation in urban and rural areas. Reactive compounds and products in the ambient air as well as in chamber studies must be identified and measured, taking into consideration the mass and composition of compounds emitted, as determined in source assessment research. These data will help predict changes in the photochemical transformation potential resulting from the use of alternative fuels. For example, O<sub>3</sub>-forming potential for the first day could be reduced (which implies that population exposure to O<sub>3</sub> within the first day is reduced), but O<sub>3</sub> formation (and hence exposure) on the second day could be unaffected. Present downwind photochemistry is controlled primarily by the availability of NO<sub>x</sub> and not by VOCs; downwind areas are generally low in NO<sub>x</sub> and therefore have high VOC/NO<sub>x</sub> ratios. Decreasing the reactivity of VOCs in urban areas will allow more NO<sub>x</sub> to be transported downwind, which may increase the photochemical formation of O<sub>3</sub> downwind. Ozone levels in rural areas arising from urban pollutant transport, therefore, may be unaffected or may even increase with the use of alternative fuels. As a consequence, exposure of populations may extend relatively far in time and space from the emission sources. The potential impact of the use of alternative fuels on O<sub>3</sub> depends on several local variables, such as the VOC/NO<sub>x</sub> ratio, the relative significance of the varied sources (i.e., anthropogenic and biogenic), meteorology, boundary conditions (e.g., the characteristics of the pollutant mix into which the alternative fuel associated emissions are being injected), and others. The impact of alternative fuels in varied scenarios can best be studied by a combination of approaches, including controlled chamber studies, ambient air monitoring, and city and regional modeling. Studies of O<sub>3</sub> exposure, given the potential for second day impact, should also be designed and implemented.



1 Studies of the impacts of alternative fuels on air toxics are needed. Previous  
2 smog-chamber studies on pure compounds (e.g., propylene and toluene) with conventional  
3 gasoline auto exhaust have shown that mutagenicity increases with photochemical  
4 transformation of the emissions. The use of alternative fuels will decrease or eliminate many  
5 air toxics usually associated with the use of conventional gasoline (e.g., benzene, toluene,  
6 and xylenes), but research is needed to determine if any unusual and potentially toxic air  
7 pollutants are produced from photochemical transformations (e.g., DMS from methanol-  
8 based fuel).

9 Airborne pollutants related to fuels may be deposited on terrestrial and freshwater  
10 ecosystems, contributing to soil and surface water acidification and the exposure of biota to  
11 toxic substances. Although local pollutant deposition may impact agroecosystems, air  
12 currents may carry the pollutants great distances, resulting in their deposition onto remote  
13 terrestrial and aquatic ecosystems. Changes in both wet and dry deposition processes  
14 expected from fuel shifts need to be estimated; these estimates can then be used in various  
15 aquatic and terrestrial exposure assessment models.

#### 16 17 ***1.4.1.2.2 Soil and Groundwater Fate***

18 Groundwater quality may be impacted by discharges from the production of fuel  
19 feedstocks and/or from the manufacture, storage, distribution, and use of fuels.  
20 Contaminants may be introduced at the soil surface or in the unsaturated zone and leached  
21 into the underlying aquifers, or in some cases contaminants may be emitted directly into the  
22 aquifer. Discharges may result from acute, large-quantity releases or from chronic,  
23 lower-level releases. Both the rate and the duration of a contaminant release may  
24 significantly determine the impact on groundwater quality. Additionally, groundwater quality  
25 may be altered by the solubilization or mobilization of native or previously introduced  
26 chemicals through changes in the hydrogeology, geochemistry, or solution chemistry of the  
27 system. For example, the introduction of high concentrations of methanol into porous media  
28 previously contaminated by conventional fuels could significantly enhance the mobility of the  
29 residual hydrocarbons.

1       The magnitude of groundwater quality changes may be estimated through the  
2 application of solute transport and fate models. These models must account for all the  
3 processes that significantly influence the transport and attenuation of the chemicals, including  
4 phase partitioning in complex multiphase systems. The application of these models requires  
5 specific characterization of the hydrology, hydrogeology, chemistry, and biology of the  
6 system; however, for comparative assessments of fuels, quantifying the changes resulting  
7 from a fuel, without site specific parameterization, may be sufficient. To assess its utility,  
8 this generic modeling approach must be evaluated over a broad range of subsurface  
9 conditions. For any modeling approach, factors of primary importance are liquid phase  
10 mobility, the rate and extent of biotransformation, and the effects of the contaminants on  
11 subsurface microbial ecology and geochemistry.

#### 13 ***1.4.1.2.3 Surface Water Fate***

14       The transport and fate of fuels in freshwater systems could result in pollutant exposures  
15 to aquatic ecological resources and to humans via contaminated drinking water. Source  
16 characterizations and release scenarios need to be evaluated for their relevance to freshwater  
17 fate. Modeling can be used to project fate of releases in the near field, where mixing and  
18 dispersion dominate the exposures, and in the far field, where chemical and biological  
19 (e.g., microbial degradation) processes can transform and reduce the fuel residues. For fuel  
20 mixtures (e.g., reformulated gasolines), the differential fate of fuel components is important  
21 because effects will vary among components and their transformation products. Chemical  
22 properties of the fuels will largely determine their fate when spilled, with the possibility of  
23 sediment and water column contamination. In addition, attention must be given to dynamic  
24 procedures and models to capture the time series nature of fate processes and subsequent  
25 effects.

26       Although the deposition of airborne toxics from the use of alternative fuels is not  
27 expected to have a dramatic impact on freshwater ecosystems, urban watersheds provide  
28 efficient transfer of toxics deposited in wet- and dry-fall and from fuel and oil leaks to  
29 stream systems. Accordingly, multimedia evaluations of the extent of such problems must be  
30 considered to determine the need for further research on this topic.

1       Near-coastal waters and wetlands are thought to be the most vulnerable to accidental  
2 releases into marine systems. The same general approach used for freshwater systems must  
3 be followed here, including the examination of emission sources and release scenarios for  
4 their relevance to marine systems. However, some noteworthy differences exist. Near-  
5 coastal system transport fields are dominated by tidal processes and winds. Near-field  
6 problems will be predominantly affected by mixing, but far-field processes will be dominated  
7 by both fate processes and tidally driven transport. Many near-coastal zones have  
8 contaminated sediments deposited from freshwater inflows. Sudden releases of highly  
9 concentrated fuels may significantly alter the local water chemistry and result in releases of  
10 stored pollutants to the water column, thus creating secondary effects. Such problems need  
11 to be investigated.

### 13 **1.4.1.3 Integration of Exposures**

14       As can be observed in Figure 1-2, similarities and differences exist among the pathways  
15 that culminate in human or biota exposures. The purpose of this section is to combine the  
16 previous information from source characterization and fate, to apply monitoring and  
17 modeling approaches, to identify and characterize sensitive populations, and, finally, to link  
18 these elements together to develop either human or biota exposure assessments.

#### 20 ***1.4.1.3.1 Human Exposure Assessment***

21       Exposures resulting from production, distribution, storage, and use of fuels, especially  
22 conventional fuels, are known to have the potential for adverse health effects. Fuel  
23 switching will change these exposures, requiring the linkage between quantitative exposure  
24 assessments and health effects. The pathways of potential human exposure include each of  
25 the media (i.e., air, water, food, and soil) as well as accidents related to use (e.g., spilling  
26 on hands during refueling or accidental ingestion). Occupational exposures and effects are  
27 also of interest because they will be altered as a result of fuel switching. They are not part  
28 of this Research Strategy, however, because it focuses on environmental exposures and  
29 impacts and emphasizes exposures via the atmosphere because such exposures will be  
30 widespread and could, therefore, potentially affect the entire populace.

1       Exposures from accidental swallowing are expected to have a major health impact  
2 because of the possibility of very high doses, even though relatively few individuals are  
3 likely to be exposed via this route. In the case of methanol, which is acutely toxic, the  
4 consequence of exposure can be severe. A significant amount of information on this topic is  
5 available for conventional gasoline. This Strategy identifies the need for a quantitative  
6 exposure assessment of accidental ingestion scenarios to evaluate the magnitude of their  
7 potential risks.

8       Dermal exposure during refueling is expected to be very infrequent for any given  
9 individual. The frequency and potential risks of such exposures must be assessed more  
10 quantitatively before further research needs can be identified. Some individuals use fuels as  
11 solvents and degreasers, raising the potential for dermal exposures; but relative to other types  
12 of exposures, few individuals are assumed to be involved. Because only some fuels are  
13 effective degreasers, this route of exposure is of only minor general concern. Because the  
14 toxicity is poorly defined and the doses involved could be high, however, the potential for  
15 exposures and health effects needs to be assessed. Research on this topic must await the  
16 results of such an assessment.

17       Oral exposure through water, as a result of groundwater contamination, or through  
18 food, as a result of contamination of organisms in the food chain or of plant foodstuffs  
19 through atmospheric deposition, is possible and, hence, must be considered. The potential  
20 for such exposure is poorly understood, however, creating a need for results of the research  
21 on source characterization and fate before exposure assessment (and health effects) research  
22 can be designed. Exposure assessment research on drinking water and food contamination is  
23 deferred and not discussed further in this Strategy. However, the potential for food-chain  
24 contamination needs to be evaluated in the ecosystem effects research program.

25       In summary, initial human exposure assessment research in this Research Strategy will  
26 focus on inhalation exposures. As potential exposures via other routes are assessed based on  
27 available data (dermal and accidental oral exposures) and future data (water and food  
28 exposures), this focus may be expanded. The key elements to be considered are: ambient  
29 air, including urban, rural, remote, and point sources; microenvironment exposures,  
30 including private and public parking garages; localized microenvironments and in-transit

1 exposure; and exposure modeling. The focus of exposure research activities in relative order  
2 of importance is to (1) characterize and validate modeled estimates of maximum exposure;  
3 (2) obtain additional data including activity patterns, food and water exposure, and total  
4 exposure measurements; (3) measure air quality; and (4) enhance exposure models. These  
5 priorities are based on needs to provide estimates of exposure for human health, to provide  
6 links between emissions and health, and to improve exposure estimates. This program needs  
7 to interact with the health effects program, to ensure that exposure assessments are developed  
8 for those pollutants of greatest potency and that dose-response health effects studies are  
9 conducted using probable exposure levels of pollutants likely to be encountered. The  
10 research activities associated with microenvironmental studies, atmospheric studies, exposure  
11 modeling, and oral exposures are detailed below.

12  
13 ***Microenvironmental Studies.*** Carbon monoxide exposure studies have identified  
14 various scenarios in which the public might be significantly exposed to this pollutant by  
15 mobile source emissions, either directly or indirectly. The scenarios included public and  
16 private parking garages and in-transit exposures. As expected, exposures varied according to  
17 the factors known to affect emissions (e.g., speed, temperature, and elevation). In some  
18 systematic way, the same microenvironments should be studied under the same or similar  
19 conditions, to the extent that prototypes allow, in order to compare and contrast the pollutant  
20 concentrations from vehicles using alternative fuels with those from vehicles using  
21 conventional fuels.

22  
23 ***Ambient Air.*** The primary focus of ambient air studies should be to characterize the  
24 impact of alternative fuels on populations exposed to O<sub>3</sub>. Atmospheric fate research should  
25 provide data for assessing O<sub>3</sub> exposures in both urban and rural settings. This fate research  
26 should also characterize air toxics, such as formaldehyde, acetaldehyde, DMS, and PAN,  
27 that would require future exposure assessment. For example, ambient air exposures to  
28 formaldehyde could change as a result of increased methanol use; such a change should be  
29 quantified for a benefits analysis. The objective in all cases would be to compare changes in  
30 ambient air exposures.

1       **Exposure Modeling.** The goal of any exposure modeling effort would be to develop  
2 and validate exposure models to estimate the sources, transport and fate, pollutant  
3 concentrations, and interaction of emission products with human activity patterns for use in  
4 the development of exposure assessments that can be used in risk assessments. The current  
5 model used to generate the potential exposures for methanol-fueled automobiles, the modified  
6 National Ambient Air Quality Standards (NAAQS) Exposure Model (NEM), has not been  
7 evaluated for use as an adequate predictor of exposures resulting from automotive emissions,  
8 nor has it been validated for conventional fuels. The exposure research should begin to  
9 address this need by ensuring that the current NEM and exposure scenarios can be evaluated  
10 and validated using conventional fuels, at least for the worst-case predictions. If it can, then  
11 further model refinement and/or development would not be warranted in the near future.  
12 Otherwise, further model work would be required. In addition, studies of time patterns of  
13 people likely to be in contact with the maximum exposures must be undertaken so that health  
14 risks can be better determined. This information is common to all fuel choices.

#### 16       **1.4.1.3.2 Biota Exposure Assessment**

17       **Terrestrial Ecosystem Exposure.** The primary issue for terrestrial ecosystem exposures  
18 is the change in air quality. Although other types of exposure (e.g., contaminated water)  
19 may also present a risk, they are of secondary concern. Both direct (ambient air), especially  
20 rural, and indirect (wet/fog and dry deposition) exposures are of high interest. The source  
21 characterization and atmospheric fate research would provide information on changes in the  
22 ambient air and deposition of alternative fuel pollutants compared with conventional fuel  
23 pollutants. The ambient air exposure assessment research should focus on O<sub>3</sub>, due to its  
24 known adverse phytotoxicities. Other pollutants of interest include NO<sub>2</sub> and air toxics (e.g.,  
25 formaldehyde and acetaldehyde); their specific identities and quantities will depend upon the  
26 specific fuel. Key elements include monitoring and modeling of exposure patterns to  
27 terrestrial ecosystems, with a focus on sensitive vegetation, which would require research on  
28 terrestrial plant exposure and effects. For exposures via atmospheric deposition processes,  
29 the primary approach should be to apply models such as those developed as part of the  
30 National Acid Precipitation Assessment Program and other multimedia compartmental

1 models. These models can evaluate pollutant emission patterns, environmental partitioning,  
2 and vegetation exposure scenarios to determine the risks posed to terrestrial ecosystems  
3 resulting from fuel switching.

4  
5 ***Aquatic Ecosystem Exposure.*** Aquatic exposure assessments need to include fuel  
6 spills, chronic inputs of fuels, and wet and dry intermittent deposition inputs of combustion  
7 and emission products to freshwater, estuarine, and marine ecosystems. Research on source  
8 characterization and multimedia environmental fate must be integrated with information on  
9 the habitat and characteristics of the populations of organisms at risk, considering the  
10 requirements of effects models to be used in the risk assessment. Depending upon the nature  
11 and level of detail of the desired risk assessment, this final exposure characterization may  
12 address various factors. Aquatic populations at risk must be identified and their  
13 microenvironments must be specified so that appropriate environmental concentrations can be  
14 derived from source characterizations and environmental fate models. The computed  
15 environmental exposure must be compatible with effects models, providing information, as  
16 needed, on average environmental concentrations, time dependence of exposure, multiple  
17 routes of exposures, bioavailability, and environmental attributes that may affect toxic  
18 response. For some fuel components, food-chain transfers must also be considered.  
19 Depending upon the effects models to be applied, characterization of the populations and  
20 individuals at risk may also include attributes that regulate toxicokinetics and toxicodynamics.

21 In addition to such prospective exposure assessments, attempts should be made to assess  
22 exposure in field situations, so as to provide some directly usable empirical information and  
23 to assist model development. Both retrospective examination of past spills and participation  
24 in monitoring of future spills and chronic contamination should be considered. Such  
25 retrospective evaluation could also be used to empirically assess exposure of aquatic systems  
26 to contamination from fuel feedstock production.

#### 27 28 **1.4.1.4 Global Climate Impacts**

29 Global climate research and risk assessments are described in a separate EPA research  
30 strategy; however, feedstock and fuel production, and the transport, storage, and use of fuels

will result in emission of RITGs, which may influence global climate. Characterizing changes in emission rates of such RITGs associated with fuel switching is within the purview of the Alternative Fuels Research Strategy (Table 1-3). Research on stationary and mobile source characterization of air emissions and atmospheric fate will produce data on numerous compounds, including those that are radiatively important, such as methane, CO<sub>2</sub>, and N<sub>2</sub>O. The data on RITGs will be transferred to EPA's Global Climate Research Program, so that the evaluation of global climate effects can incorporate fuel-related impacts.

**TABLE 1-3. SUMMARY OF RADIATIVELY IMPORTANT GASES IMPACTED BY ALTERNATIVE FUEL USE**

| Gas  | Primary Lifetime, Years       | Anthropogenic Sources   | Indirect Effects on Chemistry of             |                                  |
|--|-------------------------------|---|--|----------------------------------|
|  |                               |   | Troposphere                                  | Stratosphere                     |
| Carbon dioxide                               | 500<br>(air-biosphere-oceans) | Fossil fuel burning; land use conversion  | None   | O <sub>3</sub>                   |
| Methane                                      | 7 - 10                        | Domestic animals; rice paddies; biomass burning; natural gas production, distribution, and use; coal mine leaks | OH, CO, and O <sub>3</sub>                   | H <sub>2</sub> O, O <sub>3</sub> |
| Carbon monoxide                              | 0.4                           | Energy use; agriculture; forest clearing  | OH, CH <sub>4</sub> , and O <sub>3</sub>     | Not sig.                         |
| Nitrous oxide                                | 150                           | Fossil fuel burning; cultivation and fertilization of soils   | None   | O <sub>3</sub>                   |
| Nitrogen oxides<br>(= NO + NO <sub>2</sub> ) | ≤0.02                         | Fossil fuel burning; biomass burning  | OH, CO, CH <sub>4</sub> , and O <sub>3</sub> | O <sub>3</sub>                   |
| Ozone (tropospheric)                         | <0.1                          | Photochemical transformation of NO <sub>x</sub> and VOCs  | Many species                                 | Many species                     |

Source: Adapted from Wuebbles et al. (1989).



#### 1.4.1.5 Analytical Methodology

Analytical procedures will be required to support characterization of emissions from sources using alternative fuels, to monitor the atmospheric transport and transformation of these emissions, and to monitor population/ecosystem exposures to associated compounds. Source emissions characterization will require accurate, precise methodologies for the sampling and analysis of many compounds in complex mixtures, the composition of which can vary dramatically with source and fuel specifications. Classical vehicular certification procedures for total hydrocarbon, CO, CO<sub>2</sub>, NO<sub>x</sub>, and total PM must be reexamined and modified, if necessary, to assure adequate performance with the varied alternative fuels at concentrations dictated by new emission standards. Procedures for new compounds of interest (e.g., methanol, ethanol, methane, MTBE, formaldehyde, acetaldehyde, and others) must be developed and/or validated. "Real-time" continuous analyzers for examination of transient emissions will also be required. Air monitoring systems must be compatible with widely variant possible climatic conditions. Human exposure monitoring will require passive sampling devices that cause little interference with normal activity patterns, and possibly the measurement of metabolites and/or biomarkers. The procedures must provide selective, accurate measurements that are free of artifactual chemistry and that can be used for very complex mixtures that often include oxidants such as O<sub>3</sub>, NO<sub>2</sub>, and hydrogen peroxide.

#### 1.4.2 Effects Assessment

The character and magnitude of the effects of conventional fuel pollutants on human health and ecosystems are expected to change with increased use of alternative fuels. Evaluating the net change in effects is a complex undertaking. For example, assume that ambient air O<sub>3</sub> levels decrease, accruing benefits to public health and terrestrial ecosystems, but that microenvironmental exposures to a given air toxic increase to the point where an adverse effect can be expected. Insofar as the change in multiple categories of risks can be quantitatively assessed, they will need to be compared and the relative trade-offs in risks will need to be evaluated.

A plethora of health and ecosystem studies are possible, given the large number of individual compounds and mixtures involved, exposure scenarios, subpopulations that may be

1 exposed, and effects that might be produced. Scientific needs must be ranked to produce a  
2 feasible and efficient research program. To this end, a decision-tree analysis can be applied  
3 to the hazard identification and dose-response elements of effects assessment, in concert with  
4 progressive levels of research on exposure assessment. In the broadest sense, this involves  
5 first completing the hazard identification phase through either new research or evaluation of  
6 existing literature (depending on the state of knowledge) and evaluating the hazards in light  
7 of a preliminary exposure assessment data. This process will help indicate whether effects  
8 are possible or likely as a result of various exposure scenarios. Developing such an  
9 understanding will be an interactive process between exposure and effects research.

10       Once the hazard identification phase is completed, the results must be evaluated to  
11 decide whether to pursue the findings through dose-response assessment and full exposure  
12 assessment to reach a quantitative risk assessment. Criteria for reaching judgments would  
13 include, but not be limited to, the following: (1) the severity of the effects; (2) the size of  
14 the population potentially affected; (3) the risk potential of conventional fuels appears to be  
15 substantially different from those of alternative fuels; or (4) major investments in risk  
16 prevention/reduction appear necessary to reduce risks.

17       A complicating feature of effects research on fuel-related pollutants is the issue of the  
18 study of individual compounds vs. the study of complex mixtures. An exposure to a  
19 complex mixture will ultimately be responsible for the effects; however, knowledge of the  
20 effects of key constituents of a mixture can assist in understanding the effects of the mixture.  
21 Because the number of mixtures and individual compounds is too large to make complete  
22 study feasible, a balanced approach in concert with exposure assessment is required. The  
23 general approach, utilized in this Strategy, will be to focus first on chemicals or mixtures  
24 with known effects that cannot be easily interpreted in terms of application to public health  
25 and environment. Secondly, effects evaluations for chemicals with no or less certain data,  
26 relative to hazard, will be expanded to additional chemicals and mixtures as the exposure  
27 evaluations dictate (including likely market share penetration). For example, the evaluation  
28 of the developmental risks of the methanol is a high priority, whereas the evaluation of DMS  
29 will be postponed for improved exposure analyses. This broad approach requires some  
30 major exceptions, which will be addressed in the subsequent fuel-specific discussions.

1       The discussion that immediately follows is categorized into human health effects and  
2       ecosystem effects. Because the scope of each is relatively large, details are reserved for the  
3       fuel-specific chapters.

#### 5       **1.4.2.1 Human Health Effects**

6       The goal for health research is to provide a scientific basis for comparative,  
7       comprehensive, quantitative health risk assessment between alternative fuels and conventional  
8       fuels. The collection of adequate data is the first important step towards developing the  
9       health assessment component of a comprehensive risk assessment. In addition, the  
10      development of health assessment methods (e.g., biologically-based dose-response models)  
11      with which to assess the data are also necessary. Table 1-4 is based on a review of the  
12      current literature and depicts the types of health effects that could occur following exposure  
13      to fuel-related air pollutants. Although this table indicates that pollutants known to be  
14      associated with fuels can cause carcinogenic and noncarcinogenic effects, several of these  
15      effects are poorly understood and, for many, exposure-response relationships are unknown.  
16      Also, because emissions and atmospheric transformation products have not been adequately  
17      characterized, chemically or toxicologically, this table is far from complete. It should be  
18      noted that O<sub>3</sub>, NO<sub>2</sub>, and CO have been reviewed elsewhere and are the subject of other  
19      research programs. Therefore, they are not directly addressed in this Research Strategy, but  
20      would be incorporated into any comprehensive risk assessment of fuels.

21      To be most useful, alternative fuels health effects research should be designed to  
22      address the exposure scenarios (estimated concentrations and exposure durations) that are  
23      expected to occur in ambient air and microenvironments (e.g., personal garages).  
24      Consequently, health effects associated with repeated acute and chronic low-level exposures  
25      are of particular interest. Inhalation is the most likely route of human exposure and therefore  
26      should be emphasized. The extent to which consideration is given to other routes (i.e.,  
27      ingestion of fuels, dermal exposures to spilled fuel) will depend upon the results of exposure  
28      assessments.

29      Research efforts should proceed in a step-wise fashion. In general, these steps should  
30      include replication of published results, development of pharmacokinetic models (to aid in the

**TABLE 1-4. TYPES OF POTENTIAL INHALATION HEALTH EFFECTS OF INDIVIDUAL CHEMICALS OR COMPLEX MIXTURES RELATED TO CONVENTIONAL AND ALTERNATIVE FUELS USE<sup>a</sup>**

| Compound <sup>b</sup>   | Status of Data Base <sup>c</sup> | Types of Potential Effects <sup>d</sup>  | Susceptible or At-Risk Subpopulations                     |
|---|----------------------------------|--|---|
| <b>I. Alternative Fuels and Extenders</b>                     |                                  |  |   |
| Methanol  | ++                               | Neurobehavioral impairments; reproductive toxicity; developmental toxicity; other systemic effects | Children; folate-deficient people; adult males; fetuses   |
| Ethanol   | +                                | Neurobehavioral impairments; developmental toxicity; reproductive hormone decrements               | Children; adult males; fetuses                            |
| CNG   | +                                | Simple asphyxiant  | Not yet identified  |
| MTBE  | +                                | Neurotoxicity, other systemic effects  | Not yet identified  |
| ETBE  | 0                                |  |   |
| Gasoline-alcohol blends                                       | +                                | Developmental effects plus gasoline effects  | Not yet identified  |
| <b>II. Complex Mixtures of Conventional Fuels</b>             |                                  |  |   |
| Gasoline combustion emissions with or without UV irradiation  | +                                | Respiratory tract effects  | Not yet identified  |
| Gasoline evaporative emissions                                | +                                | Carcinogenic and noncarcinogenic effects   | Not yet identified  |
| Diesel combustion emissions                                   | +++                              | Class B2 carcinogen; respiratory tract effects   | Not yet identified  |
| <b>III. By-Products of Alternative and Conventional Fuels</b> |                                  |  |   |
| Formaldehyde  | ++                               | Class B1 carcinogen; lung irritation and hypersensitivity  | Asthmatics (for lung effects)                             |
| Other aldehydes   | ++                               | Some are carcinogens (e.g., acetaldehyde is B2 carcinogen); lung irritation and hypersensitivity   | Asthmatics (for lung effects)                             |
| NO <sub>x</sub>   | ++++                             | Lung function and structure changes; respiratory infections  | Children; exercising people; asthmatics                   |
| O <sub>3</sub>  | ++++                             | Lung function and structure changes; respiratory infections  | Exercising people; those with preexisting lung disease    |
| CO  | ++++                             | Cardiovascular effects   | People with preexisting heart or obstructive lung disease |
| PAN   | ++                               | Eye irritation; lung function decrements; potential carcinogenic effects                           | Not yet identified  |
| DMS (methanol fuel)   | +                                | Class B2 carcinogen; irritation; systemic toxicity   | Not yet identified  |
| Benzene   | +++                              | Class A carcinogen; hematopoietic changes  | Not yet identified  |
| 1,3-Butadiene   | ++                               | Class B2 carcinogen  | Not yet identified  |

<sup>a</sup> Note that the exposures to some of the compounds will increase, and exposures to others will decrease. See the section on mobile source characterization in fuel-specific chapters for a discussion of possible directional changes.

<sup>b</sup> Abbreviations: CNG = compressed natural gas; MTBE = methyl-tertiary-butyl ether; ETBE = ethyl-tertiary-butyl ether; UV = ultraviolet; NO<sub>x</sub> = nitrogen oxides; O<sub>3</sub> = ozone; CO = carbon monoxide; PAN = peroxyacetyl nitrate; DMS = dimethyl sulfate.

<sup>c</sup> +++++ extensive information available; + limited information; 0 no information.

<sup>d</sup> See health effects discussion in fuel-specific chapters for a more detailed presentation and exposure scenarios that might cause these effects.

1 interpretation of these results), additional investigation of identified hazards, development of  
2 biologically-based dose-response models, and determination of human relevance, as  
3 warranted. Initially, shorter-term studies should be used to focus subsequent in-depth  
4 studies. When the health and exposure data bases are sufficiently developed to adequately  
5 guide the design of studies, then chronic bioassays should be conducted for those fuels  
6 associated with significant market penetration. Chronic bioassays are needed in order to  
7 identify possible additional health effects and to help determine risks from long-term  
8 exposures. In conjunction with animal studies, human clinical studies (when ethically  
9 feasible) and epidemiologic data can provide invaluable additional information concerning  
10 human responses and appropriate extrapolation of animal data to humans. Field studies, such  
11 as the EPA's Integrated Air Cancer Project, also would be of value in linking actual sources  
12 with transport and fate of chemicals, resulting exposures, and biological effects. To study  
13 conventional fuels and alternative fuels, possible target areas or populations of interest for  
14 field studies might be a city before and after fuel switching and/or cohorts with personal-  
15 garage exposures. Insofar as feasible, these studies would include identification and  
16 characterization of sensitive subpopulations.

#### 18 ***1.4.2.1.1 Criteria for Ranking Research Issues***

19 The variety of fuels, pollution sources, exposure scenarios, and health effects, as shown  
20 in Table 1-5, will result in a large matrix of health effects research issues. A strategy is  
21 needed to rank these issues in order to develop a research plan. The planned research then  
22 can provide the data necessary for comprehensive quantitative risk assessment in the most  
23 efficient manner. The general criteria used for setting the health research priorities described  
24 in this document are as follows:

##### 25 (1) Pollutants for study:

- 26
- 27 • focus on chemicals specifically identified in the CAAA, particularly
- 28 Title II;
- 29 • focus on agents/mixtures with greatest exposure potential, with evidence
- 30 of potential exposure a prerequisite to initiation of health research.
- 31
- 32

**TABLE 1-5. IMPORTANT CONSIDERATIONS FOR DETERMINING  
AND PRIORITIZING HEALTH RESEARCH NEEDS TO ASSESS THE  
HEALTH RISKS OF ALTERNATIVE FUELS**

| Fuels   | Pollution Sources  | Human Exposure Scenarios  | Health Effects   |
|---|--|---|--|
| <ul style="list-style-type: none"> <li>• Conventional Fuels (Baseline)</li> <li>• Methanol</li> <li>• Ethanol</li> <li>• Compressed Natural Gas</li> <li>• Reformulated Gasoline</li> </ul> | <ul style="list-style-type: none"> <li>• Fuel Production By-Products and Emissions</li> <li>• Fuel Transportation and Distribution</li> <li>• Evaporative Emissions</li> <li>• Combustion Emissions</li> <li>• Atmospheric Transformation</li> </ul> | <p align="center"><b><u>Inhalation</u></b></p> <ul style="list-style-type: none"> <li>• Occupational</li> <li>• Ambient <ul style="list-style-type: none"> <li>-long-term</li> <li>-short-term</li> </ul> </li> <li>• Microenvironments <ul style="list-style-type: none"> <li>-parking garages</li> <li>-street canyons</li> <li>-tunnels</li> <li>-inside vehicle</li> <li>-refueling</li> </ul> </li> </ul> <p align="center"><b><u>Dermal</u></b></p> <ul style="list-style-type: none"> <li>• Incidental or Accidental Contact</li> </ul> <p align="center"><b><u>Ingestion</u></b></p> <ul style="list-style-type: none"> <li>• Accidental Swallowing</li> <li>• Contaminated Drinking Water</li> </ul> | <ul style="list-style-type: none"> <li>• Cancer <ul style="list-style-type: none"> <li>-genetic</li> <li>-nongenetic</li> </ul> </li> <li>• Noncancer <ul style="list-style-type: none"> <li>-respiratory</li> <li>-developmental</li> <li>-reproductive</li> <li>-neurologic</li> <li>-hepatic</li> <li>-immune system</li> <li>-other</li> </ul> </li> </ul> |

(2) Relevance to the real world:

- inhalation route of exposure,
- relevant exposure scenario(s),
- whole mixtures and key components of mixtures,
- implications for potentially affected human (sub)populations.

(3) Efficient use of resources:

- make maximum use of existing data,
- emphasize currently identified potential health effects,
- use short-term studies as building blocks for subsequent in-depth analyses,
- provide useful intermediate products (e.g., information helpful in making qualitative risk assessments before quantitative risk assessments are possible).

When the above criteria are applied to the existing data base on conventional and alternative fuels and their combustion and transformation products, high priority and potentially high priority fuels, fuel components and related agents can be identified (Table 1-6). In addition, general research priorities emerge. These priorities are: (1) development of pharmacokinetic data and models; (2) evaluation of dose-response relationships and implications for human health for compounds with clearly identified effects; and (3) development of health data needed to evaluate individual chemicals and/or mixtures for which substantial exposures are predicted, but health data are limited or nonexistent. These general research priorities are discussed in more detail below, and are reiterated as fuel-specific research needs in the respective sections of this document. (See Table 1-7 for an overview of the process of translating assessment and research needs into a research program.)

**1.4.2.1.2 First Priority—Pharmacokinetic Evaluations**

The development of pharmacokinetic data and models is needed (a) to facilitate the interpretation of existing data, particularly when extrapolation is needed (e.g., route-to-route, interspecies, high-to-low dose); (b) to guide the design of additional research by identifying likely target organs and the appropriate experimental species; and (c) to support exposure-response assessment by estimation of dose to target tissues. Development of these data and

**TABLE 1-6. CURRENTLY IDENTIFIED FUELS, FUEL COMPONENTS, AND RELATED AGENTS**

| <b>A. High Priority</b>  |  |   |  |
|--|--|---|--|
| Conventional Fuels   | Methanol   | Ethanol   | Reformulated Gasoline  |
| <ul style="list-style-type: none"> <li>• Benzene</li> <li>• 1,3-Butadiene</li> <li>• POMs</li> <li>• Gasoline Vapor</li> <li>• Combustion/Transformation Mixtures</li> </ul> | <ul style="list-style-type: none"> <li>• Methanol</li> <li>• Formaldehyde</li> <li>• Dimethyl Sulfate</li> <li>• Evaporative Mixtures</li> <li>• Combustion/Transformation Mixtures</li> </ul> | <ul style="list-style-type: none"> <li>• Ethanol</li> <li>• Acetaldehyde</li> <li>• Evaporative Mixtures</li> <li>• Combustion/Transformation Mixtures</li> </ul> | <ul style="list-style-type: none"> <li>• MTBE</li> <li>• ETBE</li> <li>• Evaporative Mixtures</li> <li>• Combustion/Transformation Mixtures</li> </ul> |
| <b>B. Potentially High Priority</b> <sup>*</sup>   |  |   |  |
| Acetaldehyde   | Dibenzofurans  | Methyl ethyl ketone   |  |
| Acetonitrile   | Diethyl sulfate  | Naphthalene   |  |
| Acrolein   | 1,4-Dioxane  | Phenol  |  |
| Acrylic acid   | Ethyl benzene  | Propionaldehyde   |  |
| Carbon disulfide   | Ethylene dibromide   | Styrene   |  |
| Carbonyl sulfide   | Ethylene dichloride  | Toluene   |  |
| Catechol   | Hexane   | 2,2,4-Trimethylpentane  |  |
| Chlorine   | Metals (Fe, Cu, Se,  | Xylenes   |  |
| Cresols/Cresylic acid (isomers and mixture)  | Pt, Ce, Mg)  |   |  |

\* Chemicals identified in vehicle-related emissions that are listed in Title III—Hazardous Air Pollutants or are part of the Air Toxics Study mandated in Title II—Mobile Sources of the Clean Air Act. In general, limited information currently exists for health and/or exposure.

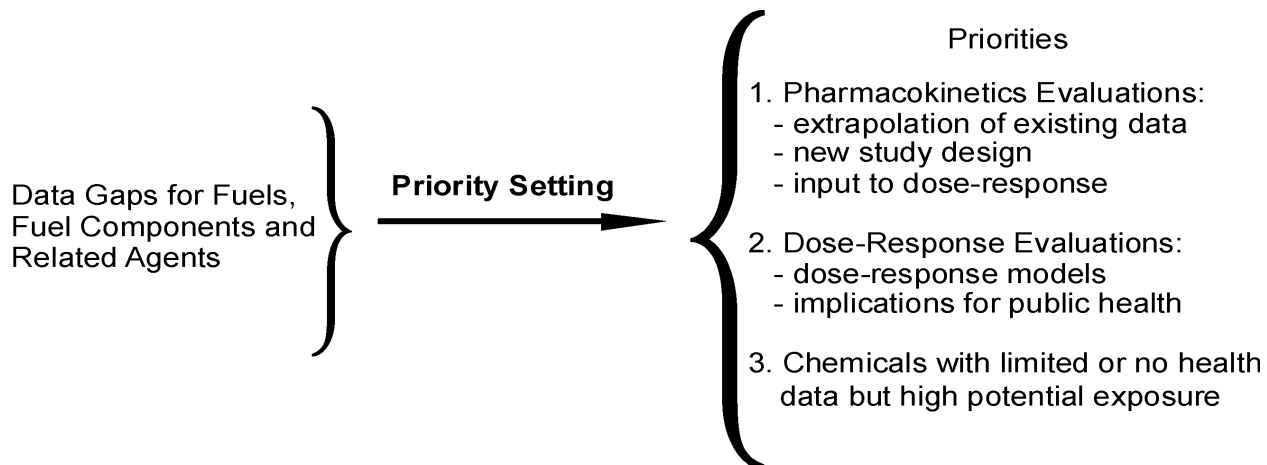
models are basic to all elements of the proposed research because of their utility in the interpretation of data for risk assessment purposes, particularly when extrapolation is needed. Pharmacokinetic research and model development should be coupled to health effects research and dose-response model development.

#### **1.4.2.1.3 Second Priority—Dose-Response Evaluations**

An understanding of dose-response relationships, including the implications for public health, is needed for estimating risks posed by alternative fuels relative to conventional fuels. For individual fuels, the highest priority research need is the development of dose-response



**TABLE 1-7. TRANSLATING IDENTIFIED ASSESSMENT AND RESEARCH NEEDS  
INTO A RESEARCH PROGRAM**



data and biologically-based dose-response models (BBDR). The development of BBDR models will require information in two major research areas: determinations of mechanism of action, and comparisons of disease initiation and progression between experimental animals and humans in order to appropriately extrapolate dose-response evaluations to humans.

Due to the complexity of combustion and transformation mixtures, the initial screening for these mixtures should be based on vehicle classes and operating conditions, using in vitro and short-term in vivo assays. These assays will be used to estimate the relative potencies of the various mixtures to induce health effects and, thereby, to focus on the vehicles and operating conditions of greatest concern. Short-term assays (in conjunction with improved estimates for emissions, exposure, and market penetration) will determine the need for chronic bioassays for combustion and transformation products. Additionally, if effects and potencies are noteworthy, based on screening results, then bioassay-directed fractionation should be used to identify components within a mixture that are associated with mutagenicity or toxicity. Subsequent to this screening effort, the research needs for the combustion and transformation products are similar to those for the individual fuels. Based on current

literature, the following endpoints are emphasized for alternative fuels: noncancer health effects, such as developmental and nervous system effects, for evaporative and uncombusted tailpipe emissions; and cancer and respiratory system effects, including pulmonary immune system effects, for combustion and transformation products. Evaluation of the health effects associated with various exposure scenarios also will be necessary.

#### ***1.4.2.1.4 Third Priority—Evaluation of Chemicals with Limited Health Data***

Data are needed to identify the potential hazards posed by chemicals and/or mixtures for which exposures are predicted to be substantial but for which health data are limited or nonexistent. This effort will, in some cases, increase confidence that the complex alterations in the environment, brought about by changes in fuel use, will not adversely impact public health. In other cases, chemicals will be identified for more in-depth evaluations. Table 1-6 lists the chemicals that have been measured in vehicle emissions that are also listed in Title III (provisions relating to hazardous air pollutants) of the CAAA. Chemicals on this list should be evaluated for potential health effects, as warranted, based on proposed assessments of emissions and exposures.

#### ***1.4.2.1.5 Summary***

In summary, the current health research priorities for the alternative fuels considered here are: (1) development of pharmacokinetic data and models; (2) development of dose-response data and models for chemicals with clearly identified adverse effects; and (3) collection of health data needed to identify the potential hazards posed by individual chemicals and/or mixtures for which health data are limited or nonexistent. The assessment of non-cancer health effects associated with evaporative and uncombusted emissions, and cancer, respiratory and pulmonary immune system effects associated with combustion and transformation products are emphasized. Evidence of exposure is a prerequisite to conducting health research. Inhalation is the primary route of concern.

Research on currently identified chemicals and mixtures should be guided by relevance to the real world and efficient use of resources. In particular, the research should: (1) allow maximal use of existing data and optimization of designs for future health effect studies,

(2) identify endpoints of greatest concern for human health, and (3) evaluate the exposure-response relationships for these endpoints as they relate to humans. The results of this health research will be integrated with those of exposure assessments in order to characterize the risk posed by alternative and conventional fuels. These results will provide support to the EPA's Office of Mobile Sources in their evaluation of the potential public health impacts associated with different exposure scenarios.

#### **1.4.2.2 Ecosystem Effects**

Ecosystem effects research should also follow a decision-tree dichotomy, similar to that for health effects research. Research should begin with hazard identification, unless adequate information on ecosystem effects is already available in the literature. If initial exposure predictions coupled with hazard identification information indicate biota/ecosystem changes of interest, then research should proceed to the exposure-response phase. The criteria pollutants are major exceptions. Although they are of primary importance (especially O<sub>3</sub>, given its effects on plants), ecosystem effects research on the criteria pollutants is already part of EPA's base program. Some interactions of the criteria pollutants, especially O<sub>3</sub>, and pollutants related to alternative fuels, however, are of interest to this Strategy. As discussed earlier, this Strategy includes a major emphasis on plant exposure assessments for O<sub>3</sub> (and other oxidative pollutants) to enable risks of alternative fuels to be compared to those of conventional fuels. Due to the major differences in types of ecosystems, the discussion below is categorized according to terrestrial and aquatic (marine and freshwater) systems.

##### ***1.4.2.2.1 Terrestrial Ecosystems Effects***

Terrestrial ecosystems could be affected by at least three different pathways: (1) land-use alterations from feedstock production, (2) chronic and acute exposures to airborne pollutants either directly (ambient air) or by atmospheric deposition processes, and (3) accidental spills/leakage. As discussed earlier, land-use impacts from feedstock production (principally biomass and grain for ethanol) should be the subject of assessments, rather than new research. Terrestrial ecosystem research, therefore, will need to focus on

1 effects resulting from atmospheric exposure and deposition and accidental spills/leakage.  
2 Feedstock production and airborne pollutant deposition and exposure are likely to pose  
3 greater risks to terrestrial ecosystems and biota than accidental spills and, therefore, should  
4 receive the major emphasis.

5       Plants and soils will serve as sinks for airborne pollutant deposition. Vegetal responses  
6 to acute or chronic exposures may include leaf injury, reduced photosynthesis, reduced  
7 reproductive capacity, and reduced community complexity through population reductions.  
8 Possible soil organism responses include population shifts, changes in nutrient cycles, and  
9 effects on plant roots. Pollutant deposition could result in ground-, irrigation-, and  
10 domestic-water contamination. The potential for bioaccumulation will vary with the pollutant  
11 but is not anticipated to be a major problem for most of the pollutants identified thus far.  
12 Trophic transfer could occur by animal consumption of contaminated forage or water.  
13 Chronic deposition may modify wildlife habitats through effects on vegetation. These  
14 potential effects need documentation through exposure-deposition and exposure-response  
15 research. A biomonitoring research project would be beneficial for assessing air quality  
16 impacts on terrestrial ecosystems (e.g., agricultural, forest) as alternative fuels gain  
17 prominence and measured changes in air quality are documented.

18       Accidental spills and tank leakage during fuel transportation to storage or delivery  
19 facilities could acutely expose terrestrial biota to toxic concentrations of alternative fuels.  
20 Acute effects of accidental spills and leakages will be localized, with potentially severe biota  
21 impacts and soil contamination. Vaporization could expose a much larger area to the fuels  
22 themselves, depending upon the prevailing atmospheric conditions and soil infiltration rates.  
23

#### 24 ***1.4.2.2.2 Aquatic Ecosystem Effects***

25       Effects on aquatic ecosystems may arise from fuel feedstock production (mining,  
26 drilling, biomass production), discharges from fuel synthesis facilities, spills and leakages of  
27 fuel to water, and deposition of fuel combustion products. Effects of the production of  
28 various feedstocks have been studied extensively; significant need for new research on these  
29 effects is not anticipated, but available information must be reviewed to assess likely impacts  
30 of increases or decreases of existing feedstock production activities that would occur due to

1 switches to alternative fuels. Fuel synthesis facilities will be regulated under existing  
2 programs, which should minimize risk to aquatic ecosystems; however, research on the  
3 toxicity of likely effluents is needed to define treatment requirements and, thus, costs. The  
4 toxicity and bioaccumulation potential of chemicals expected from atmospheric deposition  
5 must be reviewed to provide effects data needed for the risk assessment.

6 The effects of spills from fuel storage and transportation systems represent a high  
7 research priority. Although a rare event within the broad scope of the fuel distribution  
8 system, spills of conventional fuels affect aquatic communities frequently enough to be of  
9 significant concern; and effects of these spills would be expected to change markedly with  
10 switches to alternative fuels. Fuel-related pollutants may influence aquatic ecosystems  
11 directly and indirectly. These compounds, in sufficient quantities, could cause acute effects  
12 to sensitive life stages of many aquatic organisms. Depending on severity, these effects  
13 could deplete or drastically alter communities. Secondary effects of the spilled compounds  
14 could also cause damage through the production of toxic metabolites resulting from  
15 biodegradation. In addition, microbial enrichment associated with the biodegradation of the  
16 fuel could deplete oxygen levels, resulting in indirect toxic effects to the biota. Some fuel  
17 compounds may also influence the behavior or toxicity of other organic contaminants already  
18 present in aquatic systems. For example, organic compounds such as polychlorinated  
19 biphenyls and polycyclic aromatic hydrocarbons could be released from sediments and  
20 particulate material and be redistributed within the water column, possibly increasing their  
21 availability and toxicity to biota, due to the solvent properties of alcohols.

22 Available effects information must be used in developing preliminary risk assessments,  
23 which in turn are expected to show a need for better dose-response relationships for most  
24 fuels. Laboratory tests of the acute toxicity of fuels to aquatic organisms representative of  
25 species at risk should be conducted to develop kinetic-based toxicity models appropriate for  
26 predicting the lethality of fuel spills to aquatic systems. Chronic testing may also be needed,  
27 as justified by preliminary risk assessments performed in conjunction with the exposure  
28 assessment screening process. Studies using experimental aquatic ecosystems will be needed  
29 to determine the extent and persistence of community-level effects of fuel spills. To the  
30

1 extent possible, documented observations and effects of actual spills will be used to validate  
2 ambient exposure and dose-response models derived from experimental systems.  
3

### 4 **1.4.3 Scientific Assessments**

5 The CAAAs require several regulatory decisions based on compendiums and  
6 evaluations of certain sets of information. Also, the AMFA requires a report to Congress  
7 every two years, beginning December 1990, on an analysis of air quality, global climate  
8 change, and other environmental impacts, including health and ecosystem risks, of alternative  
9 fuels compared to conventional fuels. Development of this report is managerially  
10 independent from the Research Strategy. Strong scientific interrelationships exist, however,  
11 because the goal of the Strategy is to provide empirical information to enhance the  
12 quantitative nature of the comparative risk assessments of fuels.

13 For research data to be useful to policy makers, all relevant information must be  
14 evaluated and synthesized into scientific assessments. To these ends, ORD will need to  
15 develop several classes of assessments, which may be arbitrarily defined as follows:

- 16 • Major Assessments. These encompass a broad topic, such as the health and  
17 ecosystem effects of conventional gasoline, methanol fuels, etc.  
18
- 19 • Specific Topic Assessments. These are more narrowly defined and are intended to  
20 evaluate existing information to characterize the need for future research to meet a  
21 particular mandate, or to identify the need for more regulatory attention. Examples  
22 include: human health risk assessment of accidental ingestion of fuels, especially by  
23 children; characterization of accidental spills/leakages into terrestrial and aquatic  
24 ecosystems; assessment of land-use impacts from mining, drilling, and biomass  
25 production, and of their projected changes with various fuel feedstock options.  
26
- 27 • Research Impact Reports. Over the course of the research program, major research  
28 results, typically published as independent studies within the peer-reviewed  
29 literature, must be incorporated into assessments in the most timely and useful way  
30 for regulatory decision-making. For example, as major increments of data  
31 regarding the O<sub>3</sub>-forming potential of emissions from feedstock and fuel production,  
32 storage, distribution, and use become available, interim human and ecosystem risk  
33 assessments of O<sub>3</sub> will be needed. As data from source assessment and fate  
34 research become available, human and ecosystem exposure assessments will be  
35 needed to provide guidance in designing effects research. Another major issue is  
36

1 the possibility of drinking water contamination; if it occurs, health dose-response  
2 research and/or assessments may be required.  
3

4 The examples provided above do not constitute a complete listing, but they do indicate  
5 the types of scientific assessments needed. Ultimately, EPA regulatory decisions are based on  
6 EPA assessments; however, in developing these assessments, ORD examines all relevant  
7 data, much of which is expected to come from non-EPA sources. Thus, a major role exists  
8 for other interested organizations to play in the development of assessments.  
9

#### 10 **1.4.4 Risk Prevention/Mitigation**

11 As a potential adverse risk to human health, ecosystems, or global climate is identified,  
12 prevention and mitigation strategies may be developed to prevent adverse risks from  
13 presenting a barrier to an otherwise attractive fuel option. The discussion that follows is  
14 categorized according to the source (i.e. stationary, mobile, fuel transport) of the exposures  
15 to be reduced.  
16

##### 17 **1.4.4.1 Stationary Sources**

18 Stationary source risk prevention/mitigation research will be especially important  
19 because it could enable otherwise environmentally unacceptable fuel technologies to be used.  
20 For example, if producing a fuel results in hazardous emissions that currently are quite  
21 expensive to control, this fuel is less likely to be used, even if its use is environmentally  
22 attractive relative to conventional fuel. Improved control technology or risk prevention  
23 strategies could circumvent such an economic obstacle.

24 The generic approach used for risk reduction will consist of evaluating the potential for  
25 reduced emissions/discharges utilizing prevention and control technologies and practices  
26 applied to each of the processing steps in an energy trajectory and to strategic variations in  
27 the overall energy trajectories. Control technology assessments and research and  
28 development on controls need to include the following: defining the options for the best  
29 control technology, enhancing the effectiveness of existing controls, and developing  
30 innovative controls for maximum risk reduction in problem areas. Prevention technology  
31 will be evaluated from the standpoints of better application of existing prevention measures,

1 development of new prevention measures (such as process modifications), evaluation of  
2 variation in conventional energy trajectories, and entirely new or enhanced processes for fuel  
3 processing and use (e.g., alcohol from municipal waste and wood biomass). The research on  
4 stationary source prevention will be integrated with the work on stationary source  
5 characterization, because the latter depends greatly on the prevention method used. A major  
6 emphasis of the prevention research will be to develop improved approaches for reducing or  
7 preventing unacceptable health, ecosystem, or global warming risks. Although the precise  
8 definition of this research awaits the risk assessment, some issues, such as the need to reduce  
9 emissions of RITGs or O<sub>3</sub> precursors, are of substantial interest and sufficient information is  
10 available to initiate research.

11       Underground storage tanks also need to be a target of risk prevention research as well  
12 as of research on corrective action if a failure occurs. Significant progress in identifying  
13 factors that influence leakage from USTs has been made. These factors include the fuel's  
14 physical state at storage temperatures as well as its melting point, boiling point, specific  
15 gravity, vapor pressure, explosivity, flammability, combustibility, and corrosivity. Research  
16 on prevention of leaks would attempt to obtain this information (where not already known)  
17 and relate it to the adequacy of piping systems and tanks. Issues to be considered include the  
18 compatibility of these fuel factors to construction materials and procedures for inspection,  
19 maintenance, and repair of UST systems.

20       If research and assessments identify a high health or ecosystem risk from UST leaks of  
21 alternative fuels (conventional fuels are already part of the ORD base program), then  
22 research on corrective action and the development of guidance documents will be needed.  
23 Much of the supporting information can be derived from the research on the fate of fuels in  
24 soil; however, fuel-specific research and/or assessments would be needed to evaluate soil  
25 treatment technologies such as vacuum extraction, soil washing, bioremediation, and soil  
26 flushing. Groundwater treatments to be considered include air stripping, activated carbon,  
27 and biological treatment.

28       Feedstock production, especially by large-scale agricultural biomass production or  
29 mining/drilling, can be a significant source of pollutants. However, this aspect of fuel



1 impact is not addressed in the Strategy because it primarily relates to Department of Energy  
2 programs.

#### 4 **1.4.4.2 Mobile Sources**

5 A significant proportion of the U.S. fleet vehicle-miles-traveled is from vehicles as old  
6 as 20 years. Over a period of time, emission control systems deteriorate, emission rates  
7 increase, and emission compositions change. Most urban areas with excessive O<sub>3</sub> and/or CO  
8 pollution problems administer inspection and maintenance programs to identify inoperative  
9 control systems requiring repair. The long-term durability of evolving emission control  
10 technology associated with use of alternative motor vehicle fuels needs to be determined for  
11 vehicles in consumer fleet use.

12 The CAAAs contain several provisions addressing the issue of improving performance  
13 of consumer fleet emissions control. These include development of "remote sensing"  
14 emissions measurement devices permitting local authorities to identify malfunctioning  
15 vehicles on roadways, of on-board diagnostics systems providing the owner/operator with  
16 emissions control system performance information, and of enhanced inspection and  
17 maintenance programs providing more comprehensive and conclusive identification of  
18 vehicles requiring emissions control system repair. Warranty provisions for automobile  
19 emissions control systems have also changed. The current 5-year/50,000-mi equipment  
20 warranty has been extended to 8 years/80,000 mi for the catalytic convertor, electronic  
21 control unit, and onboard diagnostic unit (EPA may add other major emissions control  
22 devices). All other emissions devices on 1995 and later cars will be warranted for  
23 2 years/24,000 mi. (Certification requirements for classes of engines have been extended  
24 from 5 years/50,000 mi to 10 years/100,000 mi.)

#### 26 **1.4.4.3 Fuel Transport Sources**

27 Control technologies and/or development of fuel tankers, barges, and pipelines to limit  
28 accidental spills and leakage will reduce the entry of alternative fuels into terrestrial and  
29 aquatic ecosystems. Accidents are probably inevitable, however, and insofar as spills pose a  
30 significant adverse risk, cleanup technologies must be improved through research.

### 1.4.5 Summary

This section summarizes the risk assessment and risk prevention/mitigation issues identified above that are of greatest interest for research within the scope of this Research Strategy. The Research Strategy is circumscribed, including only public health and ecosystem risks from fuel-related emissions, characterizations of RITGs, and risk prevention/mitigation of emissions. For a total evaluation of the national impact of fuel switching, other key issues outside the scope of this Strategy must be considered and assessed. These issues include, but are not limited to, national security, economics, safety hazards (e.g., explosions and fires), land use impacts from feedstock production, occupational risks, and development of vehicular emission control devices. A point to be emphasized is that the priorities of the Research Strategy are highly dependent on currently available information and, hence, are subject to change as more information is gained and evaluated.

#### 1.4.5.1 Human Health Risk Priorities

In terms of numbers of persons exposed, the overarching concern is the health effects associated with exposures to criteria pollutants. In 1989, 66.7 million U.S. residents lived in areas that exceed the primary O<sub>3</sub> NAAQS, and about 34 million people lived in areas that exceed the CO NAAQS at some time during the year. Conventional fuel-related sources are a major contributor to the nonattainment of these standards, and a major policy goal of switching to alternative fuels is to decrease O<sub>3</sub> and CO exposures. To obtain quantitative exposure assessments for alternative fuels, research on stationary and mobile source emissions, atmospheric fate, monitoring, and modeling of exposures and impacted subpopulations must be conducted. The resulting exposure assessments can be linked to available health effects data to characterize the change in health risks/benefits for NAAQS pollutants as a function of alternative fuel usage.

The next ranked area of interest is air toxics, from the perspective of both ambient air and microenvironments. Relative to NAAQS pollutants, the impacts of air toxics on public health are not well understood. In some airsheds, approximately 50% of the ambient air carcinogenic potential is estimated to be due to conventional fuel-related emissions.

1 Monitoring data indicate that many toxic pollutants exceed levels of concern in many U.S.  
2 cities. The quantitative association between many of these pollutants and mobile source  
3 emissions is unknown. Alternative fuels are expected to alter this picture. For example,  
4 gasoline with reduced benzene and aromatic content will reduce benzene emissions. Gasoline  
5 with oxygenates will reduce the tailpipe emissions of currently recognized toxic components,  
6 except possibly for the aldehydes most closely related to the oxygenated compound itself  
7 (e.g., acetaldehyde in relation to ethanol, formaldehyde in relation to methanol).  
8 Nonpetroleum fuels of low molecular weight (CNG, neat methanol, propane) have been  
9 observed to provide large reductions in the higher molecular weight compounds such as  
10 benzene, polycyclic organic matter, and 1,3-butadiene. However, there are several hundred  
11 fuel-related air toxics that can be emitted or produced by atmospheric transformation, many  
12 of which have not been characterized. Thus, although some air toxics will be reduced, the  
13 net toxic potential of alternative fuel-related pollutants remains to be determined.

14 Because air toxics exposures in microenvironments could result in higher exposure  
15 levels than may be encountered in ambient air, there is a potential for higher risks,  
16 depending upon exposure duration and the effects of concern. The microenvironments of  
17 current interest include personal and public garages and commuting scenarios. Concern  
18 centers on potentially sensitive subpopulations exposed to complex evaporative and  
19 combustion emissions, which include not only air toxics, but  $\text{NO}_x$  and CO as well.  
20 To assess these risks, the research should focus on mobile source combustion emissions and,  
21 to a lesser extent, on primary fuel emissions, microenvironmental exposure assessment,  
22 characterization of sensitive subpopulations, types of health effects, and their dose-response  
23 characteristics.

24 Accidental swallowing of liquid fuels by children is also an issue of some concern,  
25 because even small quantities of some types of fuels can cause death or very serious effects.  
26 Such hazards must be carefully characterized so appropriate prevention measures can be  
27 taken. A risk assessment for this scenario based on available information must be performed  
28 initially. Depending upon the outcome, additional research may be needed.

29 Based on currently available information, health effects research needs to focus on  
30 pharmacokinetics, selected noncancer endpoints associated with specific fuels and fuel use

1 by-products, and the potential carcinogenicity of combustion and atmospheric transformation  
2 products. Inhalation should be the primary route of exposure considered. As the variety of  
3 exposure conditions become better characterized, additional areas of health effects research  
4 may require more attention.

#### 6 **1.4.5.2 Ecosystem Risk Priorities**

7 Two ecosystem risk pathways are of immediate and primary interest, namely the effects  
8 of O<sub>3</sub> and selected air toxics on terrestrial systems and the effects of large accidental releases  
9 of fuels into aquatic systems. Low ambient levels of O<sub>3</sub> cause adverse effects to plants.  
10 Although a secondary NAAQS for O<sub>3</sub> exists to minimize these effects, it is frequently  
11 exceeded, partially due to the influence of conventional fuel-related O<sub>3</sub> precursors. Because  
12 alternative fuels are expected to change O<sub>3</sub> patterns, quantitative terrestrial exposure  
13 assessment is a high priority. Research on source characterization, atmospheric fate, and  
14 monitoring/modeling of air quality, especially in rural areas, is needed to support such an  
15 assessment. The exposure assessment will be linked to existing terrestrial effects data to  
16 develop the O<sub>3</sub> risk assessment.

17 Formaldehyde, methanol, ethanol, acetaldehyde, PAN, and DMS are examples of air  
18 toxics that may impact both aquatic and terrestrial ecosystems. The environmental fate and  
19 effects on biota of these pollutants, individually or in combination, and their interactions with  
20 O<sub>3</sub> are not fully understood. Research projects on source characterization, environmental  
21 fate, and biota exposure and effects are needed to evaluate the risks posed to terrestrial  
22 ecosystems from the production and use of alternative fuels.

23 As events have repeatedly shown, large scale accidental releases related to the transport  
24 and storage of conventional fuels occur, causing a variety of adverse ecosystem effects.  
25 Increased transportation and storage of alternative fuels could alter these risks in various  
26 ways (e.g., by changing the potential for releases due to differences in corrosivity of the  
27 fuels in containment systems, or by changing the characteristics of the exposures and effects  
28 themselves). Greatest interest centers on supertanker and barge spills into near-coastal  
29 marine and freshwater systems. Some efforts have been made to link fate and effects models  
30 for assessing risks due to oil spills, but the components and integration of such models need

1 to be improved to allow appropriate application to the variety of fuels and situations of  
2 concern here. The predominant assessment endpoints would be ecological, although if  
3 affected freshwater systems are used as drinking water or if the food chain is affected,  
4 human health could also become an issue. To understand the potential ecosystem impacts of  
5 accidental spills, it will be necessary to evaluate and estimate potential occurrences and  
6 volumes of such spills and conduct a research program on exposure assessment (aquatic  
7 transport and fate, monitoring/modeling of exposures) and marine and freshwater effects.

8 A secondary, but still important, issue is better characterization of the other potential  
9 ecosystem risks, thereby permitting improved guidance on future research priorities. Risk  
10 pathways that require elucidation include the following: chronic ambient levels of air toxics  
11 and atmospheric deposition, which in turn are dependent on stationary and mobile source  
12 characterization and atmospheric fate; leakage from USTs and transport and fate of the  
13 released fuels to shallow urban aquifers; and chronic low-level release into aquatic systems,  
14 which also includes fate and effect issues. A prerequisite is to conduct screening exposure  
15 assessments for terrestrial, marine, and freshwater systems that can be coupled with hazard  
16 identification data gathered via research or from available literature. Initial hazard  
17 identification research would focus on selected air toxics (in the case of terrestrial  
18 ecosystems), fuels (in the case of soil or aquatic exposures), and the identification and  
19 characterization of appropriate sensitive species or assessment endpoints. This category of  
20 research is intended to determine the potential nature of the issues, rather than to provide  
21 definitive risk assessments. Numerous additional possibilities for ecosystem impacts exist,  
22 necessitating a continual evaluation of research priorities as more information becomes  
23 available.

#### 24 25 **1.4.5.3 Global Climate Change Priorities**

26 The emission of RITGs may have a major influence on global climate change and,  
27 hence, on ecosystem and health risks. Radiatively important trace gases have numerous  
28 natural and anthropogenic sources, to which fuel-related sources contribute significantly.  
29 Global climate changes will be assessed as part of another EPA program, but this Research  
30 Strategy will attempt to provide input on fuel-related RITGs. The applicable research is

1 contained within the programs on stationary and mobile source characterization of air  
2 emissions and atmospheric fate.

#### 4 **1.4.5.4 Risk Assessment Priorities**

5 The Report to Congress mandated by the AMFA involves comprehensive risk  
6 assessments, but other interim assessments and evaluations will be needed to guide research  
7 designs and decisions and to provide information to the Program Offices in a timely manner  
8 to support their regulatory decision-making. The exact nature of these assessments and  
9 evaluations depends upon regulatory needs and research progress. In the near-term, special  
10 assessments of health risks such as accidental swallowing of liquid fuels as well as major  
11 scientific assessments of the health and ecosystem effects of (1) conventional gasoline,  
12 (2) methanol, and (3) other fuels are needed.

#### 14 **1.4.5.5 Risk Prevention/Mitigation Priorities**

15 The primary issue for vehicular emissions is to ensure the adequacy of emission control  
16 devices as mileage accumulates. For stationary sources, the overriding priority is to evaluate  
17 or develop technologies that would control unacceptable risks to health, global climate, and  
18 ecosystems, thereby removing barriers to the use of more environmentally attractive fuels.  
19 The key issues relative to stationary sources are (1) the potential for an increase in stationary  
20 source VOC emissions that might offset O<sub>3</sub> reduction from the use of alternative fuels in  
21 vehicles, and (2) the potential for major contributions to global climate changes from  
22 methane and CO<sub>2</sub>. To target risk prevention/mitigation research, emissions data and  
23 qualitative risk assessments must be available. The exposure and effects assessment  
24 components of quantitative risk assessment will be used to refine and emphasize future  
25 prevention and control research needs. Utilizing existing and innovative prevention and  
26 control technologies and practices to maximize risk reduction in problem areas is important.

27 Although advanced engineering designs and applications are intended to prevent major  
28 accidents, accidents are inevitable. The history of accidents related to conventional fuel  
29 transport, including supertankers, barges, and piping systems, raises significant ecosystem  
30 concerns. Research is needed to improve cleanup procedures for both conventional and

1 alternative fuels in surface waters and sediments and in soils and groundwater. Such  
2 research is dependent upon knowledge to be gained from studies of aquatic and soils  
3 transport and fate processes.  
4  
5

## 6 **1.5 RESEARCH PRIORITIZATION APPROACHES**

7 This section describes approaches to establishing general priorities for research. Insofar  
8 as fuel-specific priorities can be identified currently, they are presented in the fuel-specific  
9 sections. Achieving comprehensive, quantitative risk assessments for every fuel is not  
10 feasible, and thus a rationale for prioritization must be developed. However, an ideal  
11 scientific rationale may well differ from that shaped by the practical realities of the research  
12 missions and commitments of various public and private institutions. Under such  
13 circumstances, it is nevertheless useful to describe the ideal goals as clearly as possible.  
14 Various funding organizations can then decide how they may wish to apply their particular  
15 institutional priorities to these goals. These ideal priorities are described in general terms  
16 below; as knowledge progresses, it may become possible to refine the logic for each of the  
17 fuels.

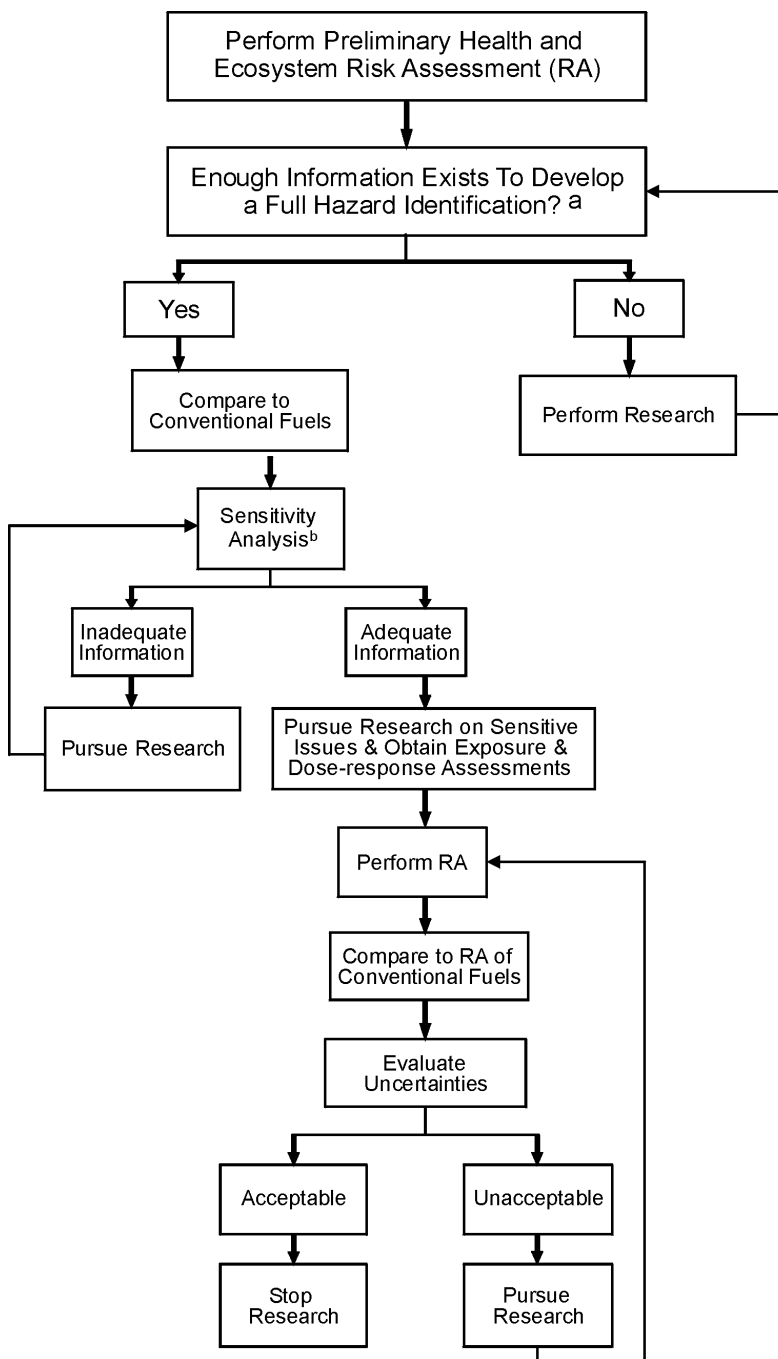
18 *The first priority is to develop quantitative health and ecosystem risk assessments of*  
19 *conventional fuels*, focusing on light-duty vehicles operated on conventional gasoline and  
20 heavy-duty vehicles operated on diesel fuels. Because conventional fuels serve as the  
21 baseline for comparisons of the benefits and risks of alternative fuels, the baseline must be  
22 available and sufficiently quantitative to permit such comparisons. Without such information,  
23 alternative fuels are likely to be judged relative to a theoretical zero risk baseline, an event  
24 that could lead to rejection of possibly preferable trade-offs of risks, which would be  
25 inconsistent with the Congressionally established principle of "substantially similar" risks  
26 (i.e., roughly equivalent to those of controlled conventional fuel emissions). Determining  
27 research priorities begins with the development of a health and ecosystem risk assessment of  
28 conventional fuels. This will indicate areas of uncertainties (e.g., ecosystem effects of diesel  
29 fuels, unit cancer risk of whole gasoline combustion emissions) that preclude comprehensive,  
30 quantitative assessments. These areas of uncertainty should then be subjected to a sensitivity

1 analysis to determine which are the most important for further research. For example, if it  
2 appears that research on the respiratory tract will have significantly more impact on  
3 developing a risk-assessment than research on neurotoxicity, the respiratory tract would be  
4 higher priority. If it appears that chronic aquatic risk is of more concern than acute aquatic  
5 risk, then this research direction is also clarified.

6 *The second priority is to evaluate alternative fuels and compare them to conventional*  
7 *fuels.* Within each alternative fuel, scientific issues will guide a rational approach to  
8 research. Priorities among the alternative fuels are not provided here, although to a certain  
9 extent technology development will guide specific fuel priorities. For example, to examine  
10 emissions from M100, there must be a prototype engine to do so. The EPA's objective,  
11 however, is to evaluate all fuels, without introducing any bias that would favor the  
12 development of one fuel over another. Other interested institutions are likely to prioritize  
13 fuel(s) according to their own missions, so no one set of specific fuel priorities will be  
14 universally useful. Figure 1-4 outlines the research prioritization steps for alternative fuels.

15 Although risk reduction is quite important, it is not described specifically in these  
16 priorities because current reduction/control activities are embedded in the exposure  
17 assessment component of the risk assessment. As risk assessments indicate adverse health or  
18 ecosystem effects, then research to reduce or prevent that risk becomes a high priority.  
19 Similarly, although RITG emissions are also quite important, they are not discussed because  
20 they will be an output of emissions research and will be used in risk assessments within  
21 EPA's global climate program, not the alternative fuels program. Certain studies mandated  
22 by the CAAAs are also not specifically identified above because they generally fall into three  
23 classes: (1) data that would support exposure assessment and therefore are contained within  
24 the broad descriptions above, (2) specific technology-based issues that have relevance to  
25 emissions controls and thus are included in risk reduction, and (3) regulatory requirements  
26 for products such as certification procedures. These studies include an assessment of the  
27 need for implementation of the more stringent Phase II light-duty motor vehicle tailpipe  
28 emissions standards, an assessment of the impact of heavy-duty vehicle emissions on air  
29 pollution and of the impact of engine rebuilding practices, an assessment of the need for and  
30 feasibility of controlling unregulated toxic air pollutant motor vehicle emissions, an





**Figure 1-4. Research prioritization of alternative fuels.**

<sup>a</sup>Full Hazard Identification - As per National Research Council (1983), this is information on likely exposures and nature of risk (e.g., carcinogen, respiratory toxicant, fish toxicant) with limited estimation of approximate dose-responses.

<sup>b</sup>Sensitivity Analysis - Determine which risk pathways and/or endpoints are likely to have significant impact on the RA. As examples, will groundwater contamination contribute a significant dose of chemicals to humans, requiring pursuit of total human exposure; are combustion, evaporative or both emissions of interest; are health or ecosystem or both RAs of interest; are cancer, noncancer, or both effects of interest?

1 assessment of the need to change emissions certification procedures to make them more  
2 representative of actual driving conditions, an assessment of the risk to public health and  
3 welfare from nonroad vehicles and engines, and an assessment of the effectiveness of the  
4 California Pilot Program to reduce urban air pollution.

5 As discussed above, this research prioritization scheme is idealized. To be effective,  
6 practical application of these priorities needs to treat the ideal as a goal to be achieved as  
7 rapidly as possible. For example, the only currently available assessments of complex  
8 mixtures of fuels are for health risks of diesel emissions (U.S. Environmental Protection  
9 Agency, 1990e) and volatilized gasoline. Much research on exposure, effects, and risk  
10 reduction is needed to support specific fuel assessments, and many effective research  
11 directions can be identified prior to development of comprehensive assessments. However,  
12 at some point the lack of an assessment will result in misdirected research and wasting of  
13 valuable resources.

## 16 **1.6 RESEARCH PLANNING ISSUES**

17 To be effective, all research performed must be part of the knowledge continuum  
18 leading to a risk assessment or leading from a risk assessment in the case of risk  
19 prevention/reduction research. The multidisciplinary, multimedia nature of the research  
20 needs for each fuel can make this difficult because the knowledge bases will need to be  
21 joined. For example, a highly refined exposure assessment is of no use if there is no health  
22 assessment; a dose-response assessment on forests or crops cannot be interpreted without an  
23 exposure assessment. Although such a need is obvious, achieving it will require coordinated  
24 planning because, typically, the required disciplines are located in different organizations  
25 within an institution or in different institutions. In some cases, higher authorities within an  
26 institution can managerially enact coordinated planning, but even then, no one institution can  
27 accomplish all the work. Thus, coordination among institutions is needed. Although  
28 individual institutions have different missions and operate independently, such independence  
29 does not prohibit coordination and collaboration.

1       Creating a mechanism for coordination should be a participatory process; hence, no  
2 details will be provided here. However, formal or informal communication from interested  
3 parties on this matter is encouraged. The ORD is developing an international conference on  
4 alternative fuels to bring all interested parties together to present their research programs and  
5 recent findings. It is hoped that sharing such information will facilitate coordination.

## 2.0 CONVENTIONAL FUELS

### 2.1 RISK ASSESSMENT RESEARCH FRAMEWORK

The benefits and risks of alternative fuels must be assessed in the context of existing fuels. Conventional petroleum-based fuels have a relatively long history of use and experience, yet much remains to be learned about their effects on the environment and on humans and biota. One reason for this is that the characteristics of the fuels themselves are subject to change. Gasoline formulations vary from season to season and from region to region. In addition, a major shift from leaded gasoline to unleaded formulations has occurred in this country since the mid-1970s. Although a considerable amount is known about the health effects of lead derived from leaded gasoline, comparatively little attention has been devoted to the health effects of unleaded gasoline. The combustion of petroleum fuels has created, and continues to contribute to, major problems of environmental pollution and effects on public health and ecosystems; within this frame of reference, alternative fuels must be assessed. Of the conventional fuel use patterns, primary interest centers on light-duty vehicles operated on conventional gasoline and heavy-duty vehicles operated on diesel fuels.

For conventional-fuel emissions, there are two major research issues: (1) whether the emissions regulations are achieving their goals and (2) the characterization of risks to serve as a baseline for comparisons to alternative fuels. Studies related to the first issue will also provide input into the second issue. Obtaining comprehensive, quantitative health and ecosystem risk assessments and information on radiatively important trace gas (RITG) emissions is even more crucial for conventional fuels because reasonably accurate baseline definitions will have a major impact on the quality of comparative risk/benefit interpretations of alternative fuels and the direction of alternative fuels research. For example, if the baseline is reasonably certain, comparisons to preliminary assessments of alternative fuels will be more credible in determining whether major benefits or risks might occur, focusing

1 attention on which fuels have high potential benefit (i.e., pursue quantitative risk assessment  
2 research for those) or high potential risk (i.e., pursue risk mitigation potential as well).

3 This chapter first highlights some key points of information and issues about  
4 conventional fuels in the format of a risk assessment. The discussion of the risk assessment  
5 research framework in Section 2.1 takes Chapter 1, the Introduction to Risk Assessment  
6 Framework for Fuels (Section 1.4), as its point of departure, but focuses on only those facets  
7 of the generic framework that are specific to conventional fuels. The risk assessment  
8 framework section is followed by a more extensive discussion of background and rationale in  
9 Section 2.2. This section is not an exhaustive evaluation of the literature; rather it highlights  
10 selected information that is likely to drive the research programs. A discussion of research  
11 that is needed to provide the foundation for a quantitative risk assessment of conventional  
12 fuels follows in Section 2.3.

## 14 **2.1.1 Exposure Assessment**

### 15 **2.1.1.1 Source Characterization**

#### 16 ***2.1.1.1.1 Emissions from Feedstock and Fuel Production, Storage, and Distribution***

17 ***Feedstocks.*** Petroleum crudes (domestic and foreign) and natural gas liquids are the  
18 feedstocks used to produce the various conventional fuels (e.g., gasoline, diesel, aviation,  
19 and stationary-source combustion fuels). Due to the similarity in composition, oil shale  
20 could be a long-range feedstock option. Crude oil varies in sulfur content and composition,  
21 which will result in different types and quantities of emissions and discharges. Major  
22 emissions from the recovery of crudes are volatile organic compounds (VOCs) and RITGs.  
23 Methane, carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), or sulfur oxides would be present  
24 from venting or flaring of the sour gases from gaseous wells. Methane and CO<sub>2</sub> are the  
25 most important global-warming gases. Spills, leaks, or releases (transient, conventional, and  
26 accidental) could involve the crude oil or various fractions such as the volatile gases. Wastes  
27 such as drilling muds are also generated. The greatest emissions potential is accidental  
28 release through the loss of containment at the well head. Emissions and discharges from the  
29 recovery of crude oils have been identified in a limited manner, but better quantification of  
30 the emissions and discharges for the variety of crude oil is needed. Operational energy

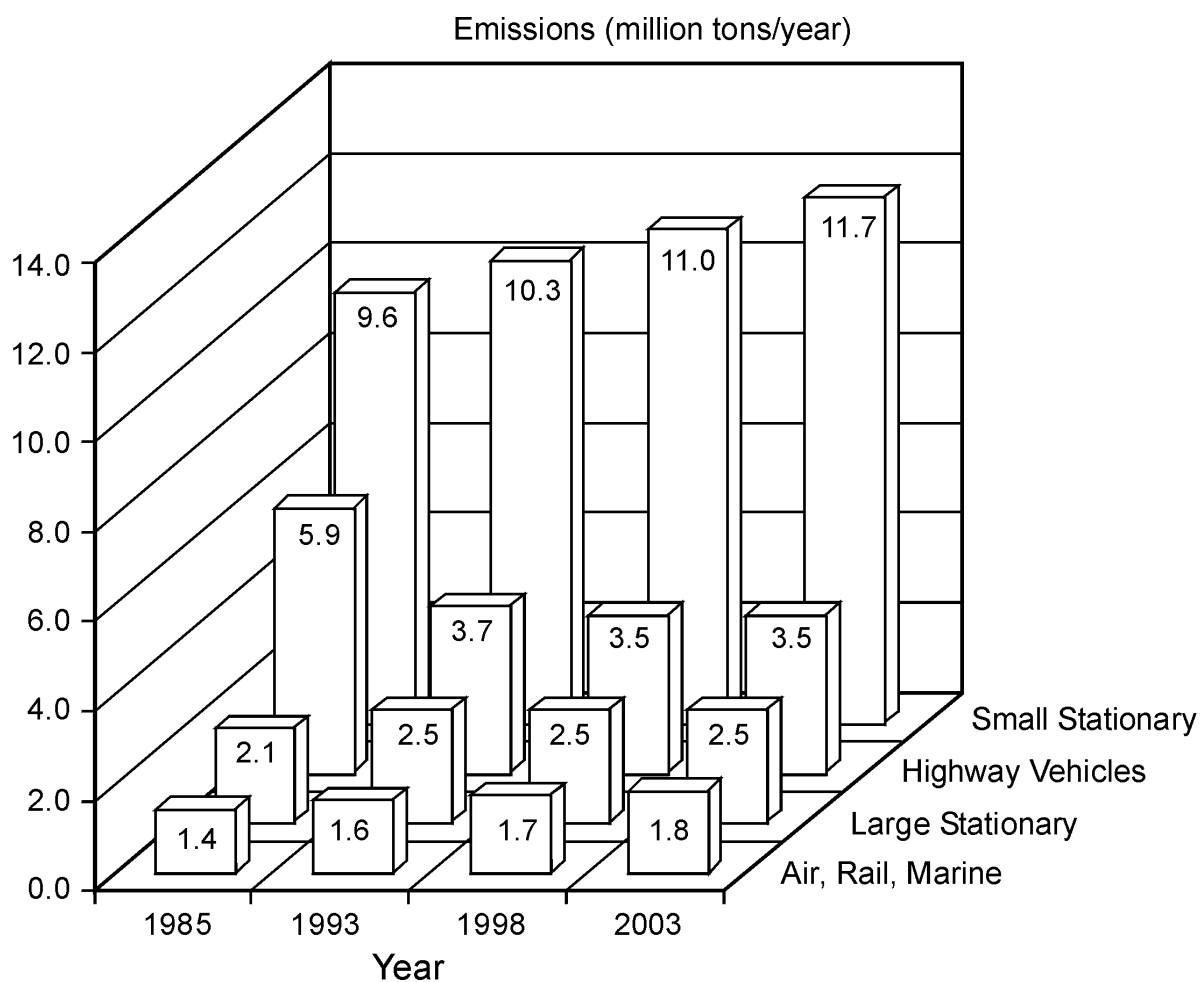
1 requirements will result in additional emissions of nonmethane RITGs. Total CO<sub>2</sub> release  
2 needs to be determined, especially release from enhanced oil recovery that is a large and  
3 increasing source of CO<sub>2</sub>.

4  
5 ***Production.*** The emissions and discharges from the refining process that produces the  
6 conventional fuels will depend upon the crudes used and the production steps required to  
7 generate the refinery products. The major emissions are VOCs, RITGs, and toxic pollutants,  
8 such as benzene. Effluents will contain a variety of organic pollutants and require treatment  
9 prior to discharge. Solid wastes include solids (coke), spent catalysts, and water treatment  
10 sludges. Although regulatory requirements (the new source performance standard [NSPS]  
11 and National Point Discharge Elimination Systems [NPDES]) have addressed many of the  
12 sources, VOC emissions have not been sufficiently reduced to alleviate the ozone (O<sub>3</sub>)  
13 nonattainment problem. The apparent effectiveness of the existing VOC controls is  
14 uncertain. Further, loss of containment in the refineries can result in major accidental  
15 releases. A significant number of these releases has resulted in fire and explosions, causing  
16 further rupture of equipment and release of additional refinery crudes or products. Spills,  
17 leaks, or releases (transient, conventional, and major accidental) could involve the crude oil,  
18 various intermediate fractions, or products. Emissions and discharges from the refining of  
19 crude oils have been identified in a limited manner, but better quantification of the emissions  
20 and discharges for the variety of crudes used, refinery configurations, and product slates is  
21 needed. Existing emission/discharge controls need to be evaluated for effectiveness and  
22 applicability, and energy efficiencies for the refinery process steps need to be determined.

23  
24 ***Storage and Distribution.*** Releases (transient, conventional, and accidental) of VOCs  
25 from the transportation, storage, and distribution of crudes and fuel products are a major  
26 concern. These releases will impact air, water, and soil quality. Air emissions of concern  
27 are VOCs and toxic air pollutants. Volatile organic compound emissions from this sector are  
28 a major issue because of their magnitude and the uncertainty of control effectiveness. These  
29 uncertainties need to be resolved. The relative importance of mobile and stationary sources  
30 for VOC emissions in the out years and the importance of small stationary sources are shown

1 in Figure 2-1. It should be noted that more recent data have indicated that VOC emissions  
2 from mobile sources may be larger than previously estimated (Walsh, 1991). Additionally,  
3 small-area VOC emission sources are very difficult to identify and quantify. The estimated  
4 values in Figure 2-1 are based on impacts of regulations and projections of increased  
5 efficiency of newer vehicles. Although the number of vehicle-miles traveled are projected to  
6 increase, the replacement of older vehicles with more efficient newer ones should result in  
7 decreased VOC emissions. The projected emissions from large stationary sources may be  
8 overly conservative due to the uncertainty of the impact of the controls required by the  
9 CAAAs because the analysis was performed before the CAAAs were passed. Increases in  
10 the number of small (less than 50 tons/year) stationary VOC emissions sources is one of the  
11 important factors that may lead to a smaller reduction in overall VOC emissions than  
12 expected; net emissions may even increase. Normally, small stationary sources are not  
13 included under existing or proposed regulations. Large volume spills are most likely to  
14 occur during offshore oil and gas exploration and drilling operations or during the transport  
15 (pipeline, tanker, or barge accidents) and storage (due to pipeline or storage tank failures) of  
16 fuels. Discharges would include a variety of hydrocarbons, depending upon the composition  
17 of the escaping fuels. Spills on or near aquatic systems would be a major concern. Chronic  
18 low-level discharges to aquatic systems are associated with transfers between tankers  
19 (or barges) and land-based storage facilities, boat fueling at marinas, and leakage from boat  
20 engines. The discharge of ballast water by tankers and barges is also a source of  
21 contamination. All spills are wasted energy; the hydrocarbon material eventually gets  
22 converted to CO<sub>2</sub>, with no energy benefits.

23 As seen in recent history, despite continual efforts to reduce or eliminate these releases,  
24 fuel spills continue to impact aquatic environments. In addition to these releases, petroleum  
25 hydrocarbons from fuels continuously enter aquatic systems as urban runoff. The sources  
26 include compounds leaked from vehicles onto roadways and combustion products or  
27 evaporative emissions in wet and dry atmospheric depositions. These hydrocarbons enter  
28 aquatic and atmospheric (as volatilized organics) systems from point sources such as sewage  
29 treatment plants and combined sewage overflows or from nonpoint sources. Sediments of



**Figure 2-1. Summary of estimated nationwide volatile organic compound emissions by source category and year. Note: "Small Stationary" = sources emitting less than 50 tons/year.**

Source: U.S. Congress (1988).

most aquatic systems located near urbanized and industrialized areas are heavily impacted by such inputs.

Releases from underground storage tanks (USTs) have been due primarily to factors such as corrosion, improper installation, and overfilling. Over 25% of existing tank systems (i.e., tanks and their associated piping) may be leaking or are expected to leak within the next 3 to 5 years, leading to significant soil and groundwater contamination. In many cases,



drinking-water aquifers will be unsuitable for public use for decades. Federal regulations regarding the storage and handling of fuels, as well as chemicals, have been promulgated; however, research is still required to optimize methodologies, equipment, standards, and guidance both for release detection and monitoring and for site investigation and assessment where leaks are suspected.

#### ***2.1.1.1.2 Emissions Related to Fuel Use***

***Stationary-Source Emissions.*** Volatile organic compounds and RITGs are the dominant emissions from stationary sources that combust petroleum-based fuels to generate heat or energy. Emissions of toxic pollutants (e.g., benzene) are also a growing concern. Identification of sources, quantification of existing emissions/discharges, and evaluation of existing controls are needed. Speciation selectivity inherent in particular control applications needs to be addressed.

***Mobile-Source Emissions.*** Conventional transportation fuels in the United States include gasolines and diesel distillates of many compositions. The characteristics of motor vehicle emissions are very sensitive to fuel composition, to the design and condition (e.g., age and malfunctions) of the engine and emissions control system, and to operating conditions (e.g., average speed, engine load, ambient temperature, and altitude). Conventional gasolines include leaded and three grades of unleaded (regular, intermediate, and premium). Leaded gasoline accounted for 13% of sales during the first 4 mo of 1989, but its market share continues to decrease. Since January 1986, the lead content of leaded gasoline has been limited to 0.1 g/gal (however, EPA's banking and trading program permitted use of levels to 0.2 to 0.3 g/gal until the end of 1987 by those suppliers previously marketing fuels with lower than permitted lead levels). Section 220 of the 1990 CAAAs prohibits the sale or distribution of any motor vehicle fuel containing lead after December 31, 1995. Regular unleaded gasoline accounted for about 58% of sales during the first 4 mo of 1989, intermediate accounted for about 5% of sales, and premium accounted for about 24% of sales. The sale of higher octane gasoline is greater than required by today's vehicle fleet and has important emissions implications because these fuels typically

1 have higher aromatic hydrocarbon fractions and associated higher toxics emissions (e.g.,  
2 benzene).

3 According to the American Society for Testing and Materials standards and EPA  
4 regulations, the composition of gasoline varies regionally/seasonally. Volatility and  
5 hydrocarbon composition are important to the characteristics of motor vehicle emissions.  
6 Depending upon the area of the country and the month, regulations require that gasoline  
7 volatility be no greater than 10.5, 9.5, or 9.0 psi Reid vapor pressure (RVP, vapor pressure  
8 at 100 °F) during the summer months (May to September) when O<sub>3</sub> levels peak, but it can  
9 be as high as 15 psi RVP during winter months. Beginning in May, 1992, RVP was to be  
10 limited to 9.0 or 7.8 psi during the summer months. During the 1989 summer period,  
11 regular unleaded gasoline composition varied from 17.7 to 42.2% aromatic hydrocarbon,  
12 1.0 to 42.8% olefinic hydrocarbon, and 33.9 to 73.2% paraffinic hydrocarbon.

13 Motor vehicles emit organic compounds from a variety of sources generally categorized  
14 according to tailpipe, parking (diurnal and hot soak) and running-loss evaporative, and  
15 refueling emissions. The relative contribution of each depends on fuel characteristics and  
16 vehicle operating conditions (e.g., speed and temperature). The aggregate organic emissions  
17 composition will depend on the relative importance of each of these sources. A number of  
18 additional combustion products, such as CO<sub>2</sub>, nitrogen oxides (NO<sub>x</sub>), carbon monoxide  
19 (CO), nitrous oxide (N<sub>2</sub>O), sulfur dioxide (SO<sub>2</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and hydrogen sulfide  
20 (H<sub>2</sub>S), are also emitted from the tailpipe.

21 Light-duty gasoline vehicles are responsible for greater than 90% of motor vehicle  
22 nonmethane hydrocarbon (NMHC) and CO emissions and for about 67% of NO<sub>x</sub> emissions;  
23 heavy-duty diesel vehicles are responsible for about one-third of NO<sub>x</sub> and particulate  
24 emissions. Nonmethane hydrocarbon and CO emission rates from motor vehicles typically  
25 increase as ambient temperatures are elevated or decreased from 70 °F and as average speed  
26 is decreased. Nitrogen oxides, although not as sensitive to these variables as NMHC and  
27 CO, also increase as ambient temperature is reduced and as average speed is decreased or  
28 increased from about 25 mph. The distribution of organic emissions among tailpipe,  
29 evaporative, and refueling sources at 75 to 100 °F diurnal range, 20 mph average speed, and  
30 9 psi RVP gasoline volatility is about 51%, 44%, and 5%, respectively. Evaporative sources

1 contribute a smaller fraction of total NMHC as average speed is decreased (although tailpipe  
2 rates increase), as fuel volatility is decreased, or as ambient temperature is decreased.

3 Gasoline and diesel motor vehicles are sources of a number of other toxic compounds  
4 of interest. Among those receiving greatest attention by the EPA are diesel particles  
5 (an estimated 178 to 860 cancer incidences per year, based on 1986 conditions),  
6 formaldehyde (46 to 86 cancer incidences per year), benzene (100 to 155 cancer incidences  
7 per year), 1,3-butadiene (236 to 269 cancer incidences per year), gasoline particles (1 to  
8 176 cancer incidences per year), and gasoline vapors (17 to 68 cancers incidences per year).  
9 Compounds (potentially sensitive to fuel composition) that are emitted from motor vehicles  
10 and influence global climate include CO<sub>2</sub>, methane, and N<sub>2</sub>O. Carbon dioxide emission rates  
11 are closely related to fuel economy. During the 1975 to 1985 decade, fleet average fuel  
12 economy improved, and CO<sub>2</sub>-emission rates decreased about 20%; however, vehicle miles  
13 traveled increased about 30% during that period. The net CO<sub>2</sub> burden from U.S. motor  
14 vehicles, therefore, has increased. The emission rate of methane has decreased. The rates  
15 of other tailpipe hydrocarbons have also decreased, but to a greater extent, because catalysts  
16 do not reduce methane as effectively as they do other hydrocarbons. Motor vehicle N<sub>2</sub>O  
17 emission rates may be increasing with catalysts; preliminary data suggest about an order-of-  
18 magnitude increase with catalyst versus noncatalyst technologies.

19 The emissions composition data available in the literature are dominated by Federal  
20 certification conditions (19.6 mph, 70 °F tailpipe, 60 to 84 °F diurnal ramp), with  
21 essentially no running-loss emissions speciation data. To examine comprehensively the air  
22 quality impact of motor vehicle emissions, an understanding of both emissions strength  
23 (g/mi) and composition is necessary under driving conditions typical of U.S. fleets. Ozone  
24 air quality problems often exist at temperatures greater than 70 °F, whereas CO problems  
25 occur at temperatures well below 70 °F.

## 27 **2.1.1.2 Environmental Fate**

### 28 **2.1.1.2.1 Air Fate**

29 Gasoline is composed of a number of paraffinic, olefinic, and aromatic compounds.  
30 All of them are photochemically reactive when exposed to sunlight in the presence of NO<sub>x</sub>.

1 The paraffins are usually the least reactive, having lifetimes from approximately 3 days to  
2 over 10 days; the aromatics are slightly more reactive, with lifetimes of 1 to 5 days; and the  
3 olefins are the most reactive, with lifetimes of only a few hours. Emissions from vehicles  
4 without catalysts and from cold starts in vehicles with catalysts are even more reactive.  
5 These tailpipe emissions contain fractionated products (e.g., acetylene and butadiene) as well  
6 as oxygenates (e.g., formaldehyde and acetaldehyde). Oxygenates are very reactive because  
7 they react with hydroxyl radicals and can also photodissociate. Butadiene is very reactive in  
8 the atmosphere and produces acrolein, a strong eye irritant, and formaldehyde.

9 Studies on dilute mixtures of auto exhaust have been conducted in smog chambers for  
10 several years. The ability of the exhaust mixture to produce O<sub>3</sub> is dependent upon the  
11 VOC/NO<sub>x</sub> ratio. At low ratios, because of nitric oxide inhibition, little O<sub>3</sub> is produced.  
12 At higher ratios, copious quantities of O<sub>3</sub> can be produced. Other products such as  
13 formaldehyde, PAN, acetaldehyde, ketones, other nitrates, and particles are also produced.

14 Dilute mixtures of automotive exhaust have been tested for mutagenicity. Irradiated  
15 and nonirradiated mixtures were tested, and the irradiated mixtures were found to be much  
16 more mutagenic. Furthermore, the gas phase components were noted to be more mutagenic  
17 than the components in the particulate phase. Further work is necessary to test the complex  
18 relationships among the VOCs, NO<sub>x</sub>, and O<sub>3</sub>. Also, additional work is needed to identify  
19 the compounds responsible for the high mutagenicity observed with irradiated auto exhaust.

#### 21 ***2.1.1.2.2 Soil and Groundwater Fate***

22 The extent to which releases of conventional, petroleum-based fuels impact groundwater  
23 quality is determined by the rate at which these hydrocarbon mixtures move through the  
24 subsurface, and by the degree to which they are attenuated during migration. Because these  
25 fuels are complex mixtures of chemicals that have a broad range of physicochemical  
26 properties, subsurface transport may occur via several mechanisms. These include aqueous-  
27 phase and nonaqueous-phase liquid (NAPL) and gaseous-phase transport. The importance of  
28 each of these mechanisms in a specific situation will be determined by the nature of the  
29 contaminant source (composition, rate, and duration of the release) and by the properties of  
30

1 the soil or aquifer. The influence of these transport mechanisms on the behavior of fuels and  
2 the aqueous-organic-vapor phase dynamics of these immiscible systems must be understood.

3 Because of the disparity in physicochemical properties, individual components of  
4 gasoline and diesel will be chromatographically separated during migration through the soil.  
5 Current knowledge permits reasonable predictions of chemical transport in predominantly  
6 aqueous systems; however, much less is known about contaminant transport and fate in the  
7 organic phase. Because important research questions concerning the physics and  
8 chemodynamics of these complex mixtures remain unanswered, current conceptual and  
9 mathematical models of contaminant transport and transformation in multiphase flow systems  
10 are suspect.

#### 11 12 ***2.1.1.2.3 Surface Water Fate***

13 Conventional fuels present an array of fate problems for freshwater and estuarine spill  
14 scenarios. First, fuels are really a complex mixture of individual compounds that will exhibit  
15 multiple fate profiles. Some components will degrade rapidly, whereas others are much  
16 more persistent. Chemical degradation will produce other products that in turn present  
17 different fate and effects behavior. Second, such fuels will separate into multiple phases in  
18 the water column, thereby complicating the transport as well as the fate of each phase.  
19 At least three distinct phases result: the product, the emulsions formed as the fuel disperses,  
20 and the product dissolved in water. The three phases move at different rates, interact as  
21 concentration and turbulence fields change, and degrade at different rates and by different  
22 mechanisms. Surface slicks form at even very low concentrations, further complicating  
23 subsequent effects (i.e., effects may be much more subtle than direct toxicity).

24 Fate processes requiring study include the identification of individual fuel components  
25 and their subsequent transformation in water systems. Biological degradation is especially  
26 important, and oxygen depletion is expected to be a major impact. Related processes of  
27 reaeration and volatilization are also important. Priority research for transport addresses the  
28 formation and movement of emulsions. The total, multiphase transport will require  
29 additional study to establish the expected frequency, volume, spatial extent, and duration of  
30 spills.

### 2.1.1.3 Exposures

#### 2.1.1.3.1 *Human Exposure Assessment*

*Air.* Information that characterizes emissions from conventionally fueled vehicles by using existing fuel characteristics and by following a standardized test protocol is currently available. This information, although incomplete, permits EPA to model likely concentrations of CO, NO<sub>2</sub>, particles, and some VOCs under different emission scenarios. The NAAQS Exposure Model (NEM) (Johnson et al., 1990; Ingalls, 1985) has been used to model exposures for criteria and noncriteria pollutants to estimate integrated lifetime exposures to carcinogenic substances emitted by motor vehicles (Adler and Carey, 1989). The updated NEM (anticipated availability, 1992) may change results. In addition, through transport and fate models, O<sub>3</sub> concentrations can also be modeled. Human exposure and microenvironmental studies of in-transit exposures to CO and VOCs provide some information about the relative relationships between indoor/outdoor and in-vehicle exposures for these compounds.

A motivation for many conventional fuel characterization studies has been to provide information to transport and fate models, especially for O<sub>3</sub>, and to estimate likely ambient O<sub>3</sub> concentrations that might result from an alternate control choice. As a first step toward understanding the impacts of the fuel choice on O<sub>3</sub> levels, calculations of O<sub>3</sub> exposure would be useful in assessing the actual health benefits of any O<sub>3</sub> reduction caused by alternative fuel substitution. This would require measuring (or modeling) the O<sub>3</sub> concentration in the important microenvironments and modeling the transport indoors from outdoors in urban, near-urban, and rural environments. Similar characterizations for NO<sub>2</sub>, particulate matter (PM), and selected VOCs (e.g., benzene, formaldehyde, and 1,3-butadiene) should also be conducted, but only after O<sub>3</sub> is adequately studied.

Likely locations of increased pollutant concentrations, including street canyons, roadway tunnels, expressways, and parking garages, should also be characterized. Finally, the mobile source contribution to complex air mixtures that originates from the use of existing fuels needs to be documented so changes in ambient concentrations resulting from emissions of alternate fueled vehicles can be measured and the risks to public health can be quantified.

1       **Oral.** Conventional fuels leaking from USTs are known to contaminate drinking water  
2 supplies, especially wells. Other major pipeline or barge spills have created potential  
3 exposures requiring temporary shut-down of intakes of contaminated water for municipal  
4 systems. Although more knowledge on such exposures would be useful, adequate  
5 information is available for an exposure assessment prior to determining the need for further  
6 research.

7       Accidental ingestion of gasoline occurs with some frequency. Approximately  
8 30,000 such cases are estimated to have occurred in the United States in 1987, based on  
9 American Association of Poison Control Centers data. Almost 30% of all gasoline ingestions  
10 occur in children aged 2 years or younger; less than half (42%) of gasoline ingestions occur  
11 in persons over age 17. This incidence and nature of occurrence (e.g., toddlers swallowing  
12 gasoline from a fuel container, adults siphoning fuel) are of major interest for comparisons to  
13 estimates of ingestion of methanol fuel, which will have more severe effects if it occurs.  
14 This topic needs to be assessed, given the extent of available information, before deciding on  
15 the need for research.

#### 16 17 **2.1.1.3.2 Biota Exposure Assessment**

18       The biota of terrestrial and aquatic ecosystems are exposed to conventional fuel  
19 pollutants (e.g., PM, CO, aromatic compounds, organic compounds, NO<sub>x</sub>, and O<sub>3</sub>) derived  
20 from fugitive emissions during fuel manufacture, transportation, storage, combustion, and  
21 vehicle refueling. Terrestrial and aquatic ecosystems are also exposed through airborne  
22 deposition and accidental spills/leakage from barges, ships, and storage tanks. Airborne  
23 pollutant deposition represents the greatest threat to terrestrial ecosystems, whereas accidental  
24 spills/leakage will have the greatest impact on aquatic ecosystems. Such exposures could be  
25 acute or chronic, frequent or infrequent, high level or low level, and local or regional.  
26 Scenario modeling efforts (e.g., models developed through the National Acid Precipitation  
27 Assessment Program [NAPAP] and ORD's Research Centers) and multimedia compartmental  
28 models will be needed to determine whether significant environmental exposures are likely to  
29 occur and pose a threat to terrestrial or aquatic biota.

1       ***Terrestrial Ecosystem Exposure.*** Air quality changes resulting from the production and  
2 combustion of conventional fuels may impact terrestrial biota through airborne exposures to  
3 O<sub>3</sub>, polycyclic aromatic hydrocarbons (PAHs), air toxics, and NO<sub>2</sub>. Key research elements  
4 include monitoring and modeling exposure patterns of individual pollutants to terrestrial  
5 ecosystems, with a focus on sensitive and important biota, such as crops and trees.  
6 Follow-up ecological effects research will be necessary. The primary approach would be to  
7 use exposure models, such as those developed as part of NAPAP, to evaluate terrestrial  
8 ecosystem exposures to the airborne pollutants. Multimedia compartmental models, such as  
9 the Spatial Multimedia Compartmental Model (SMCM) could be used to predict pollutant  
10 concentration and mass fraction in air, soil, water, and sediment through time. Exposure  
11 data could then be used to develop exposure-response studies for hazard identification at  
12 realistic ambient concentrations.

13  
14       ***Aquatic Ecosystem Exposure.*** Exposure assessments for aquatic ecosystems involve  
15 integration of research results from source characterization and environmental fate with  
16 information on the populations of organisms at risk, so the exposure assessments produced  
17 can be used for risk assessments. For exposure assessments of gasoline and diesel fuel  
18 spills, considerable care must be given to the different fates of the fuel components. Many  
19 components have limited solubility, producing slicks or emulsions; some components will  
20 volatilize readily; and others will adsorb substantially to suspended solids and sediment. The  
21 net result is to produce marked heterogeneity throughout the water column, varying  
22 bioavailability, and changes in the relative composition and, thus, the toxicity of the complex  
23 mixture represented by these fuels. The organisms at risk and their microenvironments must  
24 be carefully defined, and the concentration-time series and mixture of fuel components to  
25 which they are exposed must be carefully computed. For chronic exposures from more  
26 continuous releases and from atmospheric deposition (for which more rudimentary risk  
27 assessments will initially need to be done), only average, general exposures will be needed  
28 for comparison with effects concentrations from chronic toxicity tests; however, the mixture  
29 of fuel components to which organisms at risk actually will be exposed must be carefully  
30 characterized so suitable effects information can be applied.



#### 2.1.1.4 Analytical Methodology

Analytical methodologies for measuring source emissions, for monitoring the ambient air transport and transformation of these emissions, and for monitoring the exposure of target populations (human and ecosystem) to the pollutants of interest are prerequisites for determining the relative impacts of varied motor fuels on risk to public health and welfare.

Source emissions characterization requires accurate, precise analytical procedures. Acceptable procedures exist for measuring currently regulated total hydrocarbon (THC), CO, NO<sub>x</sub>, CO<sub>2</sub>, and total particulate emissions, as well as for measuring some unregulated toxic emissions of interest (such as benzene, formaldehyde, and 1,3-butadiene) from motor vehicles using conventional fuels. With the 1990 CAAAs requiring substantial reduction of motor vehicle regulated emissions, the adequacy (accuracy and precision) of classical certification measurement methods will require evaluation at lower pollutant concentrations. In addition to classical THC regulation, the CAAAs require measurement of NMHC emission rates. Near term procedures will measure THC and methane emissions, and NMHC emissions will be determined by subtraction. Future procedures will require direct measurement of NMHC emissions. Because available procedures are often costly and complex to implement, efforts to improve methodology performance and to simplify procedures, permitting application by lesser skilled analysts, are required. Many of the analytical procedures provide only integrated data for transient driving periods; therefore, conditions favoring emission of the toxic substance of interest are difficult to isolate. Continuous "real time" measurement procedures must be developed for this purpose. Validated chromatographic procedures are required for determining the composition of organic emissions for both O<sub>3</sub> and toxics air quality impact assessments.

Ambient air monitoring of pollutants requires many of the same techniques employed for source emissions measurements. Because pollutants are present at much lower concentrations, however, these source measurement techniques need to be modified (e.g., gas chromatographic samples need to be concentrated with the use of a cryogenic trap). Gas chromatograms of ambient air samples often have many unidentified peaks. Some of these are probably a result of direct emissions; however, many of them are a result of atmospheric transformations. Gas chromatographs (GCs) with mass spectrometry (MS) along with

1 long-path infrared spectroscopy are needed for proper identification. Some developmental  
2 work is also needed for the measurement of formaldehyde and higher aldehydes because the  
3 cartridge technique using dinitrophenylhydrazine (DNPH) may be affected by ambient levels  
4 of O<sub>3</sub>.

5 Ambient air monitoring and microenvironmental monitoring will require improvements  
6 and/or further methods development in order to measure the pollutants at the expected levels  
7 and locations of interest. In addition, an O<sub>3</sub> personal monitor will be required for accurate  
8 characterization of population exposures.

## 10 **2.1.2 Effects Assessment**

### 11 **2.1.2.1 Human Health Effects**

12 The health effects of the complex mixtures that comprise current conventional fuels  
13 have not been recently evaluated; however, a major research program to evaluate the  
14 comparative toxicology, including carcinogenicity, of synthetic fuels compared to  
15 conventional fuels was conducted during the 1970's as part of government (Department of  
16 Energy) and industry (American Petroleum Institute) programs. Although these synthetic  
17 fuel studies focused on many petroleum products that are heavier and have a higher boiling  
18 range than diesel and gasoline fuels, a number of studies included diesel No. 2 and gasoline  
19 as comparative conventional fuels. In general, the heavier, higher boiling fuels were found  
20 to be more toxic and carcinogenic than the lighter fuels, such as gasoline. These studies will  
21 provide an important comparative data set for studies proposed for new alternative fuels,  
22 such as the oxygenated and alcohol fuels.

23 The health effects of conventional petroleum products have been recently evaluated by  
24 the International Agency for Research on Cancer (IARC). The IARC reviewed the human  
25 and experimental animal and short-term bioassay data for both cancer and noncancer effects.  
26 The conventional fuel most pertinent to the comparative assessment of alternative fuels is  
27 unleaded gasoline. Unleaded gasoline was evaluated by the IARC as being possibly  
28 carcinogenic to humans (Group 2B), based on inadequate evidence for carcinogenicity in  
29 humans and limited evidence for the carcinogenicity in animals. Aerosolized whole gasoline  
30 has been studied in chronic inhalation exposures in one strain of mice and in one strain of

1 rats. Comparisons between exposure to aerosolized whole gasoline and normally occurring  
2 vapors from vapor loss, however, are uncertain because the vapors will contain a greater  
3 percentage of lower molecular weight components. An increase in the incidence of  
4 hepatocellular adenomas and carcinomas was found in female mice, but not in males.  
5 An increased incidence of adenomas and carcinomas of the kidneys was observed only in  
6 male rats. The induction of kidney tumors was preceded by nephropathy with hyaline  
7 droplet formation, necrosis, and degeneration of proximal convoluted tubules. The extent  
8 and severity of hyaline droplet accumulation parallels the extent and localization of renal  
9 tubular cell proliferation. In humans, urinary thioether excretion in service station workers  
10 was increased, and the half-life of antiprene in these workers was reduced. The only  
11 evidence for genotoxicity of unleaded gasoline is the induction of unscheduled DNA synthesis  
12 in hepatocytes of mice treated in vivo and in cultured mouse, rat, and human hepatocytes.

13 The findings in the animal studies have led to a number of investigations on the nature  
14 and mechanism of carcinogenesis of unleaded gasoline vapors. Because a number of  
15 chemicals, in addition to gasoline, have also been recently shown to induce kidney  
16 nephropathy and tumor induction in male rats, an EPA Toxicology Forum Panel was  
17 convened to determine the usefulness of these endpoints for assessing human risk. This  
18 Panel concluded that when certain criteria are met (e.g., the agents are nongenotoxic, hyaline  
19 droplets are present, etc.), then neither kidney nephropathy nor kidney tumors are  
20 appropriate for evaluating human risk. The panel, however, has not determined whether  
21 gasoline meets these criteria.

22 In contrast to gasoline research, diesel research has focused on combustion exhaust.  
23 Over the past decade, an extensive range of studies from in vitro genetic toxicity to  
24 long-term animal inhalation studies and human epidemiological studies of diesel exhaust have  
25 been conducted. The data base on leaded and unleaded gasoline exhaust is much less  
26 extensive, but it does include several important new studies conducted for comparison to  
27 diesel emissions.

28 A working group of the IARC found sufficient evidence for the carcinogenicity of  
29 whole diesel engine exhaust in experimental animals and limited evidence in humans,  
30

1 resulting in an overall evaluation of diesel engine exhaust as probably carcinogenic in  
2 humans (Group 2A).

3       The EPA has developed a draft assessment of the health effects of diesel emissions  
4 (U.S. Environmental Protection Agency, 1990e) in which it qualitatively classifies diesel  
5 emissions as a probable human carcinogen (category B1) based on limited evidence of  
6 carcinogenicity in humans. Fewer data were available to evaluate gasoline engine exhaust.  
7 In part because of this lack of data, IARC was unable to evaluate leaded and unleaded  
8 gasoline engine exhausts separately, and, for the purposes of their summary and evaluation,  
9 these two conventional combustion emissions were combined. The IARC working group  
10 found inadequate evidence for the carcinogenicity in animals of whole gasoline engine  
11 exhaust, although several studies provide evidence that gasoline engine exhaust is  
12 carcinogenic. The IARC also found that the evidence for the carcinogenicity of condensates  
13 and extracts of gasoline engine combustion emissions in animals was sufficient; however,  
14 evidence for the carcinogenicity of gasoline engine exhaust in humans was inadequate. These  
15 findings resulted in an overall evaluation of gasoline engine exhaust as possibly carcinogenic  
16 to humans (Group 2B). The EPA has not evaluated the weight-of-evidence for  
17 carcinogenicity of gasoline engine exhaust, nor has EPA developed any unit risk estimates of  
18 carcinogenic potency.

19       In contrast, the noncancer health effects associated with the combustion and  
20 transformation products of conventional fuels are better documented and impact a large  
21 portion of the U.S. population. The effects of pollutants such as CO and O<sub>3</sub> have been  
22 discussed extensively elsewhere and will not be reiterated here. Although numerous older  
23 studies evaluated the effects of inhaling combustion mixtures of leaded gasoline, virtually no  
24 studies of unleaded fuel combustion emissions have been published in the open literature.  
25 There are likely to be several similarities between the effects of leaded and unleaded gasoline  
26 emissions. However, differences in lead and organic composition may yield unknown  
27 differences in toxicity. Furthermore, most combustion emission studies were conducted  
28 many years ago using techniques that are not as sophisticated as current techniques. The  
29 issues highlight the importance and difficulties of the comparative risk assessment of  
30 alternative fuels planned by the EPA. Appropriate choices of fuels and control technologies

will involve difficult comparisons of effects on differing organ systems and of differing severities under a variety of exposure conditions. Appropriate conventional fuel studies must be conducted to ensure valid comparisons to alternative fuels.

## **2.1.2.2 Ecosystem Effects**

### ***2.1.2.2.1 Terrestrial Ecosystem Effects***

The biological and ecological effects of conventional fuel pollutants have been documented, particularly in relation to likely ambient exposure levels; however, research is still needed for comparisons with alternative fuels. Laboratory investigations of plant species show that conventional-fuel pollutants (e.g., O<sub>3</sub> and NO<sub>x</sub>) can inhibit plant growth and development through reduction in photosynthesis, transpiration, and mineral absorption. Also, these pollutants have been documented to have direct impacts on ecosystems by causing changes in plant species composition, productivity, and reproduction. Changes in the vegetal structure of ecosystems undoubtedly will affect wildlife habitat quality.

Direct effects of conventional-fuel pollutants on wildlife may, depending upon concentration and exposure duration, result in irritation of the mucous membranes, eyes, and respiratory tract and perhaps disrupt activity patterns. Trophic changes with loss of biodiversity resulting from acid rain deposition into surface waters have been documented. Chronic, sublethal exposures to vegetation may decrease productivity and reproduction, whereas wildlife may be affected through loss of competitive advantage or altered behavioral patterns.

Some information on the effects of conventional-fuel pollutants on single species is available because of research with the criteria pollutants; however, data on terrestrial ecosystem exposure-deposition and exposure-response are lacking. Potential ecological effects need documentation through microcosm/mesocosm research and biomonitoring of various terrestrial ecosystems such as agroecosystems and forests.

### ***2.1.2.2.2 Aquatic Ecosystem Effects***

Extensive research on the acute and chronic effects of petroleum on aquatic organisms and ecosystems has been conducted. Most of this work has focused on No. 2 fuel oil

(similar to diesel fuel), No. 6 fuel oil, and crude oil. Considerably less research has been conducted on gasolines, due in part to the volatility of gasoline.

Many petroleum hydrocarbons are toxic to aquatic biota, and some of the compounds, such as PAHs, have been shown to bioaccumulate in some aquatic species. Petroleum hydrocarbons can injure aquatic biota and communities due to direct acute toxicity resulting from physical processes (smothering, hypothermia due to loss of body insulation) and from chronic effects on sensitive life stages.

Although a considerable amount of information is available about the toxicity of petroleum compounds to various aquatic organisms, the impact of these fuels on aquatic systems is not yet fully understood. For example, additional mesocosm experiments are needed to better understand the community-level effects of these mixtures and the resiliency of aquatic ecosystems. This should include studies of a variety of aquatic community types that may vary greatly in their responses and sensitivities. Integrative system measurements, such as oxygen consumption and nutrient fluxes, should be included to assess the state and health of these systems. Also, due to the likely transient nature of the exposures, kinetic-based toxicity models are needed for better predictions of the effects of fuels on aquatic systems.

### **2.1.3 Risk Prevention/Mitigation**

#### **2.1.3.1 Stationary Sources**

The efficiency of existing prevention and control technologies and practices for stationary sources of VOCs must be assessed. Based on this evaluation, design and operation information must be developed to optimize existing stationary source controls, especially for emissions from gasoline storage, distribution, and marketing. Guidance is needed to develop new or improved control systems, design methods, and operating procedures that would minimize emissions/discharges from feedstock recovery, production, transportation, distribution, and use of conventional petroleum-based fuels.

Carbon-based controls are especially important for hydrocarbon recovery. Research is needed to optimize the effectiveness of carbon-based technology; however, existing oxygenates (ethanol, MTBE) in conventional fuels may have adverse impacts on the

1 control-effectiveness of existing carbon-based controls. Research to quantify this potential  
2 adverse effect and to develop improved carbon-absorption technology for minimizing or  
3 eliminating the adverse effect is needed.

4 To reduce the occurrence and severity of releases, user-oriented accidental release  
5 reference manuals/guidelines for preventing accidental releases of conventional fuels from  
6 storage, production, transportation, and marketing should be developed. Special emphasis  
7 needs to be placed on prevention and control of the major and growing CO<sub>2</sub> releases  
8 associated with petroleum extraction, especially enhanced oil recovery.

9 Existing Federal regulations offer state-of-the-art guidance for the prevention of releases  
10 from USTs; however, continued research is required to optimize design and installation  
11 procedures; corrosion prevention methodologies; and procedures to inspect, identify,  
12 maintain, and repair potential internal and external UST system problems to prevent failure.  
13 Research is also required to provide decision tools and guidance on cleanup technologies for  
14 application to leaking USTs and includes an interpretation of items such as the mobility of  
15 the contaminants at a site, site conditions that limit in-place cleanup, site conditions that  
16 suggest the site is stable and not worsening, and data that show cleanup progress (i.e., when  
17 to terminate cleanup). Achieving these goals will require in-depth studies of certain site  
18 characteristics, transport and transformation processes, and subsurface conditions, as well as  
19 studies of specific corrective action technologies at actual sites of leaking USTs.

20 Research on leaking USTs to date has focused on gasoline-contaminated soils and  
21 aquifers, with only a modest effort to cover other conventional fuels, and has included  
22 (1) evaluations of the state-of-the-knowledge of gasoline fate and transport in soil,  
23 (2) evaluations of the state-of-the-art of several corrective action technologies (e.g., soil  
24 vapor extraction and soil washing), (3) limited pilot and full scale demonstration tests, and  
25 (4) the preparation of site investigation/corrective guidance manuals. Further research is  
26 required to address other conventional fuels as well as other cleanup technologies to optimize  
27 technology selection and evaluation for more cost-effective cleanup actions.

### 2.1.3.2 Mobile Sources

Motor vehicle risk reduction programs need to focus on the long-term durability of emission control technology (tailpipe and evaporative) for reducing environmentally damaging emissions and on programs to identify and repair malfunctioning vehicles in the consumer fleet.

### 2.1.3.3 Fuel Transport Sources

Technology control/development of fuel tankers, barges, and storage tankers to reduce accidental spills and leakage will reduce the entry of conventional fuels into aquatic ecosystems. Accidents are inevitable, however, and insofar as spills pose a significant adverse risk, cleanup technologies must be improved through research.

## 2.2 BACKGROUND AND RATIONALE

### 2.2.1 Exposure Assessment

#### 2.2.1.1 Source Characterization

##### 2.2.1.1.1 Stationary Source Characterization

The potential benefits and risks of alternative fuels must be assessed in the context of existing fuels. Conventional petroleum-based fuels have a relatively long history of use and experience, yet much remains to be learned about their emissions and effects on the environment, humans, and biota. Without accurate data on emissions and discharges from crude oil recovery, refining, storage, transportation, distribution, and use of conventional fuels, a factual data base will not be available for quantitative determination of existing levels and types of emissions and discharges, for projecting future levels, or for providing an adequate basis for alternative fuels comparisons. One reason for this information gap is that the characteristics of the fuels themselves are subject to change. Gasoline formulations will vary by type of crudes, from season to season, and from region to region. The production and combustion of petroleum-based fuels (stationary and mobile) has created, and continues to be a major contributor to, problems of VOC emissions, impacting O<sub>3</sub> nonattainment, releases of toxic substances, and RITGs affecting global climate change (U.S. Congress,

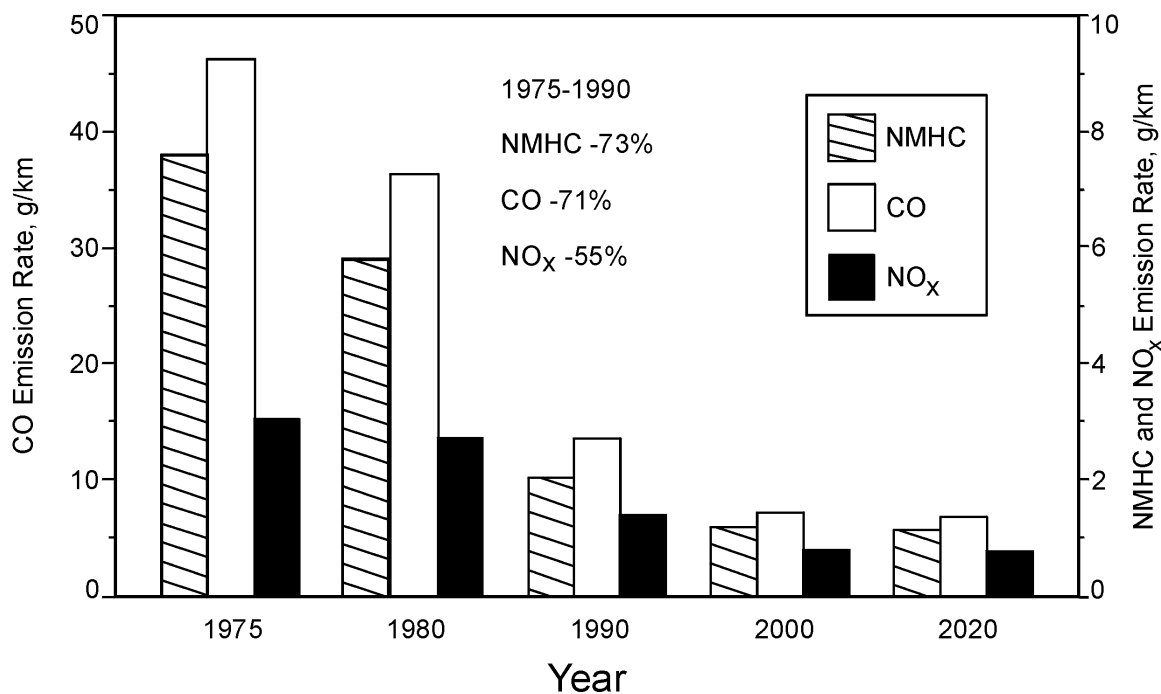


1988; DeLuchi et al., 1987). Although regulatory requirements (NSPS and NPDES) have reduced emissions, VOC emissions have not been sufficiently reduced to alleviate the O<sub>3</sub>-nonattainment problem. Because petroleum-based transportation fuels will be used for many years, the apparent effectiveness of existing VOC controls is uncertain and needs to be evaluated. Although emissions and discharges from the petroleum industry have been identified in a limited manner, better quantification for the variety of crudes used, refinery configurations, and product slates is needed. This information is necessary if additional reduction of pollutant emissions is to be obtained through application of existing or improved control systems. Existing emission/discharge controls need to be evaluated for effectiveness and applicability, and energy efficiencies for the various steps and processes need to be determined. The greatest emissions potential is through spills, leaks, or releases (transient, conventional, and accidental from loss of containment), and the major emissions of concern related to the petroleum industry are VOCs, RITGs, toxic air pollutants, and sulfur species. Information on CO<sub>2</sub> emissions is not available, with the exception of emissions from required energy generation sources. Data on total carbon emissions are needed, particularly for enhanced oil recovery, which is a large and increasing source of CO<sub>2</sub>.

#### ***2.2.1.1.2 Mobile Source Characterization***

Efforts by the U.S. government and motor vehicle industries to improve air quality in U.S. cities have resulted in a dramatic reduction of emissions from roadway motor vehicles. Figure 2-2, based on the EPA mobile source emissions model MOBILE 4 (U.S. Environmental Protection Agency, 1989b), suggests that during the period from 1975 to 1990, fleet average NMHC and CO emission rates were reduced by about 70%, and NO<sub>x</sub> emission rates were reduced by about 55%. During that same period of time, however, vehicle-miles-traveled (VMT) increased about 45%, substantially offsetting the emission-rate reductions. Most of the improvements have resulted from the technology-forcing Federal Emission Standards summarized in Table 2-1.

The history of motor vehicle emissions control in the United States has involved both progressively reduced standards and improved test procedures. For example, 1971 light-duty vehicle tailpipe emissions, certified at 2.2 g/mi THC and 23 g/mi CO, were determined



**Figure 2-2. Fleet average NMHC, CO, and NO<sub>x</sub> emission rates, 1975 to 2020.**  
**Note: 60 °F to 84 °F; 11.5 psi, 10.5 psi (89) RVP; 31.5 kph;**  
**inspection and maintenance, anti-tampering.**

Source: U.S. Environmental Protection Agency (1989b) .

1 using a 7-mode steady-state driving schedule; and evaporative emissions, certified at 6 g/test,  
 2 were determined using a gravimetric carbon-trap technique. Beginning in 1978, evaporative  
 3 emissions were determined using the Sealed Housing for Evaporative Determination (SHED)  
 4 technique, in which the entire vehicle is enclosed to collect emissions from all sources. The  
 5 current evaporative emissions standard is 2 g/test. A progression of transient driving  
 6 schedules more representative of urban driving conditions was used beginning in 1972, with  
 7 the current Constant Volume Sampling-1975 (CVS-75) procedure beginning in 1975.  
 8 Current tailpipe emission standards are 0.41 g/mi THC and 3.4 g/mi CO (both of which  
 9 represent 90% reductions from 1970 vehicle baselines), along with 1.0 g/mi NO<sub>x</sub> and

**TABLE 2-1. U.S. MOTOR VEHICLE EMISSIONS AND FUEL ECONOMY STANDARDS<sup>a</sup>**

| Model Year        | Vehicle Category | Tailpipe Hydrocarbon | Carbon Monoxide | Oxides of Nitrogen | Evaporative Hydrocarbon | Particles | Fuel Economy |
|-------------------|------------------|----------------------|-----------------|--------------------|-------------------------|-----------|--------------|
| 1970 <sup>b</sup> | LDV, LDT         | 2.2 g/mi             | 23 g/mi         | -                  | -                       | -         | -            |
| 1971              | LDV, LDT         | 2.2 g/mi             | 23 g/mi         | -                  | 6 g/test <sup>c</sup>   | -         | -            |
| 1972 <sup>d</sup> | LDV, LDT         | 3.4 g/mi             | 39 g/mi         | -                  | 2 g/test                | -         | -            |
| 1973              | LDV, LDT         | 3.4 g/mi             | 39 g/mi         | 3.0 g/mi           | 2 g/test                | -         | -            |
| 1974 <sup>e</sup> | HDGV, HDDV       | -                    | 40 g/bhphr      | -                  | -                       | -         | -            |
| 1975 <sup>f</sup> | LDV              | 1.5 g/mi             | 15 g/mi         | 3.1 g/mi           | 2 g/test                | -         | -            |
|                   | LDT              | 2.0 g/mi             | 20 g/mi         | 3.1 g/mi           | 2 g/test                | -         | -            |
| 1977              | LDV              | 1.5 g/mi             | 15 g/mi         | 2.0 g/mi           | 2 g/test                | -         | -            |
| 1978              | LDV              | 1.5 g/mi             | 15 g/mi         | 2.0 g/mi           | 6 g/test <sup>g</sup>   | -         | 18 mpg       |
|                   | LDT              | 2.0 g/mi             | 20 g/mi         | 3.1 g/mi           | 6 g/test                | -         | -            |
| 1979              | LDV              | 1.5 g/mi             | 15 g/mi         | 2.0 g/mi           | 6 g/test                | -         | 19 mpg       |
|                   | LDT              | 1.7 g/mi             | 18 g/mi         | 2.3 g/mi           | 6 g/test                | -         | -            |
|                   | HDGV, HDDV       | 1.5 g/bhphr          | 25 g/bhphr      | -                  | -                       | -         | -            |
| 1980              | LDV              | 0.41 g/mi            | 7.0 g/mi        | 2.0 g/mi           | 6 g/test                | -         | 20 mpg       |
| 1981              | LDV              | 0.41 g/mi            | 3.4 g/mi        | 1.0 g/mi           | 2 g/test                | -         | 22 mpg       |
|                   | LDT              | 1.7 g/mi             | 18 g/mi         | 2.0 g/mi           | 2 g/test                | -         | -            |
| 1982              | LDV              | 0.41 g/mi            | 3.4 g/mi        | 1.0 g/mi           | 2 g/test                | -         | 24 mpg       |
| 1983              | LDV              | 0.41 g/mi            | 3.4 g/mi        | 1.0 g/mi           | 2 g/test                | -         | 26 mpg       |
| 1984              | LDV              | 0.41 g/mi            | 3.4 g/mi        | 1.0 g/mi           | 2 g/test                | -         | 27 mpg       |
|                   | LDT              | 0.8 g/mi             | 10 g/mi         | 2.3 g/mi           | 2 g/test                | -         | -            |
| 1985              | LDV              | 0.41 g/mi            | 3.4 g/mi        | 1.0 g/mi           | 2 g/test                | 0.6 g/mi  | 27.5 mpg     |
|                   | LDT              | 0.8 g/mi             | 10 g/mi         | 2.3 g/mi           | 2 g/test                | 0.6 g/mi  | -            |
| <sup>h</sup>      | HDGV (<14K)      | 2.5 g/bhphr          | 40.1 g/bhphr    | -                  | 3 g/test                | -         | -            |

**TABLE 2-1 (cont'd). U.S. MOTOR VEHICLE EMISSIONS AND FUEL ECONOMY STANDARDS<sup>a</sup>**

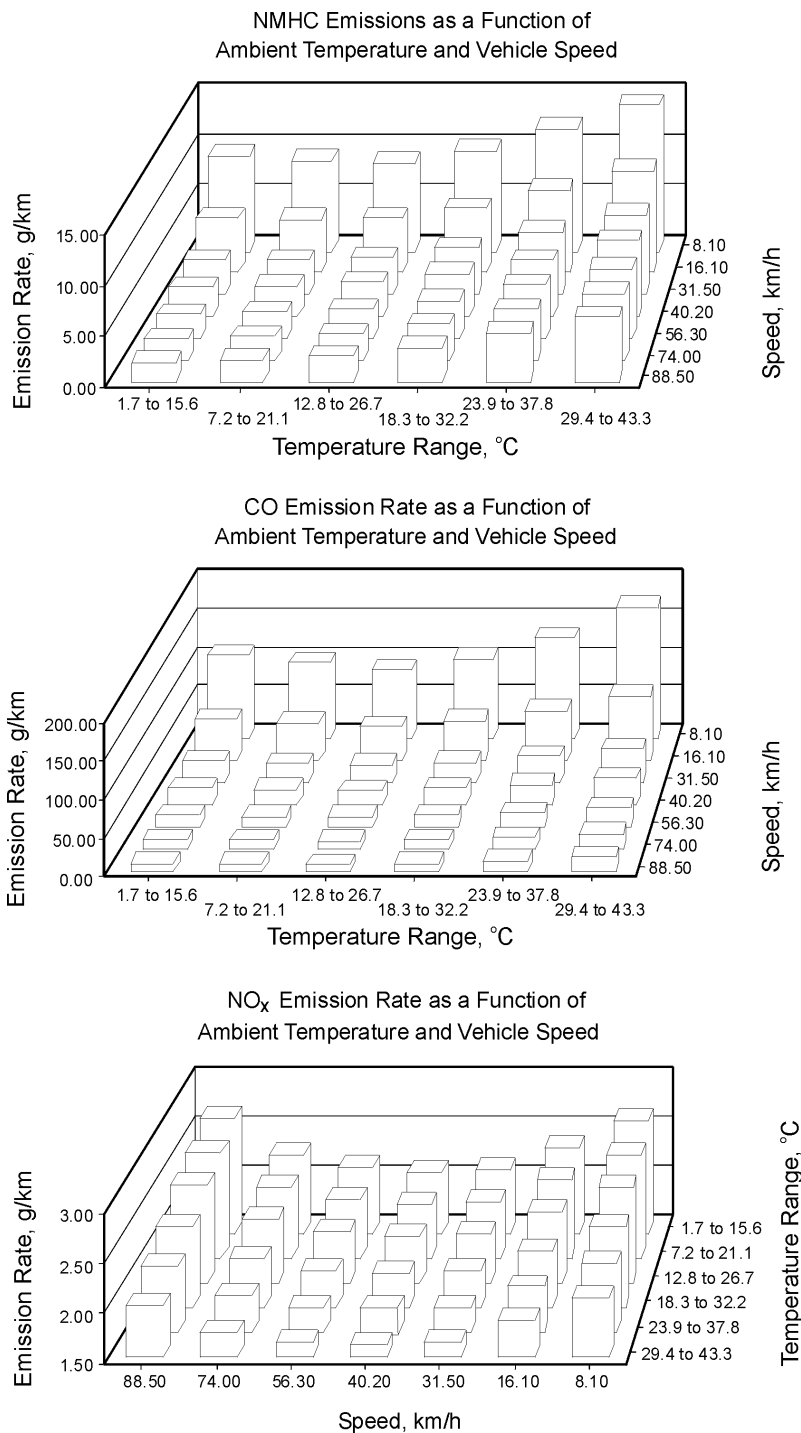
| Model Year        | Vehicle Category | Tailpipe Hydrocarbon | Carbon Monoxide | Oxides of Nitrogen | Evaporative Hydrocarbon | Particles                         | Fuel Economy |
|-------------------|------------------|----------------------|-----------------|--------------------|-------------------------|-----------------------------------|--------------|
| <sup>h</sup>      | HDGV (>14K)      |                      |                 |                    | 4 g/test                | -                                 | -            |
| <sup>h</sup>      | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | -                  | -                       | -                                 | -            |
| 1987              | LDV              | 0.41 g/mi            | 3.4 g/mi        | 1.0 g/mi           | 2 g/test                | 0.2 g/mi                          | 27.5 mpg     |
|                   | LDT              | 0.8 g/mi             | 10 g/mi         | 1.2 g/mi           | 2 g/test                | 0.26 g/mi                         | -            |
|                   | HDGV (<14K)      | 1.3 g/bhphr          | 15.5 g/bhphr    | 6.0 g/bhphr        | 3 g/test                | -                                 | -            |
|                   | HDGV (>14K)      | 2.5 g/bhphr          | 40 g/bhphr      | 6.0 g/bhphr        | 4 g/test                | -                                 | -            |
|                   | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | 6.0 g/bhphr        | -                       | -                                 | -            |
| 1988              | HDGV (<14K)      | 1.1 g/bhphr          | 14.4 g/bhphr    | 6.0 g/bhphr        | 3 g/test                | -                                 | -            |
|                   | HDGV (<14K)      | 1.9 g/bhphr          | 37.1 g/bhphr    | 6.0 g/bhphr        | 4 g/test                | -                                 | -            |
|                   | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | 6.0 g/bhphr        | -                       | 0.6 g/bhphr                       | -            |
| 1991              | HDGV (<14K)      | 1.1 g/bhphr          | 14.4 g/bhphr    | 5.0 g/bhphr        | 3 g/test                | -                                 | -            |
|                   | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | 5.0 g/bhphr        | -                       | 0.25 g/bhphr                      | -            |
| 1993              | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | 5.0 g/bhphr        | -                       | 0.1 g/bhphr (bus)                 | -            |
| 1994 <sup>i</sup> | LDV              | 0.25 g/mi            | 3.4 g/mi        | 0.4 g/mi           | 2 g/test                | 0.08 g/mi                         | 27.5 mpg     |
| <sup>i</sup>      | LDT              | 0.32 g/mi            | 4.4 g/mi        | 0.7 g/mi           | 2 g/test                | 0.26 g/mi                         | -            |
|                   | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | 5.0 g/bhphr        | -                       | 0.1 g/bhphr<br>0.05 g/bhphr (bus) | -            |
| 1995 <sup>j</sup> | LDT              | 0.32 g/mi            | 4.4 g/mi        | 0.7 g/mi           | 2 g/test                | 0.08 g/mi                         | -            |
| 1998              | HDDV             | 1.3 g/bhphr          | 15.5 g/bhphr    | 4.0 g/bhphr        | -                       | 0.1 g/bhphr                       | -            |

Key: <sup>a</sup>LDV = Light-duty vehicle, LDT = Light-duty truck, HDGV = heavy-duty gasoline vehicle, HDDV = heavy-duty diesel vehicle, g/mi = grams per mile, g/bhphr = grams per brake horsepower hour, mpg = miles per gallon; <sup>b</sup>7-mode steady-state driving procedure; <sup>c</sup>carbon trap technique; <sup>d</sup>CVS-72 transient driving procedure; <sup>e</sup>13-mode steady-state driving procedure; <sup>f</sup>CVS-75 transient driving procedure; <sup>g</sup>SHED technique; <sup>h</sup>transient driving procedure; <sup>i</sup>phased in from 1994 to 1996; <sup>j</sup>PM phased in from 1995 to 1997.

0.2 g/mi particles. Heavy-duty vehicle tailpipe emissions were regulated using a 13-mode steady-state driving schedule from 1974 to 1985, when transient procedures were adopted. The tailpipe emission standards have ranged from 40 g/bhphr CO in 1974 to current gasoline truck and bus standards of 1.1 g/bhphr THC (1.9 g/bhphr for >14,000 lb gross vehicle weight [GVW]), 14.4 g/bhphr CO (37.1 g/bhphr for >14,000 lb GVW), and 6.0 g/bhphr NO<sub>x</sub>. Diesel truck and bus standards are 1.3 g/bhphr THC, 15.5 g/bhphr CO, 6.0 g/bhphr NO<sub>x</sub>, and 0.6 g/bhphr particles. The current heavy-duty gasoline truck and bus evaporative emission standard is 3 g/test (4 g/test for >14,000 lb GVW).

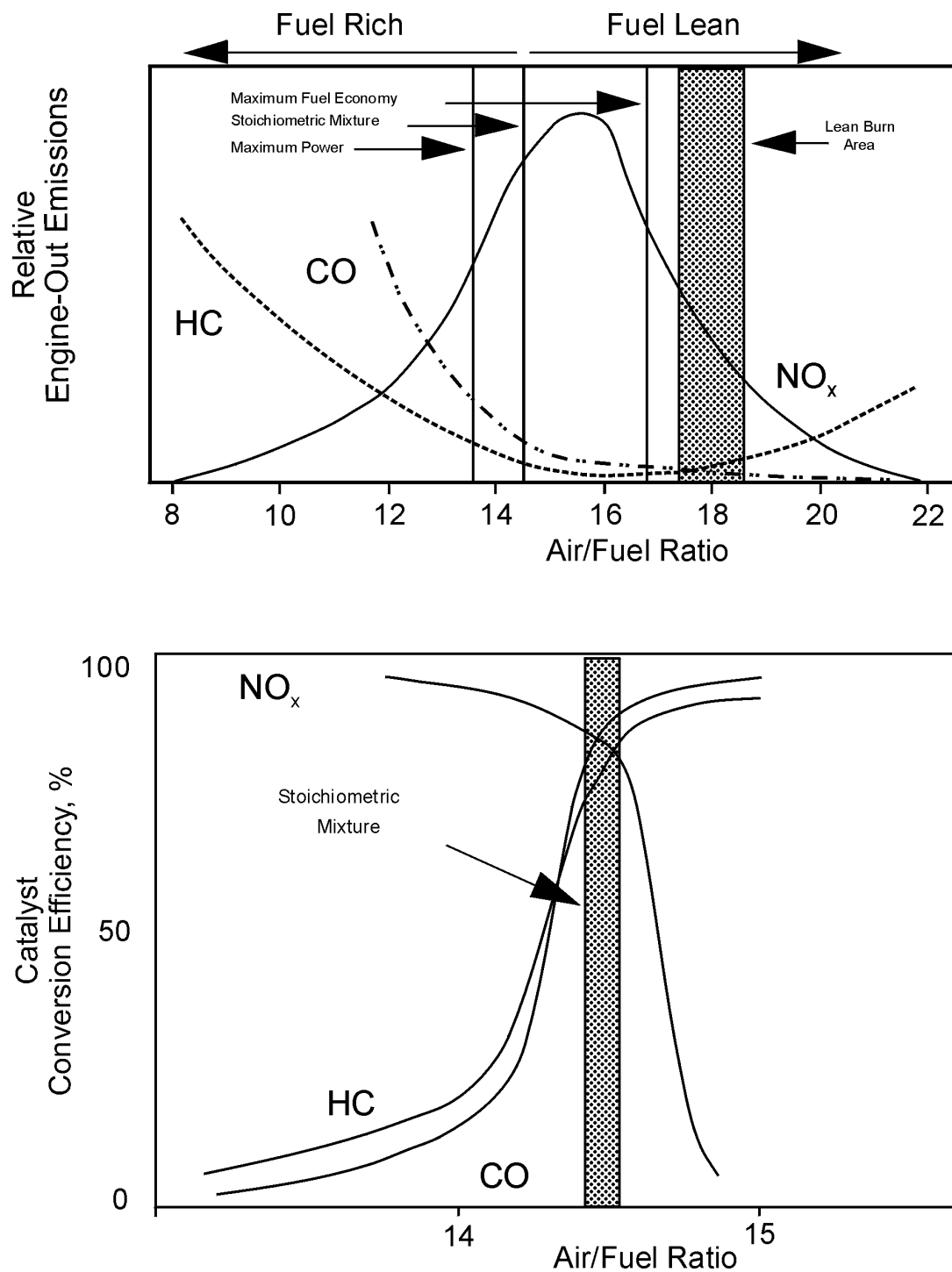
If current VMT growth continues, during the mid- to late-1990s, the pollution burden of motor vehicles is projected to "bottom-out" and begin to grow in magnitude unless further improvements are realized (Walsh, 1990). The 1990 CAAAs require both reduction of motor vehicle emissions and changes in fuel formulation (e.g., reduction of gasoline volatility and aromatic hydrocarbon fractions, and addition of oxygenated organics).

In 1988, light-duty gasoline passenger cars and trucks were responsible for greater than 90% of the motor vehicle NMHC and CO emissions and about 67% of NO<sub>x</sub> and particulate emissions, and heavy-duty trucks and buses were responsible for about 30% of NO<sub>x</sub> and particulate emissions (U.S. Environmental Protection Agency, 1990g). The emissions (especially those of gasoline-fueled vehicles) are sensitive to changes in operating conditions such as ambient temperature, average speed, altitude, and age (malfunctions). Figure 2-3 illustrates the variations of NMHC, CO, and NO<sub>x</sub> with ambient temperature and speed as projected by MOBILE 4. Federal emissions certification involves a rather narrow "window" within this range of conditions [i.e., 19.6 mi/h (31.5 km/h), 70 °F (21.1 °C) average temperature with a 60 to 84 °F (15.6 to 28.9 °C) diurnal ramp]. The ratio of air to fuel in the engine combustion chamber is very important to gasoline vehicle emissions. Any operating condition that shifts the air/fuel ratio towards fuel rich or fuel lean of the stoichiometric mixture will influence emissions as indicated in Figure 2-4. Hydrocarbons are emitted from tailpipes and evaporative (running-loss) sources when vehicles are operated on roadways, from evaporative (diurnal and hot soak) sources when vehicles are parked, and from the gasoline tanks when vehicles are refueled. Figure 2-5 illustrates the relative contribution of each at varied average speeds and ambient temperatures for 11.5 psi RVP and



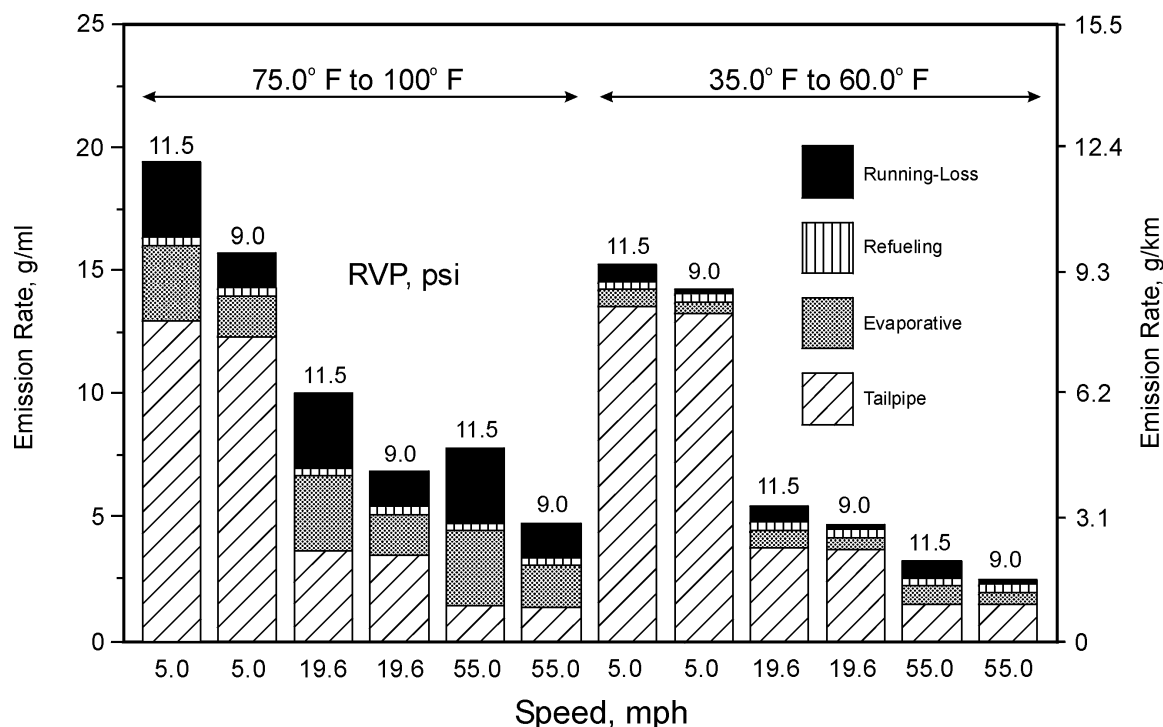
**Figure 2-3. NMHC, CO, and NO<sub>x</sub> emission rates as a function of ambient temperature and vehicle speed.**

Source: U.S. Environmental Protection Agency (1989b); Black (1991a).



**Figure 2-4. Emissions versus air/fuel ratio.**

Source: Black (1991a).



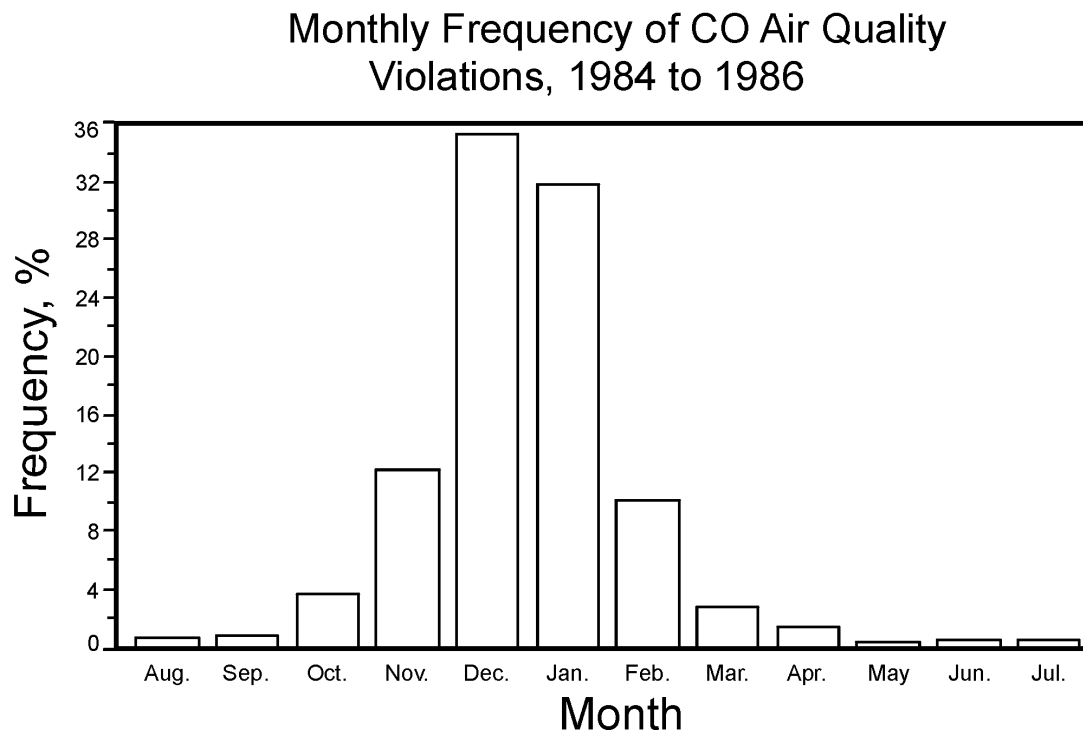
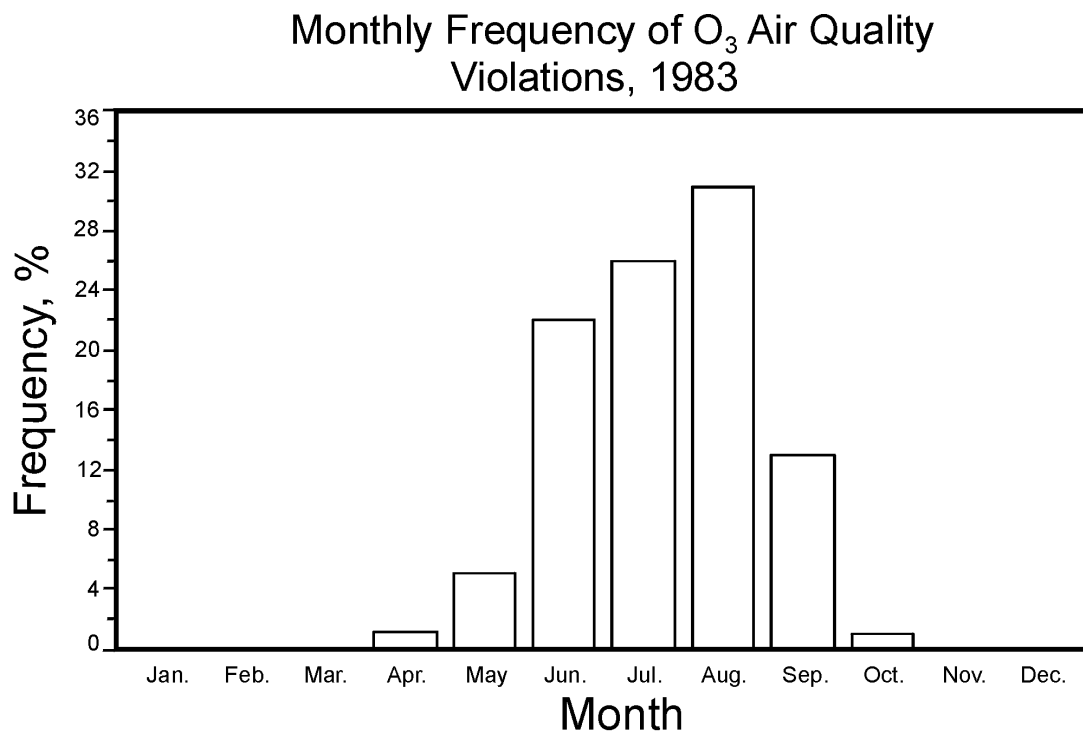
**Figure 2-5. 1985 Motor vehicle NMHC emissions distribution: tailpipe, evaporative (diurnal and hot soak), refueling, and running-loss.**

Source: U.S. Environmental Protection Agency (1989b); Black (1991a).

9.0 psi RVP gasolines. The relative contribution of evaporative sources is much greater at higher summer temperatures. It should be noted that the MOBILE 4 model manipulates neither evaporative emissions for average speed variance nor refueling emissions for fuel volatility or average speed variance. Available data are not adequate to define the necessary mathematical algorithms.

As illustrated in Figure 2-6, O<sub>3</sub> and CO air quality vary seasonally. Ozone air quality problems are more common during high temperature summer conditions (U.S. Environmental Protection Agency, 1989d), and CO air quality problems are more common during low temperature winter conditions (U.S. Environmental Protection Agency, 1989e). The impact





**Figure 2-6. Seasonal nature of O<sub>3</sub> and CO air quality.**

Source: Black (1991a).

1 of motor vehicle emissions on O<sub>3</sub> is sensitive to many variables, including meteorology  
2 (ambient temperature, ultraviolet [UV]-light intensity, wind, etc.), the relative importance of  
3 other O<sub>3</sub> precursor sources, organic emissions composition (reactivity), and local  
4 hydrocarbon/NO<sub>x</sub> ratios. The relative contribution of motor vehicles and other sources  
5 (anthropogenic and biogenic) will vary from one region to another and with ambient  
6 temperature, traffic congestion (average speed), and many other manageable and  
7 unmanageable variables. The emissions composition will depend on many of these same  
8 variables, the composition of the fuel, and the characteristics (e.g., age; distribution of  
9 trucks, buses, cars) of the vehicle fleet. Table 2-2 provides an example of the compositional  
10 variance of commercial gasoline and diesel fuels. Motor vehicle hydrocarbon emissions  
11 composition will vary with the fuel. As indicated in Table 2-3, emissions compositional  
12 differences are expected for tailpipe, evaporative, and refueling sources; and the vehicle  
13 aggregate composition will depend on the relative contribution of each category (which varies  
14 with speed, temperature, etc.) (Black, 1991a). Because the sensitivities of hydrocarbon and  
15 NO<sub>x</sub> emissions to operating variables are different (see Figure 2-3), the emissions  
16 hydrocarbon/NO<sub>x</sub> ratio will also vary with operating conditions according to Figure 2-7.

17 The emission rates of toxics are sensitive to many of the previously discussed variables.  
18 For example, benzene emission rates are sensitive to the fuel content of benzene and of  
19 higher molecular weight fuel aromatics (e.g., toluene and xylenes), which are responsible for  
20 tailpipe benzene through dealkylation processes during combustion (Black et al., 1980; Raley  
21 et al., 1984; Seizinger et al., 1986). Limited available data suggest that tailpipe benzene-  
22 emission rates increase as temperature is decreased but that the benzene fraction of total  
23 hydrocarbon emissions remains relatively constant (Stump et al., 1989). Data on the  
24 sensitivity of evaporative emissions composition to ambient temperature are very limited.  
25 As would be expected from distillation theory, aromatic hydrocarbons constitute a larger  
26 fraction of the emissions at higher temperatures.

27 Estimates of cancer risk from motor vehicle emissions suggest that attention should be  
28 directed to diesel particles, gasoline particles, 1,3-butadiene, benzene, and formaldehyde.  
29 The largest potential risk has been identified with diesel particles (Adler and Carey, 1989).  
30 These emissions have been the subject of much study, and ORD has developed a draft

TABLE 2-2. NATIONAL FUEL SURVEY (SUMMER 1989)

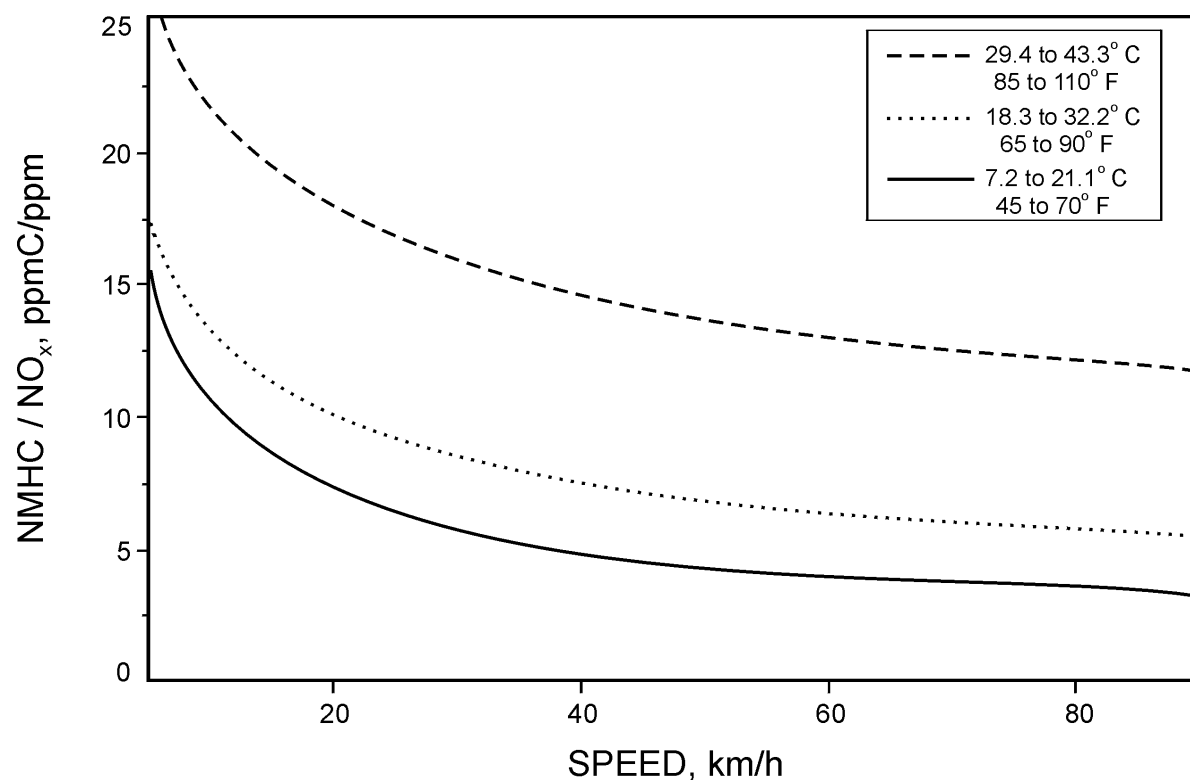
|                     | Aromatics | Olefins | Saturates | MTBE | RVP  | Sulfur | Octane   | Cetane No. |
|---------------------|-----------|---------|-----------|------|------|--------|----------|------------|
|                     | %         | %       | %         | %    | psi  | wt %   | (R +N)/2 |            |
| <b>Premium</b>      |           |         |           |      |      |        |          |            |
| <b>Unleaded</b>     |           |         |           |      |      |        |          |            |
| Maximum             | 67.0      | 17.8    | 82.5      | 10.3 | 10.9 | 0.071  | 97.3     |            |
| Minimum             | 11.0      | 1.1     | 30.6      | <0.1 | 5.9  | <0.001 | 87.0     |            |
| Average             | 37.1      | 6.2     | 56.6      | <1.9 | 8.9  | <0.016 | 92.3     |            |
| <b>Intermediate</b> |           |         |           |      |      |        |          |            |
| Maximum             | 48.6      | 23.1    | 66.6      | 8.3  | 10.3 | 0.111  | 91.1     |            |
| Minimum             | 25.1      | 2.9     | 37.6      | <0.1 | 8.2  | 0.005  | 87.2     |            |
| Average             | 32.5      | 11.4    | 55.9      | <1.6 | 9.1  | 0.036  | 89.3     |            |
| <b>Regular</b>      |           |         |           |      |      |        |          |            |
| <b>Unleaded</b>     |           |         |           |      |      |        |          |            |
| Maximum             | 42.2      | 42.8    | 73.2      | 5.4  | 10.9 | 0.187  | 94.9     |            |
| Minimum             | 17.7      | 1.0     | 33.9      | <0.1 | 7.7  | <0.001 | 84.4     |            |
| Average             | 29.9      | 11.8    | 58.1      | <0.2 | 8.9  | <0.037 | 87.3     |            |
| <b>#2 Diesel</b>    |           |         |           |      |      |        |          |            |
| Maximum             | 43.3      | 2.3     | 86.1      |      |      | 0.60   |          | 56.4       |
| Minimum             | 13.3      | 0.4     | 55.3      |      |      | 0.03   |          | 39.2       |
| Average             | 32.7      | 0.9     | 66.2      |      |      | 0.32   |          | 45.4       |

Adapted from Motor Vehicle Manufacturers Association (1989).

**TABLE 2-3. HYDROCARBON COMPOSITION OF GASOLINE MOTOR VEHICLE TAILPIPE, EVAPORATIVE, AND REFUELING EMISSIONS**

| Organic Classification | Tailpipe Emissions (%) | Evaporative Emissions (%) | Refueling Emissions (%) |
|------------------------|------------------------|---------------------------|-------------------------|
| Paraffinic             | 55                     | 72                        | 85                      |
| n-Butane               | 5                      | 23                        | 32                      |
| Isopentane             | 4                      | 15                        | 19                      |
| Olefinic               | 18                     | 10                        | 11                      |
| Aromatic               | 25                     | 18                        | 4                       |
| Acetylenic             | 2                      | 0                         | 0                       |

Source: Black (1989).

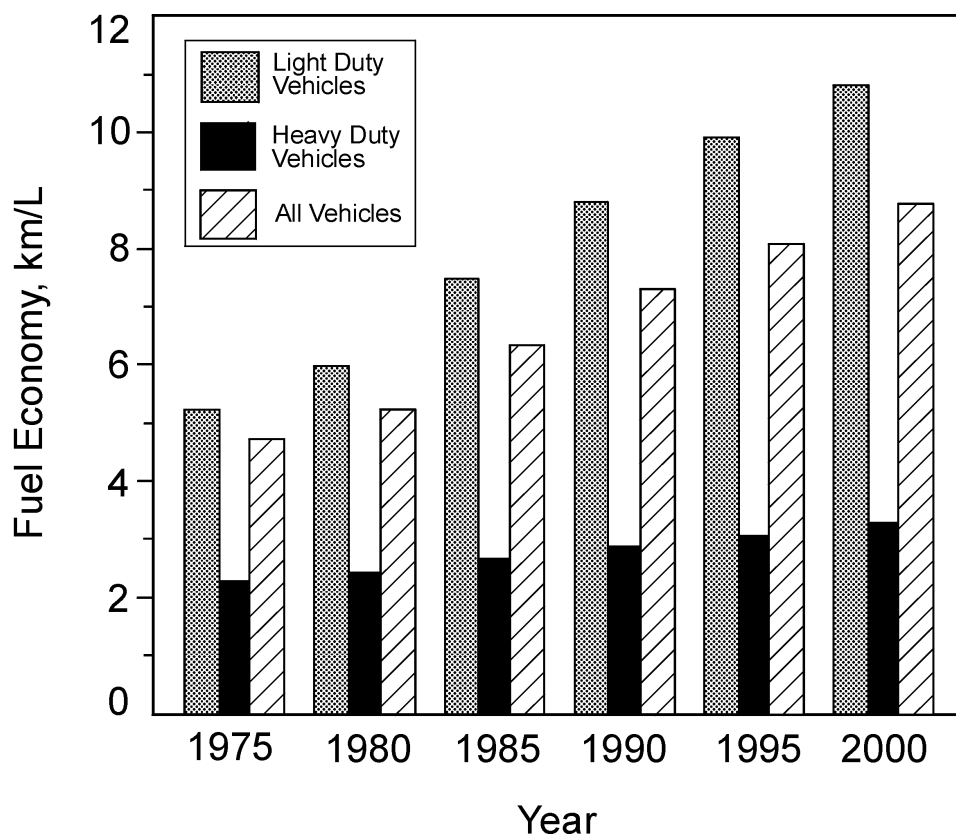
**Figure 2-7. 1985 Fleet average NMHC/NO<sub>x</sub> ratio as a function of ambient temperature and vehicle speed.**

Source: U.S. Environmental Protection Agency (1989b); Black (1991a).

comprehensive diesel hazard assessment, which includes a revision of the cancer unit risk (U.S. Environmental Protection Agency, 1990e). Diesel particles include elemental and organic carbon, sulfate, and small amounts of trace metals (Hare and Black, 1981; Black et al., 1985a).

Technology-forcing particulate-emissions standards (see Table 2-1) have resulted in improved engine designs and fuel reformulations (Alson et al., 1989; Ullman, 1989; U.S. Environmental Protection Agency, 1990a). Diesel fuel sulfur content will be reduced to 0.05 wt % by 1993 (during the summer of 1989, the national average was 0.32 wt % [see Table 2-2]).

Motor vehicles also contribute to the atmospheric burden of RITGs that influences global climate (Unnasch et al., 1989; DeLuchi et al., 1987). The motor vehicle emissions (associated with fuel combustion) of greatest importance are CO<sub>2</sub>, methane, and N<sub>2</sub>O. Chlorofluorocarbon emissions from automobile air conditioners are also important, but they are not sensitive to fuel choice and will not be discussed further in this Research Strategy. Considering emissions associated with production, distribution, and motor vehicle use, CO<sub>2</sub> is responsible for about 77% of the motor vehicle global warming effect from conventional gasoline fuels and for about 91% from conventional diesel fuels (Unnasch et al., 1989). Carbon dioxide emission rates are directly related to fuel economy, and fleet average fuel economy has improved in response to Federal Standards (see Table 2-1) and consumer market demands as indicated in Figure 2-8. Table 2-4 provides CO<sub>2</sub> emission rates for 1975, 1985, and 1995 (estimated) (Black, 1989). During the 1975 to 1985 decade, fleet average emissions decreased about 22%, but VMT increased 30%, increasing the motor vehicle atmospheric burden of CO<sub>2</sub>. Fleet average methane emission rates are estimated at about 0.1 g/mi by MOBILE 4 at 75 °F, 9.0 psi RVP fuel, for Calendar Year 1989. Catalyst control systems do not reduce methane as effectively as other hydrocarbon compounds, so the historical reduction has not been equivalent to that illustrated in Figure 2-2 for NMHC. Typically, methane represents an increasingly larger fraction of the total as the THC emission rate is reduced. In a recent examination of consumer passenger cars, methane accounted for 7.2% (0.33 g/mi) of 4.58 g/mi THC from 1975 model year cars, and for 24% (0.14 g/mi) of 0.57 g/mi THC from 1982 model year cars (Sigsby et al., 1987).



**Figure 2-8. Motor vehicle fuel economy, 1975 to 2000.**

Source: Mobile 3 Fuel Consumption Model, Wolcott and Kahlbaum (1985).

**TABLE 2-4. MOTOR VEHICLE CARBON DIOXIDE EMISSION FACTORS (g/km)**

|      | LDGV  | LDGT  | HDGV  | LDDV  | LDDT  | HDDV   | ALL   |
|------|-------|-------|-------|-------|-------|--------|-------|
| 1975 | 352.4 | 395.8 | 614.4 | 283.3 | 204.2 | 1293.7 | 426.2 |
| 1985 | 270.0 | 330.8 | 532.5 | 236.1 | 271.0 | 1076.1 | 334.1 |
| 1995 | 208.8 | 284.8 | 555.3 | 199.5 | 252.0 | 908.1  | 268.2 |

Key:

LDGV = Light-duty gasoline vehicle, LDGT = Light-duty gasoline truck,  
 HDGV = Heavy-duty gasoline vehicle, LDDV = Light-duty diesel vehicle,  
 LDDT = Light-duty diesel truck, HDDV = Heavy-duty diesel vehicle.

Source: Black (1989).

Very few data on motor vehicle N<sub>2</sub>O emissions are available, but a recent analysis provided the estimates given in Table 2-5 (Black, 1989). Nitrous oxide emission rates may be increased about an order of magnitude by the catalyst used to reduce other emissions.

**TABLE 2-5. MOTOR VEHICLE NITROUS OXIDE EMISSION FACTORS**

| Vehicle Category   | Emission Factor (Range)<br>mg/km |
|--------------------|----------------------------------|
| LDGV (no catalyst) | 3.7 (1.9-9.9)                    |
| LDGV (catalyst)    | 37.9 (1.9-145.4)                 |
| LDDV               | NA (6.8-29.8)                    |
| HDGV               | 45.4 (29.8-60.3)                 |
| HDDV               | 29.2 (19.3-46.6)                 |

Key:

LDGV = Light-duty gasoline vehicle, LDDV = Light-duty diesel vehicle,  
HDGV = Heavy-duty gasoline vehicle, HDDV = Heavy-duty diesel vehicle,  
NA = Not available.

Source: Black (1989).

Most of the previously discussed data have been developed using laboratory simulations of roadway driving conditions, with engineering prototypes and vehicles obtained from consumer fleets with owners' consents. A suggestion has been made that such vehicles may not provide a representative sampling of in-use malfunctioning vehicles, and because of the cost, such tests involve relatively small numbers of vehicles and fuels. The results of the 1988 Motor Vehicle Tampering Survey (15 cities, 7,259 vehicles) suggest that for one out of every five U.S. passenger cars and light-duty trucks, at least one component of the emission control system was tampered with (U.S. Environmental Protection Agency, 1989f).

1 An additional 12% were classified as "arguably tampered," meaning that a determination  
2 could not be made as to whether the vehicle's condition was due to tampering or to poor  
3 maintenance. Tampering and misfueling can cause dramatic increases in VOC, CO, and  
4 NO<sub>x</sub> emissions (U.S. Environmental Protection Agency, 1983g). For example, disconnected  
5 air pumps (found on 11% of the surveyed vehicles so equipped) can increase VOC emissions  
6 200% and CO emissions 800%, and disconnected exhaust-gas-recirculation systems (found on  
7 7% of surveyed vehicles so equipped) can increase NO<sub>x</sub> emissions 175%. Misfueling  
8 catalyst equipped vehicles with leaded gasoline (found on 10% of vehicles requiring unleaded  
9 fuel) can increase VOC emissions 475% and CO emissions 425%. The survey indicated that  
10 locally administered Inspection and Maintenance Programs and Antitampering Programs  
11 reduced tampering by 30%.

12 To contend with these uncertainties, a number of roadway studies have been conducted  
13 wherein the emissions from large numbers of actual in-use motor vehicles using actual  
14 market fuels were examined (Gorse, 1984; Gorse and Norbeck, 1981; Hampton et al., 1983;  
15 Lonneman et al., 1986; Bullin et al., 1980; Ingalls, 1989; Zweidinger et al., 1988). Such  
16 studies are limited by uncertainties associated with the sensitivity of emissions to operating  
17 mode (e.g., cold start emissions, average speed variation, acceleration, and deceleration) and  
18 with difficulty in defining the dilution process between the vehicles and the sampling site  
19 (i.e., estimating the emission strength at the vehicle). The data suggest that available  
20 emissions models may significantly underestimate (by a factor of 2 to 4) hydrocarbon and  
21 CO emission rates; observed ratios of hydrocarbon and CO to NO<sub>x</sub> are generally larger than  
22 predicted by models (e.g., MOBILE 4 and EMFAC7C) (Pierson et al., 1990).

23 Available laboratory data providing motor vehicle emissions speciation are dominated  
24 by certification driving conditions (20 mph, 70 °F average temperature, 60 to 84 °F diurnal  
25 temperature ramp, etc.), with essentially no compositional data for vehicle running-loss  
26 evaporative emissions. A broader understanding, including those conditions prevailing when  
27 air quality problems arise, is necessary for detailed risk assessments and contrasts with  
28 alternative fuels. The differences in laboratory/model predictions and roadway observations  
29 must be resolved.



## **2.2.1.2 Environmental Fate**

### **2.2.1.2.1 Air Fate**

Gasoline vapors and exhaust gases emitted from automobiles are composed of very complex mixtures containing several hundred compounds. These include aromatics, olefins, paraffins, oxygenates (aldehydes and ketones), NO, NO<sub>2</sub>, CO, and CO<sub>2</sub>. The hydrocarbons and organic oxygenates in the presence of sunlight and NO<sub>x</sub> (NO + NO<sub>2</sub>) will undergo degradation through a series of complex reactions, resulting in the production of photochemical smog (reduced visibility and high levels of O<sub>3</sub>, PAN, aldehydes, etc.).

Smog chamber studies on auto exhaust from conventionally fueled vehicles have shown that the irradiated exhaust is more mutagenic than raw exhaust. Also, the gaseous components are more biologically active than the particles (Shepson et al., 1987). Other studies have shown that PAN is mutagenic and a strong phytotoxicant. Another PAN type compound, peroxybenzoyl peroxyxynitrate, has been observed from the photooxidation of aromatics (Heuss and Glasson, 1968; Meijer and Nieboer, 1978) and is a very strong eye irritant.

Although many studies have been made with irradiated auto exhaust, the detailed chemistry is understood for only the simplest organics. The aromatic chemistry is poorly understood for very few of the organic products identified (Finlayson-Pitts and Pitts, 1986). Apparently, many of the oxygenated ring fragments are deposited on the walls of the reaction vessels and have not been adequately analyzed. Further work is needed in this area of product identification for the aromatics and for the higher molecular weight paraffinic hydrocarbons.

### **2.2.1.2.2 Soil and Groundwater Fate**

Gasoline is only sparingly soluble in water and exists in the subsurface primarily as a separate liquid phase. In the subsurface, movement of gasoline or its constituents may occur through the water or air phase; or when present in relatively large amounts, gasoline may move as a separate NAPL. If present in sufficient volume, this NAPL (gasoline) can reach the water table, where it forms a lens at the surface of the aquifer. The gasoline may continue to move down-gradient as a separate phase, and as in the unsaturated zone,

1 constituents of the NAPL will dissolve into the aqueous phase and will migrate through the  
2 aquifer, subject to retardation due to sorption (e.g., Schwille, 1981).

3       When the amount of the pore space filled with NAPL is reduced below a certain level,  
4 the liquid gasoline may become trapped as blobs or droplets in relatively large pores. The  
5 amount of gasoline trapped depends on the water content of the soil as well as on the soil  
6 properties. Trapping may limit the spatial extent of the gasoline contamination, but the  
7 trapped droplets may be very difficult to remove, serving as a reservoir of dissolved  
8 constituents that slowly leach into the groundwater (Wilson and Conrad, 1984).

9       For both continuous and discontinuous NAPLs, the dynamics of constituent dissolution  
10 into the aqueous phase is a function of the physical and chemical properties of the two phases  
11 and the hydraulic characteristics of the system. Because of dissolution and volatilization, the  
12 chemical composition of the NAPL will be time dependent, causing temporally variable flow  
13 and partitioning properties of the gasoline phase.

#### 14 15 **2.2.1.2.2 *Surface Water Fate***

16       Conventional fuels present an array of fate problems for freshwater and estuarine spill  
17 scenarios. First, fuels are really a complex mixture of individual compounds that will exhibit  
18 multiple fate profiles. Some components will degrade rapidly, whereas others are much  
19 more persistent. Chemical degradation will produce other products that in turn present  
20 different fate and effects behavior. Second, such fuels will separate into multiple phases in  
21 the water column, thereby complicating the transport as well as the fate of each phase.  
22 At least three distinct phases result: the product, the emulsions formed as the fuel disperses,  
23 and the product dissolved in water. The three phases move at different rates, interact as  
24 concentration and turbulence fields change, and degrade at different rates and by different  
25 mechanisms. Surface slicks form at even very low concentrations, further complicating  
26 subsequent effects (i.e., effects may be much more subtle than direct toxicity).

27       Fate processes requiring study include the identification of individual fuel components  
28 and their subsequent transformation in water systems. Biological degradation is especially  
29 important, and oxygen depletion is expected to be a major impact. Related processes of  
30 reaeration and volatilization are also important. Priority research for transport addresses the

1 formation and movement of emulsions. The total, multiphase transport will require  
2 additional study to establish the expected frequency, volume, spatial extent, and duration of  
3 spills.

### 5 **2.2.1.3 Exposures**

#### 6 **2.2.1.3.1 Human Exposures**

7 Conventional transportation fuels include gasolines and diesel distillates of many  
8 compositions, which vary with respect to time of year and location/elevation. In addition to  
9 varying fuel composition, emissions are sensitive to the engine and emission control design  
10 and operating conditions. With an understanding of these factors, information about specific  
11 combustion products, such as CO<sub>2</sub>, NO<sub>x</sub>, CO, N<sub>2</sub>O, SO<sub>2</sub>, H<sub>2</sub>S, and organics (e.g., benzene  
12 and 1,3-butadiene), has grown over the years. This information can be incorporated into  
13 models that permit prediction of the likely impact on ambient air quality of changes in  
14 emissions, fuel composition, or both. In fact, the need to reduce O<sub>3</sub> concentrations to  
15 acceptable levels has been the motivating force behind much of the research effort to develop  
16 new fuels. Transport and fate models that incorporate the current understanding of the  
17 atmospheric sciences are available for this purpose.

18 Based on 1989 monitoring data, about 66.7 million Americans live in an area out of  
19 compliance with the current O<sub>3</sub> National Ambient Air Quality Standard (NAAQS) of  
20 0.12 ppm for 1 h. However, the concentration of O<sub>3</sub> to which individuals are exposed and  
21 the numbers and population subgroups exposed to levels that may exert adverse health effects  
22 remain uncertain. Improved exposure assessment will require research to enhance  
23 understanding of these concerns, the incorporation of these types of data into improved  
24 exposure models, field validation of these models, and development of methods that will  
25 improve estimations of dose.

26 There is no comparable national monitoring requirement for the states to measure  
27 ambient levels of the common volatile organics. However, based on a 10-site research  
28 network run by the U.S. EPA in Boston, Chicago, Houston, and Seattle/Tacoma for two  
29 years, 25 target compounds were measured. Results from this network indicated that the  
30 24-h ambient levels were comparable in all urban areas and were generally quite low

( $<0.10$  to  $20$  ppbv), with averages below  $3.0$  ppbv. Mobile source generated pollutants that exceeded mean concentrations above  $1.0$  ppbv include benzene, toluene, xylene, and formaldehyde. Furthermore, interpollutant correlations were extremely high for the aromatic VOCs (benzene, toluene, xylene, and ethylbenzene) at all sites, suggesting the importance of a common source (vehicular emissions) (Evans, 1990).

As the first step toward understanding the impact of automotive emissions on  $O_3$  exposure, measurements will be obtained in important microenvironments, and exposure models of the transport indoors from outdoors in urban, nonurban, and rural environments should be developed. Similar characterization studies of other emission products such as VOCs (especially benzene and 1,3-butadiene),  $NO_2$ , and PM (especially diesel particles) should follow in sequence behind  $O_3$ , if concurrent studies are not feasible.

Oral exposure also requires assessment to permit comparisons to alternative fuels. The two scenarios of interest are drinking water contaminated with gasoline and accidental ingestion (an incidence of about 30,000 cases) resulting from fuel siphoning or other actions (Litovitz, 1988). The latter is important insofar as the factors involved in accidents with gasoline can be used to project the potential incidence of accidents with methanol, which can have a more severe outcome (i.e., death or blindness). For both of these scenarios, considerable information exists. Thus an assessment is indicated prior to determining the need for future research.

#### **2.2.1.3.2 Biota Exposures**

**Terrestrial Exposures.** Once the conventional-fuel pollutants are emitted into the atmosphere from stationary and mobile sources, they are subject to the prevailing conditions that influence their environmental fate (Schroeder and Lane, 1988). The chemical reactions that occur within the atmosphere are complex and driven by processes such as hydroxyl scavenging and solar irradiation. These reactions may result in the formation of products that can be as toxic, more toxic, or less toxic to biota than the parent compounds.

The atmosphere is also the major pathway for the transport and deposition of the pollutants (Schroeder and Lane, 1988) from stationary and mobile sources to terrestrial ecosystem receptors—vegetation and soils (Foster, 1991). Vegetation and soil have large

1 surface areas in contact with the atmosphere and thus are recipients of the majority of  
2 pollutant deposition. Exposure may occur via wet deposition (e.g., fog, rain, dew) and dry  
3 deposition (e.g., gaseous, particulate). Cloud water and fog water have the potential to  
4 concentrate pollutants and therefore represent an important pathway of exposure to  
5 vegetation, more so than rain and dry deposition. The prevailing meteorological conditions  
6 and the physicochemical properties of the pollutants will dictate atmospheric residence times  
7 and pollutant deposition to the receptors (Schroeder and Lane, 1988). Such exposures could  
8 be acute or chronic, frequent or infrequent, high level or low level, and local or regional.  
9 Local pollutant deposition will impact urban and agricultural ecosystems, whereas remote  
10 ecosystems will be exposed to the pollutants via long-range atmospheric transport and  
11 deposition. The degree of ecological impact will depend, in part, on the exposure (duration,  
12 pattern, time, and concentration) of the pollutant to the biota (Moser et al., 1991).

13 The environmental partitioning of pollutants within terrestrial ecosystems will dictate  
14 their potential impact on vegetation and other biota (Weinstein and Birk, 1989). For  
15 example, trace metals (e.g., lead) tend to accumulate on soil surfaces via adsorption to  
16 organic matter. Trace metal accumulation may reduce plant growth and vigor through the  
17 disruption of nutrient uptake by the plant roots and may alter soil biota populations, resulting  
18 in decreased organic matter decomposition. Gas-phase pollutants (e.g., O<sub>3</sub>) reside in the  
19 atmosphere with the potential to disrupt plant-leaf biochemical processes after absorption  
20 through the stomata or cuticle. The lipophilic nature of some pollutants (e.g., PAHs) may  
21 result in their accumulation in the waxy cuticle of leaves. The contaminants may then be  
22 passed along food chains through herbivory and predation with the potential for  
23 biomagnification.

24 The exposure of conventional-fuel pollutants to terrestrial biota through the atmosphere  
25 is not fully understood. Pollutant deposition and exposure to biota in urban and agricultural  
26 systems are much better documented than for remote ecosystems such as forest and alpine  
27 habitats. Obviously, modeling efforts are needed to predict with statistical confidence the  
28 potential exposure of terrestrial ecosystem to the conventional-fuel pollutants. Therefore,  
29 reliable monitoring data from urban, rural, and remote locations are necessary to verify the  
30 model predictions.

1        ***Aquatic Exposures.*** As explained in the introduction of this chapter, exposure  
2 assessments for contamination of aquatic ecosystems by fuels and fuel transformation  
3 products must include careful characterization of the system of interest; this includes  
4 identifying organisms at risk and their microhabitats, accounting for the heterogeneous  
5 distribution of contaminants in space and time, and specifying physical and chemical factors  
6 that will alter fuel bioavailability and effects. Such characterizations have not been done in  
7 the past and require coordination between efforts on source characterization, fate and  
8 transport, and effects assessment. Reports of past spills and leakages will be useful for  
9 providing some of this information and for developing scenarios needed for generic  
10 assessments. For example, Guiney et al. (1987a,b) studied a pipeline spill of aviation fuel in  
11 October 1982 into Roaring Run Creek, in Cambria County, PA. In addition to documenting  
12 much of the fate and effects of this spill, these reports provide considerable information in  
13 areas such as specifying the types of organisms at risk, system morphometry and flows, as  
14 well as distribution of contamination within the water and sediment. Retrospective analyses  
15 of other spills, such as the fuel tank collapse on the Monongahela River during January  
16 1988, can also provide guidance (Center for Hazardous Materials Research, 1989).  
17 To parameterize surface water mixing/dissolution/fate, exposure models must be an early  
18 priority for strategy implementation. So also must be realistic spill source characterization  
19 for conventional fuel transport and storage systems.

#### 21    **2.2.1.4 Analytical Methodology**

22        A wide range of analytical procedures are required to facilitate examination of the  
23 impact of changes in motor fuels on risk to health and the environment. The procedures can  
24 generally be categorized according to procedures for characterizing source emissions,  
25 procedures for monitoring the transport and transformation of the emissions in ambient air,  
26 and procedures for monitoring human and ecosystem exposure. Procedures for both  
27 certification of regulated emissions and comprehensive characterization of unregulated  
28 emissions are required for sources. The primary concern with conventional fuel certification  
29 methodology is the adequacy (accuracy and precision) of classical procedures for  
30 measurement of pollutant (THC, NMHC, CO, NO<sub>x</sub>, and particles) concentrations at levels

dictated by lowered emission standards required by the 1990 CAAAs. All currently defined procedures will require evaluation.

The Coordinating Research Council examined the adequacy of procedures for certification of heavy-duty engine particulate emissions at 0.25 g/bhphr (1991 truck standard) and 0.1 g/bhphr (1993 bus and 1994 truck standard) as an element of the APRAC VE-1 project, "Evaluation of Fuel and Engine Variables on Heavy-Duty Diesel Engine Emissions" (Coordinating Research Council, 1990). The project identified factors contributing to the variability of particulate mass-emission rate measurements in the heavy-duty transient test procedures used in certification and suggested possibilities for method improvement.

Similar activities will be required with other procedures for measurement of regulated emissions, when required standards are enacted. The 1990 CAAAs consider phased reductions of: hydrocarbon emissions from the current 0.41 g/mi total hydrocarbon (THC) regulation to 0.25 g/mi nonmethane hydrocarbon (NMHC) in 1994 and to 0.125 g/mi NMHC in 2003 (pending an air quality study); CO emissions from the current 3.4 g/mi regulation to 1.7 g/mi; and NO<sub>x</sub> from the current 1.0 g/mi regulation to 0.4 g/mi to 0.2 g/mi. With organic emission standards requiring measurement of NMHC (a departure from current THC standards), analytical methodology will be required for determination of methane (permitting calculation of NMHC by subtraction from THC) and/or direct measurement of NMHC. The latter will probably be required for the lowest standards because of uncertainties associated with using a small difference in two large numbers (NMHC = THC - methane). Procedures for direct measurement of methane have been developed for motor vehicle emissions (Hoffman et al., 1987; Burch and Pembroke, 1973; Probst and Reschke, 1977; Society of Automotive Engineers, 1976), but procedures for direct measurement of NMHC emissions will require development.

Efforts to assess the impact of motor vehicles on O<sub>3</sub> and toxics air quality require detailed speciation of emissions. Because of the very complex nature of the mixtures, many studies have used chromatography (California Air Resources Board, 1989; Crews and Stump, 1988; Lipari, 1990; Sigsby et al., 1987; Stump and Dropkin, 1985; Stump et al., 1989; Black et al., 1980; Williams et al., 1990). Efforts to provide standardized uniform chromatographic methods and quality assurance procedures across the user community will

1 be useful, and such activities have been initiated in the Auto/Oil Air Quality Improvement  
2 Research Program (Schuetzle, 1990). Chromatographic procedures generally involve  
3 collection of an integrated sample of transient emissions in a container (generally a teflon  
4 bag) during the test period, with subsequent analysis. Continuous or "real-time" analysis  
5 provides the additional information necessary to isolate driving conditions most responsible  
6 for emissions of interest. Efforts to develop such methods have been initiated for many air  
7 toxics of interest and will continue as fuel formulations and compounds of interest change  
8 (Butler et al., 1985; Staab et al., 1985; Von Carlowitz et al., 1990; Heller et al., 1990).

9 Ambient air monitoring of pollutants requires many of the same techniques employed  
10 for source emissions measurements. Because pollutants are present at much lower  
11 concentrations, however, these source measurement techniques need to be modified (e.g., gas  
12 chromatographic samples need to be concentrated with the use of a cryogenic trap). Gas  
13 chromatograms of ambient air samples often have many unidentified peaks. Some of these  
14 are probably a result of direct emissions; however, many of them are a result of atmospheric  
15 transformations. Gas chromatographs with mass spectrometry along with long-path infrared  
16 spectroscopy are needed for proper identification. Some developmental work is also needed  
17 for the measurement of formaldehyde and higher aldehydes, because the cartridge technique  
18 using DNPH may be affected by ambient levels of O<sub>3</sub> (Arnts and Tejada, 1989).

19 Ambient air monitoring and microenvironmental monitoring will require improvements  
20 and/or further methods development in order to measure the pollutants at the expected levels  
21 and locations of interest. For example, a method for accurately measuring butadiene at  
22 ambient levels is required in order to assess the degree to which butadiene constitutes a  
23 public health risk. In addition, because the measurement of formaldehyde using the DNPH  
24 method may be affected by O<sub>3</sub> levels, comparisons of indoor and outdoor measurements will  
25 only be possible with improvements to the current methodology. In addition, an O<sub>3</sub> personal  
26 monitor will be required for accurate characterization of population exposures, because most  
27 humans spend 90% of their time indoors, where O<sub>3</sub> levels are typically lower (than  
28 outdoors).



## 2.2.2 Effects Assessment

### 2.2.2.1 Human Health Effects

Health risks from conventional gasoline and diesel fuels have resulted in rather extensive regulations of emissions to reduce the risks. Current estimates of cancer risks are summarized in Table 2-6. Noncancer effects are summarized in Table 1-4. The data base on conventional fuels is quite uneven. There is substantial information on the related criteria pollutants (i.e., O<sub>3</sub>, NO<sub>2</sub>, CO) and a very few of the related air toxics (e.g., formaldehyde, benzene, 1,3-butadiene); the health effects of these individual pollutants are presented first, with the exception of formaldehyde (which is discussed under methanol fuels, Section 3.2.2.1, because of higher tailpipe emissions of this compound with methanol fuels). A recent summary of the health effects of several mobile source-related air toxics has been developed (U.S. Environmental Protection Agency, 1991c). However, health effects are caused by exposures to complex mixtures, not just the single pollutants. Most is known about the carcinogenic potential of diesel combustion emissions and the noncancer toxic potential of leaded conventional gasoline. Information is either limited (e.g., carcinogenicity of uncombusted gasoline fuel) or nonexistent (e.g., carcinogenicity of combusted unleaded gasoline fuel) on the other important classes of complex mixtures. The ensuing discussion of complex mixtures presents gasoline and diesel separately, subdivided according to combusted or noncombusted fuels and cancer or noncancer effects.

This discussion of health effects only pertains to inhalation exposures. Oral exposures can occur from accidental ingestion or from contamination of drinking water as a result of spills or major leaks; however, oral exposure effects can be assessed separately with existing information. Until such assessments are completed, no research needs relating to oral exposures will be described, and there will be no further discussion of oral exposure effects.

#### 2.2.2.1.1 Ozone, Nitrogen Dioxide, and Carbon Monoxide

Because of adverse health effects associated with O<sub>3</sub>, NO<sub>2</sub>, and CO, criteria documents have been prepared and NAAQSs have been promulgated (U.S. Environmental Protection Agency, 1982a, 1986a, 1989g, 1990e, 1990f). For the sake of brevity, several important

**TABLE 2-6. MOTOR VEHICLE EMISSIONS RISK ESTIMATES, CANCER INCIDENCES PER YEAR**

|                               | 1986 <sup>a</sup> | 1995 <sup>a</sup> |
|-------------------------------|-------------------|-------------------|
| Diesel Particles <sup>b</sup> | 178-860           | 106-662           |
| Formaldehyde <sup>b</sup>     | 46-86             | 24-43             |
| Benzene <sup>b</sup>          | 100-155           | 60-107            |
| Gasoline Vapors               | 17-68             | 24-95             |
| 1,3-Butadiene <sup>b</sup>    | 236-269           | 139-172           |
| Gasoline Particles            | 1-176             | 1-156             |
| Asbestos                      | 5-33              | ND <sup>c</sup>   |
| Cadmium                       | <1                | <1                |
| Ethylene Dibromide            | 1                 | <1                |
| Acetaldehyde                  | 2                 | 1                 |
| Total                         | 586-1650          | 355-1236          |

<sup>a</sup>Incidences are based on 95% upper confidence limits of cancer unit risk associated with estimates of exposures and populations exposed which create the estimated ranges shown.

<sup>b</sup>These cancer risks are currently being reevaluated and values may change.

<sup>c</sup>ND = Not determined.

Source: Adapted from Adler and Carey (1989).

types of effects induced by these pollutants are summarized in Table 1-4 but, to avoid unnecessary duplication with these other documents, they are not discussed in the text.

#### **2.2.2.1.2 1,3-Butadiene**

The following discussion of 1,3-butadiene cancer risk is drawn from material supporting the 1989 assessment (U.S. Environmental Protection Agency, 1989i). Since that time, additional research has been conducted and published that is being considered as part of an imminent reevaluation of the cancer risk of 1,3-butadiene. These new papers are not summarized here, but a recent review has been written by Birnbaum (1992).

Long-term inhalation studies performed with B6C3F1 mice (National Toxicology Program, 1984) and Sprague-Dawley rats (Hazleton Laboratories Europe, Ltd., 1981) provide sufficient evidence that 1,3-butadiene is carcinogenic in animals. The rats were

1 exposed to either 1,000 or 8,000 ppm, whereas the mice were exposed to either 625 or  
2 1,250 ppm. Rats exhibited an increased incidence of the following tumors: Leydig cell  
3 adenomas, exocrine adenomas of the pancreas, multiple mammary gland tumors, follicular  
4 cell adenomas, and carcinomas of the thyroid and uterus. The most prevalent tumor types in  
5 B6C3F1 mice were malignant lymphomas associated with the hematopoietic system, and  
6 hemangiosarcomas.

7 Three studies have been reported to date for workers specifically exposed to  
8 1,3-butadiene. In a cohort study, none of the standard mortality ratios (SMRs) for cancer  
9 were found to be significantly elevated (Matanoski et al., 1982). In a second cohort study,  
10 increases of borderline significance in the SMRs for lymphatic and hematopoietic cancer  
11 were detected (Meinhardt et al., 1982). In a cross-sectional study, no evidence for  
12 hematological effects were noted (Checkoway and Williams, 1982). An association between  
13 employment in the synthetic rubber industry and elevated cancer risk was reported in two  
14 studies (McMichael et al., 1976; Andjelkovic et al., 1976). Synthetic rubber, however, is  
15 manufactured from styrene, a possible carcinogen, as well as butadiene. Because of possible  
16 exposure to other potential carcinogens in rubber plant workers, methodological limitations  
17 of the studies, and borderline or no effects in workers exposed to butadiene alone, the results  
18 of epidemiology studies are considered inadequate to assess the carcinogenic effects of  
19 1,3-butadiene.

20 Based upon inadequate data for carcinogenicity in human studies, but "sufficient"  
21 positive data from animal experiments, 1,3-butadiene has been classified into EPA  
22 weight-of-evidence category B2 and is thus considered to be a probable human carcinogen.  
23 An upper-bound unit risk value of  $2.8 \times 10^{-4}$  per  $\mu\text{g}/\text{m}^3$  (i.e., the cancer risk of lifetime  
24 exposure to  $1 \mu\text{g}/\text{m}^3$ ) was derived from the National Toxicology Program (1984) mouse  
25 study.

#### 26 27 **2.2.2.1.3 Benzene**

28 Benzene is rapidly absorbed dermally and through the respiratory and gastrointestinal  
29 tracts. Because it is fat soluble, benzene readily penetrates biological membranes. As an  
30

1 acute toxicant, benzene produces narcotic effects, with CNS stimulation followed by  
2 depression (ACGIH, 1986; Carpenter, 1944).

3 Fetotoxic effects have been reported in several experiments with different species over  
4 a range of air concentrations. Decreased fetal weight and disturbances in skeletal  
5 development were observed in Sprague-Dawley rats (Green et al., 1978; Coate et al., 1982;  
6 Kuna and Kapp, 1981), CFLP mice (Ungvary and Tatrai, 1985), and New Zealand rabbits  
7 (Ungvary and Tatrai, 1985). Overall, the data suggest that fetotoxic effects may begin in the  
8 range of 40 to 50 ppm benzene, although a well-designed 2-generation reproductive toxicity  
9 study and a teratology evaluation are needed for a definitive conclusion. The data also  
10 suggest that female offspring are more susceptible to delayed skeletal ossification effects, an  
11 aspect that warrants further attention (Green et al., 1978).

12 Benzene is unique among the hydrocarbons as a myelotoxin, with hematopoietically  
13 active bone marrow as the target tissue for longer-term exposures. Bone marrow contains  
14 precursor cells to the mature circulating blood cells (i.e., erythrocytes) various types of  
15 leukocytes, and thrombocytes. Benzene toxicity is manifested by marked decreases in the  
16 circulating levels of these formed blood elements. Chronic exposure of humans and  
17 laboratory animals to high concentrations of benzene results in blood dyscrasias, including  
18 lymphocytopenia, thrombocytopenia, and pancytopenia or aplastic anemia (Kalf et al., 1987).  
19 Benzene has been shown to inhibit lymphopoiesis and lymphocyte function, both in vivo and  
20 in vitro in various laboratory animal species, at concentrations lower than those at which  
21 reductions in cell number are observed (Irons et al., 1983; Kalf et al., 1987). Baarson et al.  
22 (1984) showed an effect on erythroid progenitor cells in the bone marrow of mice following  
23 exposure to 10 ppm benzene for 6 h/day, 5 days/week for 178 days.

24 Although there is agreement that benzene is not itself the principal molecular species  
25 responsible for the bone marrow or lymphoid toxicity, the possible metabolic pathways and  
26 potential targets for metabolites are complex, and the exact cell type(s) and critical reactions  
27 are not fully established. It is generally recognized that metabolism to phenol and subsequent  
28 excretion as the phenyl glucuronide or sulfate conjugate represent a detoxification pathway,  
29 as does conjugation with glutathione and excretion as a phenyl mercapturic acid (Sabourin  
30 et al., 1988). Benzoquinone and muconaldehyde have also been suggested as other reactive

1 metabolites responsible for the toxic effects of benzene (Latriano et al., 1986; Kalf et al.,  
2 1987). Species differences in the proportions of applied benzene (oral or inhalation) to these  
3 various pathways have been demonstrated (Sabourin et al., 1987, 1988, 1989). Benzene  
4 metabolites have been shown to accumulate in bone marrow where, it is thought, benzene  
5 can also be metabolized autonomously or benzene metabolites can be translocated from the  
6 liver and metabolized to the ultimate reactive metabolite (Travis et al., 1990). Benzene has  
7 been shown to be metabolized and covalently bound in bone marrow of F344 rats in situ to a  
8 slight extent (Irons et al., 1980), and some physiologically-based pharmacokinetic (PBPK)  
9 model simulations are closest to empirical data when bone marrow is assumed to metabolize  
10 benzene (Travis et al., 1990). Further empirical analysis of this particular issue is  
11 warranted.

12 Major conclusions based on recent PBPK modeling efforts and experimental data are  
13 that, compared to rats, mice metabolize a greater proportion of absorbed benzene (after  
14 either oral or inhalation exposure) to the hydroquinone conjugates and muconic acids and that  
15 these differences are consistent with the increased susceptibility to the toxic effects of  
16 benzene exhibited by mice in oral toxicity studies (Medinsky et al., 1989). Physiologically-  
17 based pharmacokinetic model simulations using metabolism parameters determined for mice  
18 and rats also suggest that the putative toxic metabolites (benzoquinone and muconaldehyde)  
19 may represent a larger fraction of total benzene metabolized at low inhalation concentrations,  
20 which may have implications for human risk assessment (Medinsky et al., 1989).

21 Quantification of the capacity of human tissue to form the various metabolites remains to be  
22 determined.

23 Benzene has also been shown to be an immunosuppressant agent, based on decreases in  
24 red cell lysins, agglutinins for killed typhoid bacilli, and the absence of antibacterial  
25 antibodies in benzene-exposed animals (Snyder, 1984). Although many of these observations  
26 are related to the ability of benzene to deplete leukocytes, immunosuppressant activity per se  
27 has recently been confirmed; serum levels of complement and immunoglobulin levels were  
28 shown to be reduced in benzene-exposed workers (Snyder, 1984). Benzene can also modify  
29 both host resistance to a bacterial infectious agent and aspects of cell-mediated tumor  
30 surveillance (Rosenthal and Snyder, 1985, 1987). Determining the extent to which

1 immunological processes prevent carcinogenesis is important in determining the extent to  
2 which depression of immunological function by benzene may contribute to its leukemogenic  
3 activity.

4 Benzene is a proven human carcinogen, most commonly associated with an increased  
5 incidence of acute myelogenous leukemia and some of its variants, including erythroleukemia  
6 and acute myelomonocytic leukemia (Goldstein, 1983). It is also suspected of causing  
7 chronic myelogenous leukemia, chronic lymphocytic leukemia, Hodgkin's Disease,  
8 paroxysmal nocturnal hemoglobinuria, and, possibly, acute lymphocytic leukemia (Goldstein,  
9 1983). Other hematological disorders in humans possibly associated with benzene exposure  
10 include lymphocytic lymphoma, myelofibrosis, myeloid metaplasia, multiple myeloma, and  
11 thrombocythemia (Goldstein, 1983; Kalf et al., 1987). Benzene has also been associated in  
12 laboratory rodents with an increase incidence of several solid tumors (Maltoni et al., 1983,  
13 1985) and leukemia (Cronkite et al., 1984).

14 It is important to ascertain whether some degree of aplastic anemia is requisite for  
15 benzene leukemogenesis or whether leukemia can develop after exposure to levels of benzene  
16 below those which cause serious bone marrow damage. Such information would help  
17 determine whether the early hematotoxicity of benzene should be approached as a separate  
18 noncancer toxicity endpoint or as part of a spectrum of events related to carcinogenesis.  
19 Elucidation of the toxic mechanism and identification of the pertinent benzene metabolites in  
20 laboratory animal models are needed to quantitatively address this issue, since such data are  
21 unlikely to come from epidemiologic studies (Goldstein, 1983). The toxicokinetics of the  
22 toxic metabolites in relation to benzene exposure, competitive reactions and detoxification  
23 pathways, and the appropriate laboratory animal model from which to quantify these  
24 relationships remain critically pertinent to determining whether benzene is leukemogenic at  
25 low concentrations and to determining approaches for estimating human health risk.

26 The following discussion of benzene cancer risks is drawn from material supporting the  
27 1989 cancer assessment (U.S. Environmental Protection Agency, 1989h). Since that time,  
28 additional research has been conducted and published that is being considered as part of an  
29 imminent reevaluation of the cancer risk of benzene.

1        Either an increased incidence or a causal relationship between nonlymphocytic leukemia  
2 and exposure to benzene has been reported in numerous epidemiologic studies (International  
3 Agency for Research on Cancer, 1982a). These include employees in the shoe industry  
4 (Aksoy et al., 1974), in the manufacture of rubber products (Infante et al., 1977a,b; Rinsky  
5 et al., 1981, 1987), and in the chemical industry (Wong et al., 1983).

6        Both gavage and inhalation exposure of rodents have resulted in development of  
7 neoplasia. Maltoni et al. (1983) reported significant increases in hepatomas and Zymbal  
8 gland carcinomas in Sprague-Dawley rats exposed chronically to a time-weighted average of  
9 241 ppm benzene. Slightly increased incidences of hematopoietic neoplasms were reported  
10 for male C57Bl mice exposed to 300 ppm benzene, but no significant effects were seen in  
11 either male AKR mice, CD-1 mice, or Sprague-Dawley rats exposed similarly (Snyder et al.,  
12 1981). In a National Toxicology Program (1986) study, benzene was administered by  
13 gavage at doses of 50, 100, and 200 mg/kg to F-344 rats and at doses of 25, 50, and  
14 100 mg/kg to B6C3F1 mice. Increases in Zymbal tumors were seen in both mice and rats.  
15 Rats also showed increases in oral cavity and skin tumors, whereas mice had increases in  
16 lymphomas and lung tumors in both sexes, Harderian and preputial gland tumors in males, as  
17 well as mammary gland and ovarian tumors in females.

18        Based upon several studies in which increased incidences of nonlymphocytic leukemia  
19 from occupational exposure were reported and supported by positive data in animal studies,  
20 benzene has been placed into category A and is thus considered to be a known human  
21 carcinogen. An upper-bound inhalation unit risk of  $8.3 \times 10^{-6}$  per  $\mu\text{g}/\text{m}^3$  was derived using  
22 pooled data from the Rinsky et al. (1981) and Ott et al. (1978) occupational studies, which  
23 were then adjusted using the results of the Wong et al. (1983) study.

#### 24 25 **2.2.2.1.4 Conventional Gasoline**

26        Numerous studies have been conducted in the last several decades on the health effects  
27 of gasoline vapor and the combustion emissions and atmospheric transformation products of  
28 both evaporative and combustion emissions. Components of gasoline emissions and products  
29 that have been regulated by EPA on the basis of their adverse health effects include NO<sub>2</sub>,  
30 SO<sub>2</sub>, O<sub>3</sub>, and CO. National Ambient Air Quality Standards have been promulgated for these

1 pollutants. Because they have substantial existing documentation and are the focus of ORD's  
2 base research program as single pollutants, no further discussion will be provided here.

3       The controlled studies on gasoline combustion products summarized here employed  
4 (1) urban ambient air, which is dominated by auto emissions and their transformation  
5 products, or (2) raw (nonirradiated) or photochemically reacted (irradiated) auto exhaust  
6 generated in laboratories from vehicles with and without catalytic converters. Other studies  
7 cited here examined the effects of gasoline vapor. Noncancer health effects studies are  
8 described first, followed by studies on cancer. Note that raw, nonirradiated auto exhaust  
9 contains hydrocarbons, aldehydes, NO<sub>x</sub>, CO, and oxides of sulfur (SO<sub>x</sub>; SO<sub>2</sub> and sulfate  
10 aerosol), as well as trace amounts of other compounds. Irradiated exhaust contains, in  
11 addition, O<sub>3</sub> and higher concentrations of NO<sub>2</sub>, aldehydes, and PM. The use of catalytic  
12 converters has the following primary effects: conversion of certain alkenes to alkanes,  
13 decrease in concentrations of CO and acetylene, and decrease in photochemical reactivity and  
14 NO<sub>2</sub>-forming potential of the exhaust emissions (Tilton and Bruce, 1981).

15  
16       ***Noncancer Health Effects of Gasoline Combustion Emissions.*** Both acute and chronic  
17 inhalation studies of gasoline vapors and combustion mixtures (with and without  
18 photochemical oxidation) have been reported and indicate that gasoline can cause acute and  
19 chronic effects to most major organ systems. Most of this research was conducted in the  
20 1960s and 1970s and, therefore, generally does not fully represent potential effects of  
21 nonleaded conventional gasolines. Nonetheless, given the degree of similarity between these  
22 older and current conventional gasolines, similar health effects might be assumed to occur  
23 with current conventional fuels. These studies also illustrate the importance of studying  
24 whole emissions, with and without photochemical transformation. Based upon knowledge of  
25 the individual chemicals, the mixture effects observed are not entirely predictable, and the  
26 transformed mixture (with more oxidants) was frequently more toxic than the original  
27 emissions. Specific studies are summarized below.

28       Pulmonary function and morphology have long been health effects of concern in  
29 relation to auto emissions and transformation products and have been measured in both  
30 chronic and acute controlled studies. In the 2-year exposure study of Stupfel et al. (1973),



emphysema was seen in the high-NO<sub>x</sub> auto exhaust exposure group (23 ppm NO<sub>x</sub>, 0.37% CO<sub>2</sub>, 50 ppm CO, and 0.2 ppm aldehydes) but not in the low-NO<sub>x</sub> exhaust exposure group (0.2 ppm NO<sub>x</sub>, 0.07% CO<sub>2</sub>, 50 ppm CO, and 0.1 ppm aldehydes). In the Hysell et al. (1975) study (see below), extensive pulmonary changes were seen in adult rats exposed to raw or irradiated exhaust (no catalytic converter). In hamsters exposed to the same mixture, pulmonary effects included increased numbers of alveolar macrophages in terminal bronchioles, proliferation of respiratory epithelium in alveolar ducts, and thickening of alveolar septum. Purulent bronchitis, bronchiolitis, and bronchopneumonia were also observed.

Murphy (1964) exposed guinea pigs for 4 h to irradiated or nonirradiated auto exhaust, with the irradiated exhaust exposures administered in either a steady-state (square-wave) or a cyclic (simulating diurnal pollutant patterns) distribution. Steady-state pollutant concentrations in the exhaust were 2.42 ppm formaldehyde, 0.20 ppm acrolein, 0.80 ppm total oxidant, 2.66 ppm NO<sub>2</sub> and 300 ppm CO. Cyclic concentrations (over 3 h) were 1.81, 1.93, 1.32 ppm formaldehyde; 0.10, 0.09, 0.06 ppm acrolein; 0.56, 0.91, 0.95 ppm total oxidant; 2.17, 2.13, 0.79 ppm NO<sub>2</sub>; and 200, 250, 150 ppm CO. The following changes in various pulmonary function parameters were observed: increased flow resistance; decreased breathing frequency; and increased tidal volume at about 1.5 h of exposure, but decreased tidal volume by 2.5 h. Greater increases in flow resistance and tidal volume occurred in exposures to irradiated exhaust compared to nonirradiated exhaust.

Pulmonary function and morphology changes were observed in a chronic study (108 mo) of the effects of auto exhaust on dogs (Stara et al., 1980). Female beagles were divided into one control and seven experimental exposure groups: control animals (CA); raw, nonirradiated exhaust (R); irradiated exhaust (I); SO<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> (SO<sub>x</sub>); raw exhaust plus SO<sub>x</sub> (R + SO<sub>x</sub>); irradiated plus SO<sub>x</sub> (I + SO<sub>x</sub>); NO<sub>x</sub> 1 high NO<sub>2</sub>, low NO (NO<sub>x</sub> 1); and low NO<sub>2</sub>, high NO (NO<sub>x</sub> 2). Estimated exposure concentrations (in ppm unless noted otherwise) for the respective experimental exposure groups were: (a) CO: R, 100; I, 100; (b) hydrocarbon, as methane: R, 24 to 30; I, 24 to 30; (c) NO<sub>2</sub>: R, 0.1; I, 0.5 to 1.0; NO<sub>x</sub> 1 (high NO<sub>2</sub>), 0.5 to 1.0; NO<sub>x</sub> 2 (high NO), 0.2; (d) NO: R, 1.5 to 2.0; I, 0.1; NO<sub>x</sub> 1, 0.2; NO<sub>x</sub> 2, 1.5 to 2.0; (e) total oxidant, as O<sub>3</sub>: I, 0.2 to 0.4; (f) SO<sub>x</sub>: SO<sub>x</sub>, 0.5;

(g)  $\text{H}_2\text{SO}_4$  ( $\mu\text{g}/\text{m}^3$ ):  $\text{SO}_x$ , 100. The dogs were exposed to the respective atmospheres 16 h/day for 68 mo. They were then all exposed to clean (filtered) air for another 2 to 3 years after termination of experimental exposures.

At 18 and 36 mo of exposure, no significant changes were seen in pulmonary function. At 61 mo, however, increased diffusing capacity for carbon monoxide was seen in the R and I groups compared to the  $\text{NO}_x$  1, or  $\text{NO}_x$  2 groups. Total expiratory resistance was increased in the I and I +  $\text{SO}_x$  groups; decreased expiratory flow rates were seen in the  $\text{NO}_x$  1 (high  $\text{NO}_2$ ) group versus the CA group. Residual volume was moderately increased in the R, I, R +  $\text{SO}_x$ , and I +  $\text{SO}_x$  groups. When examined after being housed in clean air for about 2.5 years post-termination of exposure, all exposure groups had pulmonary and structural differences from the CA group; the abnormalities were greater at about 2.5 years postexposure than at the termination of exposures. Exposures to raw and irradiated exhaust appeared to injure airways and parenchyma; whereas,  $\text{SO}_x$ ,  $\text{NO}_x$  1, and  $\text{NO}_x$  2 exposures injured the parenchyma only. Functional abnormalities correlated moderately well with structural changes in the exposure groups (Stara et al., 1980).

Pulmonary lesions reported from the beagle study (Stara et al., 1980) included enlargement of air spaces in proximal acinar lesions (most severe in groups  $\text{NO}_x$  1,  $\text{NO}_x$  2,  $\text{SO}_x$ , and  $\text{SO}_x$  + I), and hyperplasia of nonciliated cells (most severe in R and R +  $\text{SO}_x$  groups). Ultrastructural examination of lungs of autopsied beagles (at about 2.5 years postexposure) showed occasional abnormalities, but no significant differences were seen in exposed versus control dogs.

Changes in blood or organ biochemistry were also reported. Increases in prolyl hydroxylase (an enzyme involved in collagen synthesis) were observed in the I, I +  $\text{SO}_x$ , and  $\text{NO}_x$  2 (high NO) exposure groups in the beagle dog study, but no significant differences in collagen content were observed. The same beagle study (Stara et al., 1980) showed clear-cut, but small, changes in phosphatidyl ethanolamine, a phospholipid in the lung; no changes in brain or heart lipids; and some changes in liver phospholipids. Hysell et al. (1975) found increases in hemolysis-resistant red blood cells (RBCs) in adult rats and hamsters exposed for 6 days to raw exhaust (no catalytic converter); the same study showed no effect on eosinophils. Lee et al. (1976) exposed lactating rats to raw exhaust continuously

1 for 7 days and found increased hematocrit and lactate dehydrogenase activity, but no effect  
2 on serum glutamic oxaloacetic transaminase. Rats exposed for 2.5 years to urban ambient  
3 air dominated by auto emissions had decreased alkaline phosphatase activity in the lung  
4 (Emik et al., 1971).

5 Using an infectivity model, Coffin and Blommer (1967) showed increased mortality in  
6 mice exposed for 4 h to irradiated auto exhaust and then challenged with bacteria  
7 (*Streptococcus sp.*). Results were similar at the following two levels of pollutants in the  
8 exhaust (achieved by different driving/engine cycles): (1)  $\geq 0.4$  ppm NO<sub>2</sub>, 0.02 ppm NO,  
9 100 ppm CO, and 0.52 to 0.67 ppm oxidants; or (2) 0.2 to 0.8 ppm NO<sub>2</sub>, 0.15 to 0.48 ppm  
10 oxidants, and 25 or 100 ppm CO.

11 Decreased body weights were reported by Lee et al. (1976) for lactating rats exposed  
12 24 h/day for 7 days to either raw or irradiated auto exhaust from a non-catalyst-equipped  
13 vehicle. Rats exposed to irradiated exhaust from a catalytic-converter-equipped vehicle  
14 showed a greater weight loss than rats exposed to exhaust from a vehicle without a catalytic  
15 converter; NO<sub>2</sub> was higher in the unconverted exhaust. Similar findings were reported by  
16 Stupfel et al. (1973), who found decreased body weights in rats exposed (6 to 8 h/day,  
17 5 days/week, for 2.5 to 24 mo) to auto exhaust containing high NO<sub>x</sub> (23 ppm), 0.37% CO<sub>2</sub>,  
18 50 ppm CO, and 2 ppm aldehydes. No effects on body weight were observed in rats  
19 exposed to exhaust containing 0.2 ppm NO<sub>x</sub>, 0.07% CO<sub>2</sub>, 50 ppm CO, and 0.1 ppm  
20 aldehydes.

21 Shortened life spans for male C57B1/6 mice exposed for 2.5 years to urban ambient air  
22 were reported (Emik et al., 1971). Female mice of the same strain and mice of both sexes  
23 of two other strains had normal life spans. In a study by Hysell et al. (1975), significantly  
24 higher rates of early mortality were seen in neonate rats (2-weeks old) exposed for 7 days to  
25 exhaust from vehicles without catalytic converters (exhaust contained 5 ppm NO<sub>2</sub>).

26 Decreased locomotor activity in rats exposed continuously for 38 to 88 days in three  
27 experiments using auto exhaust (with and without catalytic conversion) was reported (Cooper  
28 et al., 1977). The decrease was attributed to NO<sub>x</sub> or total hydrocarbons, but a 10-fold  
29 increase in NO<sub>x</sub> produced no further decrease in activity. In the chronic exposure study of  
30 beagle dogs, no significant effects on visual-evoked brain potentials were seen in any of the

1 exposed groups compared with the control groups (Stara et al., 1980). Stupfel et al. (1973)  
2 reported a decrease in sound avoidance reflexes in rats exposed to auto exhaust (see the  
3 earlier description of this study).

4  
5 ***Noncancer Health Effects of Uncombusted Gasoline Emissions.*** Although evaporative  
6 emissions from gasoline-fueled vehicles are a concern primarily because of their role in  
7 O<sub>3</sub> formation, their health effects are also a concern because benzene, a leukemogen, is a  
8 component of gasoline vapor as well as of exhaust emissions. The noncancer health effects  
9 of gasoline vapor are a minimal concern and are very briefly summarized here, using only  
10 studies on gasoline vapor itself. Other studies on hydrocarbon mixtures that partially  
11 simulate the composition of gasoline vapor are of interest, but are less pertinent.

12 Inhalation toxicity data on noncancer effects that are based on human exposure to  
13 gasoline vapors are limited and consist mainly of data on acute exposures to high  
14 concentrations. Information given here was obtained from the review of vapor-phase  
15 hydrocarbons by Tilton and Bruce (1981). Inhalation of extremely high concentrations of  
16 gasoline vapor can cause narcosis, coma, and sudden death. Death upon acute exposure to  
17 gasoline fumes is generally attributed to severe central nervous system depression that  
18 terminates in respiratory paralysis (Machle, 1941). Gasoline vapors can sensitize the  
19 myocardium, such that even small quantities of epinephrine can precipitate ventricular  
20 fibrillation. This may explain the type of sudden deaths observed in cases of accidental  
21 exposure to gasoline vapor (Ainsworth, 1960; Wang and Irons, 1961; Aidin, 1958; Nelms  
22 et al., 1970; Poklis, 1976), because the edema seen in these individuals at autopsy did not  
23 appear sufficiently severe to be fatal. Both gasoline and numerous constituents of gasoline  
24 are known to induce ventricular fibrillation in the presence of epinephrine (Chenoweth,  
25 1946).

26 Acute inhalation exposures to lesser concentrations of gasoline vapor are usually  
27 characterized by nonspecific anesthetic or narcotic effects, such as headache, vertigo, blurred  
28 vision, ataxia, tinnitus, nausea, anorexia, and muscular weakness (e.g., Tilton and Bruce,  
29 1981). Slight dizziness and eye irritation from an exposure of 4 to 5 min to 2,600 ppm were  
30 reported by Drinker et al. (1943), whereas at 10,000 ppm, marked intoxication occurred.

1 A study by Davis et al. (1960) revealed no manifestations of intoxication in humans exposed  
2 to any of three different unleaded gasolines for 30 min at concentrations of 200, 500, or  
3 1,000 ppm. The only significant effect reported was eye irritation at the 1,000 ppm level.

4 The few data available on the health effects of chronic exposures to low concentrations  
5 of gasoline vapor are limited to reports on occupational exposures and some cases of gasoline  
6 abuse ("sniffing" of vapors). In general, the symptoms of chronic exposure to gasoline  
7 vapor are ill-defined. They may consist of fatigue, muscular weakness, nausea, vomiting,  
8 abdominal pain, and weight loss (e.g., Tilton and Bruce, 1981). Chronic exposure to  
9 sufficiently high concentrations is also known to elicit neurological effects that include  
10 confusion, ataxia, tremor, paresthesias, neuritis, and paralysis of peripheral and cranial  
11 nerves (Swinyard, 1970). Based on data reviewed in Tilton and Bruce (1981), the greatest  
12 hazard associated with chronic gasoline inhalation appears to be exposure to the aromatic  
13 hydrocarbons, especially benzene, because chronic benzene intoxication can result in severe  
14 irreversible systemic effects such as encephalopathy, aplastic anemia, and leukemia.  
15 No reports were found in the literature (i.e., as of the 1981 Tilton and Bruce review) relating  
16 chronic gasoline sniffing to pathological conditions such as liver, kidney, or bone marrow  
17 lesions.

18  
19 ***Carcinogenicity of Gasoline Combustion Emissions.*** Campbell (1936) chronically  
20 exposed mice by inhalation to whole leaded-gasoline exhaust diluted to a minimum of 1:83  
21 for a lifetime and found no carcinogenic response. The high dilution rates and inadequate  
22 reporting, however, limited the usefulness of the study. Brightwell et al. (1986) reported no  
23 significant tumorigenic responses in either Fischer 344 rats or Syrian golden hamsters  
24 exposed 16 h/day to either catalyzed or uncatalyzed gasoline engine exhaust. The dilution  
25 rates are uncertain, although based upon noncancer toxic endpoints, it is unlikely that  
26 maximum tolerated concentrations were achieved in the catalyzed exhaust. No significant  
27 increases in lung tumor rates were reported. Heinrich et al. (1986) reported no significant  
28 increases in tumor induction in either rats or hamsters exposed to uncatalyzed exhaust diluted  
29 a minimum of 27-fold. No lung tumors were detected in dogs exposed for 68 mo to either  
30 untreated or photochemically treated gasoline engine exhaust and then held in clean air for an

1 additional 32 to 36 mo (Hyde et al., 1980). This study is significant because of its duration  
2 and because clear-cut evidence for noncancer toxic effects was noted; however, sample sizes  
3 were inadequate to detect a carcinogenic response unless the pollutants were extremely potent  
4 carcinogens.

5 The maximum concentrations of exhaust used in the above studies are limited by the  
6 toxic effects of CO<sub>2</sub> and CO present, especially in those studies in which the exhaust was not  
7 catalyzed. Furthermore, PM, which is thought to be responsible for cancer induction by  
8 diesel exhaust, is present at much lower concentrations in the gasoline exhaust studies at the  
9 dilutions used. The inhalation studies are therefore considered to be inadequate to rule out  
10 the possibility that inhalation of gasoline engine exhaust can induce cancer. Gasoline  
11 combustion emissions have been identified by IARC (International Agency for Research on  
12 Cancer, 1989) as possibly carcinogenic to humans based on evidence of induction of lung  
13 tumors in rats and hamsters by intratracheal instillation of exhaust condensate, induction of  
14 dermal tumors in mice following skin painting and induction of sarcomas in mice following  
15 subcutaneous injection of exhaust condensate. This evidence was supported by studies  
16 showing that gasoline particle extracts are genotoxic to bacteria and mammalian cells.  
17 Although the PM in unleaded gasoline combustion emissions is lower than either diesel or  
18 leaded gasoline, there is some evidence that the genotoxic potency of the extractable organic  
19 matter is higher than most diesel vehicles, especially heavy duty vehicles. Unfortunately, the  
20 studies of gasoline combustion emissions are very limited and include studies of leaded  
21 gasoline. No cancer research has been conducted on the high emitting older unleaded  
22 gasoline vehicles classified as "superemitters".

23 No epidemiology studies in which individuals were exposed solely to gasoline engine  
24 exhaust are available (International Agency for Research on Cancer, 1989). In one cohort  
25 study of workers exposed predominantly to gasoline engine exhaust (vehicle examiners), the  
26 risk of total cancer increased with latency, but no particular site accounted for the increase.  
27 In one case-control study, no consistent increase in risk was observed.

28 Although direct evidence for carcinogenicity of gasoline engine exhaust via inhalation is  
29 lacking, this route cannot be assumed to be hazard-free. The positive effects observed using  
30 exhaust condensates and the presence of carcinogenic chemicals in both the vapor phase and

PM are illustrative of the potential hazard. The concentrations, effects, and projected cancer risks of carcinogenic components in gasoline engine exhaust have been reported (Carey, 1987; Carey and Somers, 1988; and Adler and Carey, 1989). The agents present in gasoline engine exhaust with a weight-of-evidence classification of B2 or B1, for which a unit risk cancer potency estimate has been made, include acetaldehyde, benzo[*a*]pyrene, 1,3-butadiene, particles, and formaldehyde. At the time this evaluation was made, another potential carcinogen, ethylene, was not considered to have an adequate data to calculate a unit risk value. However, new data on the conversion of ethylene to ethylene oxide in humans and carcinogenic potential of ethylene oxide may permit future revisions of the cancer risk of gasoline engine exhaust. See Table 2-6 for cancer risk estimates. The EPA has not evaluated the weight of evidence for the carcinogenicity of gasoline engine exhaust emissions.

***Carcinogenicity of Uncombusted Gasoline Emissions.*** The primary evidence for carcinogenicity of gasoline is based upon a study in which mice and rats were chronically exposed to a whole aerosol of unleaded gasoline (MacFarland et al., 1984). These studies reported significant increases for kidney tumors in male rats and liver tumors in female mice. Although no other chronic cancer bioassays have been conducted, a variety of shorter term studies to determine which components are responsible for toxic effects and to attempt elucidation of the mechanisms for carcinogenesis have been undertaken.

Epidemiology studies collectively provide limited evidence that employment in the petroleum industry, resulting in exposure to gasoline as well as other petroleum products, is associated with certain types of cancer. The evidence presented from studies in which gasoline was considered the primary source of exposure, however, was considered inadequate for evaluating gasoline per se as a human carcinogen. No studies in which exposure is considered to be exclusively gasoline are currently available in the open literature. A recently completed epidemiology study, supported by the American Petroleum Institute will soon become available.

The only individual component of gasoline that has been clearly shown to be a human carcinogen is benzene. Based upon a previously derived potency estimate and assuming a

1 2% concentration in gasoline, benzene could theoretically contribute 20% of the total tumor  
2 response; however, no quantitative evidence indicates that benzene actually contributes to the  
3 response. Although the MacFarland et al. (1984) study predicted the maximum tumor  
4 response due to benzene to be 3%, the design of this experiment was not sufficiently  
5 sensitive to detect this level of response. Two important issues must be addressed. The first  
6 concerns the relevance of male-rat kidney tumors for human risk assessment. The male rat  
7 produces alpha<sub>2μ</sub>-globulin, a filterable protein, in large quantities. When male rats are  
8 exposed to gasoline, certain hydrocarbon components present in the mixture are thought to  
9 bind to the alpha<sub>2μ</sub>-globulin. Binding prevents metabolism of the protein after uptake by the  
10 kidney tubule cells. As a result, alpha<sub>2μ</sub>-globulin with the bound organics accumulates as  
11 hyaline droplets in the tubule cells, followed by the development of kidney pathology.  
12 In later life, kidney tumors also develop in some of these animals. The EPA's Risk  
13 Assessment Forum has recently conducted an evaluation of the utility of male rat kidney  
14 tumors for assessing human cancer risk. They concluded that, although definitive  
15 mechanistic proof was lacking, the development of tumors in animals with alpha<sub>2μ</sub>-globulin-  
16 induced nephropathy is likely due to progression of the pathologic lesions. The Forum panel  
17 therefore recommended that when kidney tumors occur in male rats and certain criteria are  
18 met (i.e., hyaline-droplet-related nephropathy is present, the chemical agent is nongenotoxic,  
19 etc.), then the kidney tumor response should not be used in assessing human risk. Although  
20 unleaded gasoline produces nephropathy in male rats, the Forum has not determined if  
21 gasoline meets the above criteria.

22 The second issue concerns the composition of the gasoline in the MacFarland et al.  
23 (1984) study. The animals in this study were exposed to aerosols of whole gasoline. This  
24 aerosol contained a greater proportion of the toxic components than gasoline vapor, which is  
25 made up primarily of the nontoxic short-chain volatile hydrocarbons. If the toxic  
26 components are also responsible for cancer induction, then any quantitative assessment of  
27 gasoline-vapor risk based upon this study is likely to be in error. Additional bioassays are  
28 necessary to determine the relationship between the toxicity and carcinogenicity of the  
29 individual components.



1 Evidence for the carcinogenicity of gasoline was evaluated by the U.S. Environmental  
2 Protection Agency (1987c). Based upon adequate evidence for carcinogenicity in animal  
3 studies combined with inadequate evidence in humans, gasoline was considered to fit best  
4 into category B2 and was, thus, considered a probable human carcinogen. If the rat kidney  
5 data are discounted, liver tumors in female mice are the only positive responses remaining.  
6 Even if the rat kidney tumor data are discounted, it is uncertain if the weight of evidence for  
7 carcinogenicity would change. The entire data base would require reevaluation, including the  
8 fact that carcinogenic chemicals are present in gasoline. An upper bound unit risk estimate  
9 of  $3.5 \times 10^{-3}$  per ppm (the risk of cancer resulting from lifetime exposure to 1 ppm) was  
10 derived from kidney tumor incidence data in rats. Again, if the rat kidney tumor data are  
11 discounted and the risk based upon liver tumors, the upper bound unit risk estimate decreases  
12 slightly to  $2.1 \times 10^{-3}$  per ppm.

13 In March of 1988, the IARC convened a working group to evaluate the carcinogenic  
14 risks to humans from occupational exposures in petroleum refining and from exposures to the  
15 crude oil and major petroleum fuels themselves (International Agency for Research on  
16 Cancer, 1989). The working group found limited evidence for the carcinogenicity of  
17 unleaded automotive gasoline in experimental animals and inadequate evidence for  
18 carcinogenicity in humans. This resulted in an overall evaluation of gasoline fuel in humans  
19 as possibly carcinogenic (Group 2B).

#### 21 **2.2.2.1.5 Diesel**

22 The carcinogenic and noncarcinogenic health effects of diesel combustion products have  
23 been studied extensively over the last 10 years. Considerable information regarding both  
24 classes of endpoints has been published. These data are presently being reviewed by the  
25 EPA, and a Health Assessment Document is being prepared (U.S. Environmental Protection  
26 Agency, 1990e). This document contains an evaluation of both carcinogenic and  
27 noncarcinogenic effects, along with a quantitative estimate of cancer potency. Information  
28 regarding the health effects of uncombusted diesel fuel is much more limited. Studies  
29 relating to the health effects of both diesel fuels and combustion products are summarized  
30 below.

1       ***Noncancer Health Effects of Diesel Combustion Emissions.*** Diesel exhaust particles  
2 are in the submicrometer size range and can be carried deep into the lungs. Fine-mode  
3 particles, in general, have been implicated as etiological factors in various types of chronic  
4 lung disease, such as chronic bronchitis. They may also increase the lung's susceptibility to  
5 bacterial and viral infections or aggravate preexisting disease states, such as bronchitis,  
6 emphysema, or asthma (U.S. Environmental Protection Agency, 1982b, 1986b). Other  
7 components of diesel exhaust (e.g., SO<sub>2</sub>, NO<sub>2</sub>, formaldehyde, acrolein, and H<sub>2</sub>SO<sub>4</sub>) may  
8 contribute to some of these potential health effects. The health effects of diesel emissions  
9 have been summarized recently (U.S. Environmental Protection Agency, 1990e).

10       Symptoms of acute human occupational exposure to diesel exhaust include mucous  
11 membrane and eye irritation, headache, light-headedness, nausea, vomiting, heartburn,  
12 weakness, numbness and tingling in the extremities, chest tightness, and wheezing. Exhaust  
13 odors can cause nausea, headache, loss of appetite, and psychological stress. Respiratory  
14 symptoms and changes in pulmonary function were generally found to be minimal and not  
15 statistically significant in workers exposed to diesel exhaust over the course of a workshift  
16 (Reger, 1979; Jorgensen and Svensson, 1970; Ames et al., 1982); however, in one study of  
17 bus-garage workers, an increased frequency in symptoms of cough, labored breathing,  
18 itching, eye irritation, chest tightness, and wheezing was observed (Gamble et al., 1987).  
19 In one study, reductions in pulmonary function were observed in exposed workers and were  
20 attributed to NO<sub>2</sub> (Ulfvarson et al., 1987).

21       Chronic effects of diesel exhaust have been evaluated in epidemiological studies of  
22 occupationally exposed workers (Battigelli et al., 1964; Reger et al., 1982; Attfield et al.,  
23 1982; Gamble and Jones, 1983; Purdham et al., 1987). A few of these studies reported a  
24 higher prevalence of respiratory symptoms, but they were usually accompanied by significant  
25 changes in pulmonary function.

26       Animal studies on the effects of diesel exhaust have involved acute, subchronic, and  
27 chronic exposure regimens. Short-term exposures resulted in minimal effects on pulmonary  
28 function, even when concentrations were sufficiently high to cause histological and  
29 cytological changes in the lungs (Inhalation Toxicology Research Institute, 1980; Mauderly  
30 et al., 1981; Pepelko, 1982). Exposure for several months or longer resulted in

1 accumulation of particles in the lungs, increased lung weight, increases in macrophages and  
2 leukocytes, macrophage aggregation, hyperplasia of the alveolar epithelium, thickening of the  
3 alveolar septa, altered pulmonary function, and reduced growth rates (U.S. Environmental  
4 Protection Agency, 1990e). Acute and chronic exposures to diesel exhaust have been  
5 associated with increased susceptibility to respiratory tract infections (Campbell et al., 1981).  
6 Behavioral effects have been observed in a few studies of animals exposed to diesel exhaust  
7 (Laurie et al., 1980).

8  
9 ***Noncancer Effects of Uncombusted Diesel Emissions.*** Little work has been done on  
10 the health effects of diesel fuel vapors. Gaworski et al. (1985) exposed three animal species  
11 to vapors of diesel fuel for 90 days and reported renal damage and mild changes in weight  
12 gain and erythrocyte parameters. Renal damage in male rats exposed to diesel vapor was  
13 observed by Mattie et al. (1986). Acute exposure of rats to aerosolized diesel fuel resulted  
14 in depression of body weight and slower growth, histological changes in the lung, and an  
15 increase in lung weight (Dalbey et al., 1987).

16  
17 ***Carcinogenicity of Diesel Combustion Emissions.*** The 1978 EPA report of the  
18 relatively high mutagenic activity of diesel particle extracts (Huisinigh et al., 1978) led to a  
19 major increase in research on the carcinogenicity of diesel exhaust by EPA, industry, and  
20 other organizations. The cancer research completed between 1978 and 1986 has been  
21 reviewed in two books (Lewtas, 1982; Ishinishi et al., 1986). The first animal studies to  
22 report the tumorigenicity of diesel combustion particle extracts were conducted in 1955  
23 (Kotin et al., 1955). The EPA conducted a wide range of cancer studies using available  
24 animal models (Pepelko, 1982), of which, the mouse skin tumorigenicity studies in Sencar  
25 mice resulted in dose-response data suitable for potency estimations (Nesnow et al., 1982).  
26 The first cancer unit risk estimates of diesel combustion emissions were based on the  
27 comparative potency method (Lewtas et al., 1981; Albert et al., 1983; Lewtas, 1985) using  
28 the mouse skin tumor potency of diesel particle extracts (Nesnow et al., 1982) compared to  
29 emissions for which both mouse skin tumor potency data and human lung cancer unit risks  
30 were available (coke oven, roofing coal tar, and cigarette smoke). The strongest animal

evidence for the carcinogenicity of diesel emissions is provided by inhalation studies. Positive results have been reported in at least five separate experiments with rats (Mauderly et al., 1987; Brightwell et al., 1986; Stoeber, 1986; Ishinishi et al., 1986; Iwai et al., 1986). The largest responses were reported by Brightwell et al. (1986), in which tumor incidences of 23 and 54% occurred in male and female Fischer 344 rats exposed to diesel engine emissions diluted to produce particle concentrations of  $6.6 \text{ mg/m}^3$ , with smaller increases at particle concentrations of  $2.2 \text{ mg/m}^3$ . Evidence for lung tumor induction by inhalation of diesel exhaust was also reported for NMRI mice (Stoeber, 1986) and Sencar mice (Pepelko and Peirano, 1983). On the basis of the above results, the evidence for carcinogenicity of diesel exhaust in animals is considered to be sufficient.

In earlier studies, excess risk from exposure to diesel engine emissions could not be detected in epidemiology studies. The implications of these studies, however, were limited by inadequate exposure characterization; lack of validation of surrogate measures of exposure; confounding effects of smoking, asbestos, coal and other physical and chemical agents; and absence of quantification of risks by duration of exposure, latency, and histologic type of malignancy.

More recently, an excess risk of lung cancer was observed in three of seven cohort studies and six of seven case-control studies. Most of these studies involved railroad workers or truck drivers (U.S. Environmental Protection Agency, 1990e). The most convincing were the case-control and cohort studies of Garshick et al. (1987, 1988) with railroad workers. Potential confounding factors were adequately controlled, and interactions between diesel exhaust and lung cancer risk factors were tested. Nevertheless, because of the lack of data on actual exposure to diesel exhaust in these studies as well as other methodological limitations, such as lack of latency analysis, etc., the evidence for carcinogenicity of diesel exhaust in humans is still considered to be limited. Diesel exhaust is therefore considered to best fit into cancer weight-of-evidence category B1 (U.S. Environmental Protection Agency, 1990e).

An attempt was made to develop inhalation cancer unit risk estimates based upon epidemiology data as well as chronic animal bioassays. For reasons stated above, the

1 epidemiology data were found to be inadequate for this purpose. A quantitative cancer risk  
2 estimate was therefore developed based upon chronic animal cancer bioassays.

3 In the development of a unit risk estimate, it was necessary to (1) determine the site of  
4 tumor induction in order to adequately model target tissue concentration, (2) determine the  
5 component or components of exhaust responsible for lung tumor induction, and (3) develop a  
6 dosimetry model allowing for both low-dose extrapolation as well as extrapolation of dose  
7 from experimental animals to humans (U.S. Environmental Protection Agency, 1990e). The  
8 primary tumor site was in the lungs, although marginal increases in kidney tumors were seen  
9 in some of the epidemiology studies and hematopoietic tumors were reported to be increased  
10 in one of the animal experiments (Stoeber, 1986). More specifically, the tumors originated  
11 from the epithelial lining of the small airways and alveoli, rather than connective tissue  
12 (Mauderly et al., 1987). Dosimetry was therefore based upon concentration per unit surface  
13 area of the tissue lining the lungs.

14 Diesel exhaust is made up of three major components, a vapor phase, an insoluble  
15 particle core consisting of inorganic carbon, and particle-adsorbed organics. The vapor  
16 phase contains few known carcinogens. Moreover, exposure to the vapor phase alone did  
17 not result in detectable increases in lung tumors (Brightwell et al., 1986). While the particle  
18 adsorbed organic fraction does contain carcinogenic polycyclic aromatic hydrocarbons, their  
19 concentrations are quite low and are probably inadequate to alone account for the  
20 tumorigenic responses reported. In recent, as yet unpublished studies (Heinrich, 1990;  
21 Mauderly et al., 1991), it was reported that carbon black, which is similar to the  
22 biochemically inert carbon core of the diesel particle, is capable of inducing lung tumors at  
23 inspired concentrations similar to those used in the diesel studies. Based upon the failure of  
24 the vapor phase alone to induce detectable increases in lung tumors, the low concentration of  
25 polycyclic aromatic hydrocarbons in the particle-adsorbed organics, and the ability of pure  
26 carbon particles to induce lung cancer at the same concentration as diesel exhaust particles, it  
27 was concluded that the tumor responses noted could be accounted for by a particle effect  
28 alone.

29 A dosimetry model was developed, taking into account animal-human differences in  
30 particle clearance rates, particle deposition efficiency, respiration rates, and lung surface area

1 as well as high dose inhibition of particle clearance and particle transport to lung associated  
2 lymph nodes. The target organ dose was based upon particle concentration per unit of lung  
3 surface area.

4 An important component of this model is an adjustment for high dose inhibition of  
5 particle clearance from the lungs. This slowing of clearance results in a disproportionate  
6 increase in lung burdens at the concentrations used in the animal bioassays. Failure to adjust  
7 for this factor will result in erroneous estimates of lung burden during extrapolation to low  
8 exposure concentrations. Since the vapor phase compounds or the particle-adsorbed organics  
9 do not accumulate in the lungs to any appreciable extent, estimated lung burdens will differ  
10 from those of particles following low-dose extrapolation. Risk estimates will therefore vary  
11 depending upon which exhaust component the target organ dose is based upon.

12 Using the dosimetry model to estimate particle concentration per unit lung surface area,  
13 95% upper bound inhalation unit risk estimates were developed from chronic bioassay data  
14 reported by Brightwell et al. (1986), Ishinishi et al. (1986), and Mauderly et al. (1987). The  
15 geometric mean of estimates derived from these three studies is equal to  $1.7 \times 10^{-5}$  per  
16  $\mu\text{g}/\text{m}^3$ . While this estimate is recommended in EPA's Draft Health Assessment for Diesel  
17 Engine emissions (U.S. Environmental Protection Agency, 1990e), it is still preliminary and  
18 subject to change.

19  
20 ***Carcinogenicity of Uncombusted Diesel Emissions.*** No information regarding the  
21 carcinogenicity of diesel fuel is available from either animal experiments or epidemiology  
22 studies. Although diesel fuel contains many of the same components as gasoline, the relative  
23 concentrations may be very different.

24 Human populations for epidemiological studies of uncombusted diesel fuel are not likely  
25 to be found because of the low likelihood of exposure resulting from its more limited use and  
26 lower vapor pressure, compared to gasoline. The relative carcinogenicity of diesel fuel  
27 should be initially assessed by determining the known carcinogens present and estimating  
28 overall potency from available data regarding concentrations of these individual components  
29 and their cancer potency. If such preliminary estimates are sufficiently large to be a  
30 concern, chronic bioassays should be undertaken.

## 2.2.2.2 Ecosystems Effects

### 2.2.2.2.1 Terrestrial Ecosystem Effects

The use of conventional fuels for the past several decades has resulted in significant threats to terrestrial biota and ecosystems. Indeed, the environmental integrity of many terrestrial ecosystems has been compromised from exposures to conventional-fuel pollutants and their transformation products. A good example is the San Bernadino Mountains near Los Angeles, CA, where significant vegetal and ecosystem changes have occurred in response to conventional-fuel pollutant (e.g., O<sub>3</sub>) exposure (Miller et al., 1989). The ecological effects on terrestrial biota from conventional fuel combustion products (e.g., CO, CO<sub>2</sub>, NO<sub>x</sub>, VOCs, PAHs, PM, SO<sub>x</sub>, and lead) and transformation products (e.g., O<sub>3</sub> and PAN) are documented in the various Air Quality Criteria documents (e.g., U.S. Environmental Protection Agency, 1982a,b; 1986a) and other literature sources (e.g., Smith, 1990; Newman and Schreiber, 1988). In an effort to improve environmental quality, new formulations of these fuels and suitable control technology have resulted in the reduction of a few pollutants in terrestrial ecosystems. The reformulation of conventional gasoline from leaded to unleaded may have decreased lead concentrations in plant communities, such as the watersheds associated with the Mississippi River drainage system (Trefry et al., 1985); however, new formulations to compensate for lead removal resulted in high gasoline volatility with increased emissions of photoreactive VOCs, which are the precursors to the photochemical pollutants.

Despite improved fuel formulations and control technology, conventional-fuel usage still presents environmental hazards to biota (e.g., high atmospheric concentrations of O<sub>3</sub> due to VOC and NO<sub>x</sub> production from fuel combustion [Graedel and Crutzen, 1989]). Another ecological problem associated with conventional fuel combustion is the production of NO<sub>x</sub> and SO<sub>2</sub>, which are major contributors to acid rain. Furthermore, PM, CO, and CO<sub>2</sub> are other pollutants that can impact terrestrial biota; indeed, CO<sub>2</sub>, an RITG, may indirectly influence terrestrial biota through global climate change (Schneider, 1989). The atmospheric transformation products arising from conventional-fuel pollutants that are the best understood are O<sub>3</sub> and PAN; both are highly phytotoxic and influence plant growth/yield and plant

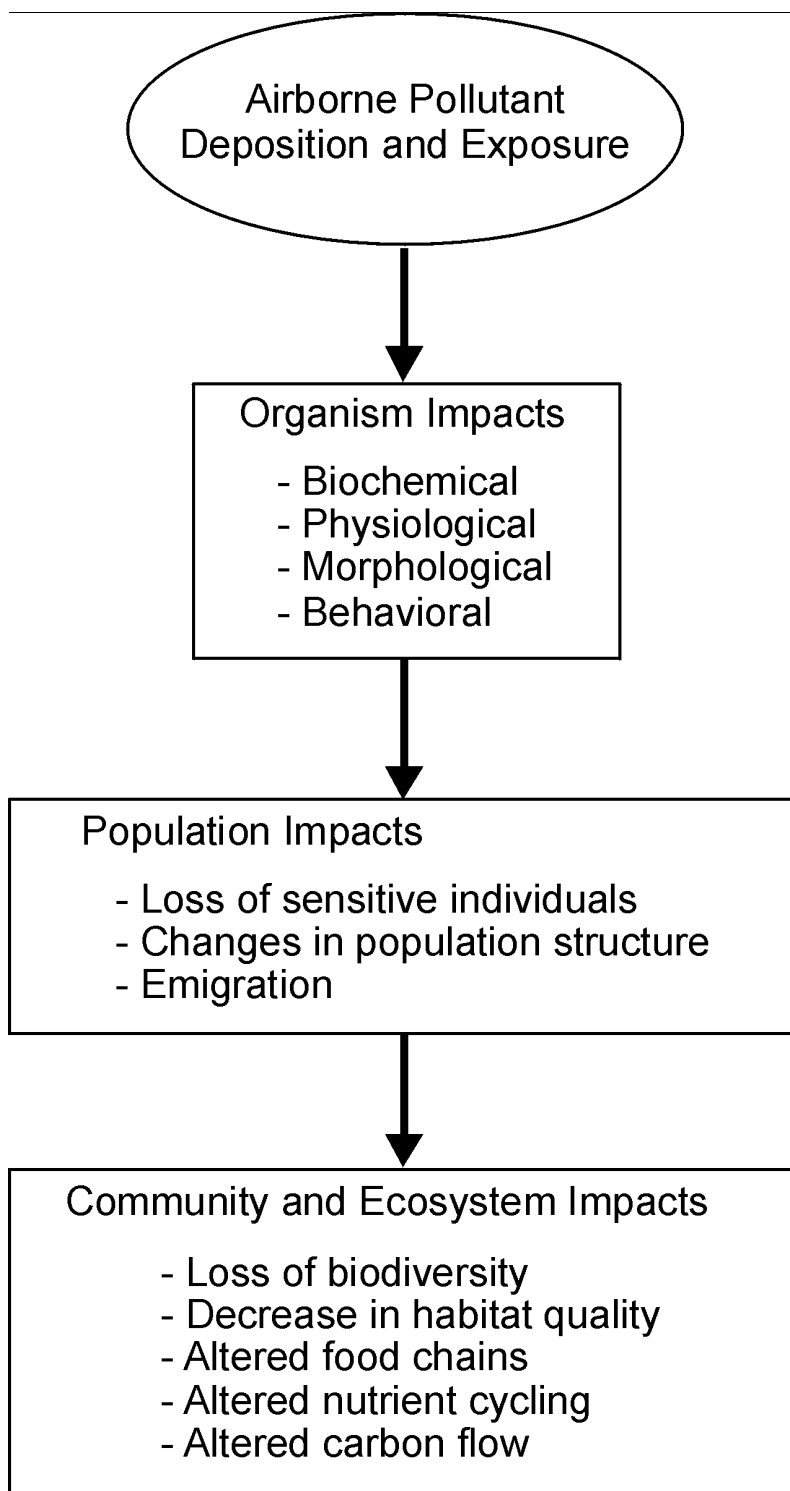
1 community structure through action on individual plants (National Research Council, 1976,  
2 1977).

3 The degree of ecological impact of conventional-fuel pollutants and transformation  
4 products on terrestrial ecosystems will depend upon emission patterns and concentrations,  
5 season, biota exposure to the pollutants, and biota sensitivity (Weinstein and Birk, 1989).  
6 Each item represents an area that will require investigation by specific research projects for  
7 conventional-fuel risk assessments to be completed. An analysis of the impact of  
8 conventional-fuel pollutants on terrestrial ecosystems can probably be achieved through  
9 literature reviews; however, limited research will still be necessary for comparative purposes  
10 with alternative fuels.

11 Ecological perturbations caused by conventional-fuel pollutant deposition on terrestrial  
12 ecosystems may have ramifications through all levels of biological organization, depending  
13 on the duration and severity of pollutant exposure and organism sensitivity (Figure 2-9).  
14 Although the adverse impacts of air pollution effects on ecosystems cannot be specified in  
15 detail as biota react differently to air pollution stress, the following generalized events may  
16 be observed and apply similarly to plants and animals, even through differences in the  
17 pathway of exposure exist (Bormann, 1985): (1) disruption of biochemical or physiological  
18 processes; (2) reduction in growth, reproduction, and abundance of sensitive individuals or  
19 populations; and (3) changes in the composition, structure, and function of communities and  
20 ecosystems. The impacts of air pollution on vegetation are better documented than for  
21 wildlife or soil biota.

22 Vegetation and soil are receptors of wet and dry pollutant deposition because of the  
23 large surface areas exposed to the atmosphere (Foster, 1991). Pollutants enter into plants  
24 through the leaves or roots depending on the site of deposition, physicochemical properties of  
25 the contaminants, and plant morphology. Biochemical processes are the first site of action  
26 within the plant (Foster, 1991). If enzymatic degradation detoxifies the pollutant, then no  
27 injury will occur. However, if the pollutant or its metabolites are not rendered harmless,  
28 then alterations in plant metabolism may result in foliar injury, altered carbohydrate and  
29 nutrient allocation, and reduced growth and reproductive capability. The degree of impact to  
30 the plant will depend on the pollutant toxicity, exposure pattern, and plant sensitivity. Acute





**Figure 2-9. Potential ecological effects of conventional-fuel pollution deposition and exposure to ecosystems.**

1 exposures usually cause observable morphological damage within a short time, such as leaf  
2 lesions, stunted growth, or even death. However, plant damage resulting from acute  
3 exposures is generally limited in time and space because of control technology mandated by  
4 legislation.

5       Chronic, sublethal pollutant exposures to vegetation are much more common and  
6 widespread than acute exposures (Moser et al., 1991). Sublethal exposures may not induce  
7 observable morphological damage, but altered biochemical processes may decrease plant  
8 vigor and productivity, alter phenology, or reduce reproductive potential. Altered  
9 physiological processes may render the plant more susceptible to insect damage, disease, and  
10 other natural stressors. Decreased reproduction will impact populations through the loss of  
11 new recruitments to the plant community. With continual exposure, sensitive plant  
12 populations may decrease in numbers, allowing tolerant species to become dominant. Thus,  
13 shifts in plant community structure and composition could result in decreased biological  
14 diversity and altered ecosystem functions.

15       Pollutant deposition to soils will affect soil biota (Shafer, 1985). Possible soil biota  
16 responses may include species mortality, gene-pool alterations, population shifts, alterations  
17 of species competition, changes in nutrient cycles, and effects on plant roots. Such changes  
18 may indirectly impact vegetation growth and development. The effects of pollutant  
19 deposition to soil are not very well documented in the literature.

20       Conventional-fuel pollutants can affect animals/wildlife through inhalation, dermal  
21 contact, and food and water consumption (Schreiber, 1985). The direct effects on animals  
22 may vary from mucous membrane and respiratory tract irritation to alterations in activity  
23 patterns, depending upon exposure duration and concentrations. Indirect effects may reduce  
24 competitive ability, foraging behavior, or predator escape mechanisms. Reduced plant cover  
25 and habitat quality will result in animals being more susceptible to predation and disease.  
26 Adequate birthing sites may be reduced because of changes in vegetation architecture. Many  
27 of the conventional-fuel pollutants should have low bioaccumulation potential, with the  
28 obvious exception of lead. Trophic transfer of these toxic chemicals may occur by animal  
29 consumption of contaminated forage (Moriarty, 1978) and water (Newman and Schreiber,  
30 1988).

#### 2.2.2.2.2 *Aquatic Ecosystem Effects*

***Freshwater Effects.*** The potential hazard of transportation fuels to freshwater aquatic systems is evident from the consequences of spills from fuel storage and transportation facilities. Although a rare event, considering the scope of the fuel distribution system, spills occur with sufficient frequency and severity to merit considerable concern. A portion of all fish kills reported each year are attributed to oil and refined oil products. Molag and Jansen (1988) reported 41 "major" oil spills (>100,000 L of oil or fuel products introduced where significant environmental damage could occur) from 1980 through 1986 into U.S. rivers, canals, and harbors. One of the most recent notable spills was 700,000 gal of diesel fuel from a collapsed storage tank into the Monongahela River in January, 1988. Acutely lethal conditions for aquatic organisms, with consequent fish kills, occurred in that river and downstream in the Ohio River (Center for Hazardous Materials Research, 1989). In September 1989, 23,000 gal of gasoline spilled from a ruptured pipeline crossing Mill Creek in Salem, OR. Substantial mortality occurred both in resident fish species and in salmon migrating upstream at this time (ENSR Consulting and Engineering, 1989).

A spill of 50,000 gal of aviation fuel in October 1982 into Roaring Run Creek in Cambria County, PA, resulted in almost complete mortality of fish and invertebrates for several kilometers of this stream, Howell Run, and the Little Conemaugh River into which it flows (Guiney et al., 1987b). Unlike most spills, the impacts of this spill were relatively well documented; recoveries of ecosystem components were observed within several months to one year, although measurable sediment contamination by fuel hydrocarbons persisted for 14 to 21 mo (Guiney et al., 1987a). Given the transient and unexpected nature of such events, however, exposure concentrations associated with initial mortalities were not documented. Lethal concentrations are typically based only on exposure calculations made after the mortality occurs.

Sufficient laboratory toxicity data are needed to properly compute and compare risks among different spill scenarios and different fuel formulations. The toxicity of conventional transportation fuels is difficult to study and predict because these fuels are complex mixtures of chemicals, containing a variety of paraffins, naphthenes, olefins, and aromatics. The relative amounts of classes of compounds and compounds within a class can vary widely

1 within a fuel type, due to seasonal and regional formulations, as well as between different  
2 fuel types.

3 Toxicity tests on aquatic organisms have been conducted with various representative  
4 constituents of conventional fuels. Acutely lethal concentrations to fish and invertebrates  
5 vary from a few tenths of a milligram per liter to a few hundred milligrams per liter,  
6 whereas more chronic endpoints may occur at 5 to 10 times lower concentrations (Pickering  
7 and Henderson, 1966; LeBlanc, 1980; DeGraeve et al., 1982; Brooke et al., 1984; Geiger  
8 et al., 1985, 1986, 1988). Adverse effects on the survival and growth of the alga *Chlorella*  
9 *vulgaris* require higher concentrations than for these animals (Kauss and Hutchinson, 1975).  
10 The toxicity of the individual compounds is highly correlated with their hydrophobicities, but  
11 the capability to predict the toxicity of a fuel based on its detailed composition or a profile of  
12 chemical properties has not yet been developed.

13 Some toxicity tests have been conducted on actual fuels, especially diesel fuel. These  
14 tests have frequently used the water-soluble fraction of the fuel by equilibrating a mixture of  
15 one part fuel with several parts water and then characterizing the toxicity of the water  
16 fraction by the extent of effects as a function of dilution with uncontaminated water. The  
17 rationale for such a test method is that it approximates the dissolved concentration an  
18 organism would experience in a water body subject to a fuel spill, because dissolution of the  
19 chemical is considered necessary for absorption by the organism. The water-soluble fraction  
20 of No. 2 diesel fuel has been reported to be not acutely lethal at full strength to flagfish and  
21 fathead minnow (Hedtke and Puglisi, 1982) and to freshwater snails (Millemann et al.,  
22 1984); however, it has been reported to be lethal to *Daphnia* at 10 to 30% strength (Geiger  
23 and Buikema, 1981; Ullrich and Millemann, 1983) and to inhibit drastically *Scenedesmus*  
24 *capricornutum* growth and photosynthesis at full-strength (Giddings and Washington, 1981).  
25 For *Daphnia*, the effect levels corresponded to several ppm of actual oil constituents in  
26 solution. When oil:water emulsions and mixtures were tested, acutely lethal concentrations  
27 (96 h LC<sub>50</sub>s) were reported to be 40 to 60 mg/L for flagfish and minnow (Hedtke and  
28 Puglisi, 1982) and to be in a similar range for a marine copepod (Barnett and Kontogiannis,  
29 1975). Barnett and Kontogiannis also reported gasoline to be more toxic than diesel fuel in  
30 the first day or two of exposure, but less toxic after several days, presumably reflecting that

1 lighter fractions in gasoline have lower, but more rapid, toxicity and are more volatile and  
2 are lost from solution.

3       These results are limited and difficult to interpret and apply. The composition of the  
4 water-soluble fraction changes with the initial fuel:water ratio, with the exact formulation of  
5 the fuel, and with aging, particularly in static toxicity tests. The presumption that the  
6 organism reacts only to the dissolved fraction is contraindicated by the results of Hedtke and  
7 Puglisi (1982), who found no toxicity in the water-soluble fraction, but found substantial  
8 toxicity in an emulsion, which should not have dissolved components higher than the water  
9 soluble fraction. This phenomenon may reflect depletion of sparingly soluble, but toxic,  
10 components from the water-soluble fraction in static tests; in emulsions, however, the  
11 dissolved concentrations of these components may be renewed from the undissolved phase.  
12 In fact, some authors have noted apparent effects of loss of components from solution in  
13 dictating the course of toxicity (Barnett and Kontogiannis, 1975; Kauss and Hutchinson,  
14 1975).

15       A deficiency in available data on fuel toxicity is the lack of any tests on contaminated  
16 sediments, where significant exposure might occur. Information on the combined toxicity of  
17 the mixture of fuel components and transformation products expected in urban waters  
18 exposed not only to spills, but also to atmospheric deposition, effluents, leakage, and runoff  
19 is also lacking. The kinetics of toxicity have not been well examined, but are important,  
20 given the transient nature of some exposures and the markedly different toxicokinetics of  
21 different fuel components. Above all, adequate data on the response of actual ecosystems to  
22 exposure to fuels are lacking. The effects of conventional fuels on experimental ecosystems  
23 need to be evaluated in order to screen effects at expected exposures, to measure direct  
24 effects on selected organisms, and to examine effects in the context of an integrated  
25 community.

26  
27       ***Marine Effects.*** A substantial amount of research on the effects of some petroleum  
28 products on marine organisms has been conducted. Most of this research, however, has  
29 focused on No. 2 Fuel Oil, No. 6 Oil, and a few crude oils (Hyland and Schneider, 1976;  
30 Whittle et al., 1982). Additional work has been done on a limited number of individual fuel

1 components, such as naphthalene and phenanthrene. Very little research has focused on  
2 gasolines. In order to compare the effects of alternative fuels with the base case, more  
3 information is needed about the fate and effects of various gasolines and gasoline components  
4 on marine organisms and communities.

5 Many petroleum hydrocarbons are toxic to aquatic biota and some compounds, such as  
6 PAHs, have been shown to bioaccumulate in some species. Petroleum hydrocarbons can  
7 injure marine biota and communities due to direct acute toxicity, as a result of physical  
8 processes (smothering, hypothermia due to loss of body insulation), and as a result of chronic  
9 effects on sensitive life stages.

10 Although a considerable amount is known about the toxicity of some petroleum  
11 compounds and mixtures to various marine organisms, much still needs to be done to  
12 understand fully how these fuels impact marine ecosystems. Due to the likely transient  
13 nature of the exposures, kinetic-based toxicity models will also need to be developed to better  
14 predict the effects of fuels on marine ecosystems.

### 16 **2.2.3 Global Warming**

17 Global climate warming is directly affected by the emissions of RITGs (CO<sub>2</sub>, methane,  
18 N<sub>2</sub>O, CO, and NO<sub>x</sub>) and VOCs. As discussed under stationary source characterization  
19 (Section 2.2.1.1.1), the production and utilization cycle of petroleum-based transportation  
20 fuels will emit both RITGs and VOCs. Critical quantification of these emissions is needed to  
21 assess the impact on global warming (being addressed by ORD's Global Climate Research  
22 Program) and to provide the necessary data needed to assess the health and ecological risks  
23 to the nation. This information will also provide a basis for identifying the location and  
24 nature of control measures needed to maximize emission reduction.

### 26 **2.2.4 Risk Prevention/Mitigation**

#### 27 **2.2.4.1 Stationary Sources**

28 Conventional petroleum-based fuels have a relatively long history of use and  
29 experience, including application of control technologies to emissions and discharges. The  
30 major emissions are VOCs; RITGs; and toxic pollutants, such as benzene. Effluents will

1 contain a variety of organic pollutants and require treatment prior to discharge. Solid wastes  
2 include solids (coke), catalysts, and water treatment sludges. Emissions and discharges from  
3 petroleum processing, storage, and transportation are from (1) conventional sources (vents,  
4 pressure-relief valves, bleed steams, etc.), (2) fugitive sources (leaking valves, piping or  
5 tanks), and (3) large scale accidental releases. Although regulatory requirements (NSPS,  
6 National Emission Standards for Hazardous Air Pollutants [NESHAP], and NPDES) have  
7 addressed many of the sources, emissions have not been sufficiently reduced to alleviate the  
8 adverse impact of petroleum-based fuels on the O<sub>3</sub> nonattainment and global warming  
9 problems. Conventional sources are generally controlled by a variety of systems, such as  
10 chemical or physical adsorption, flaring and incineration, and condensation. If properly  
11 designed, maintained, and operated, these systems can operate at efficiencies in the high  
12 nineties. There are also small conventional sources that do not fall under the regulations.  
13 Fugitive emissions are controlled by a preventive maintenance program. In the Superfund  
14 Amendments and Reauthorization Act of 1986 (SARA) (Statutes-at-Large, 1986), Title III  
15 specifically addresses emergency planning to alleviate the consequences of accidental releases  
16 (Davis et al., 1987).

17 The effectiveness of existing technologies and practices for stationary emission and  
18 discharge control must be assessed. Based on this evaluation, development of design and  
19 operation information is necessary to optimize existing stationary source controls and to  
20 apply them to now uncontrolled sources. Guidance is needed to develop new or improved  
21 control systems, design methods, and operating procedures to minimize emissions and  
22 discharges.

23 Approximately 2.5 million UST systems and 250,000 aboveground tank systems that  
24 contain petroleum motor fuels exist in the United States. The environmental impact of leaks  
25 from these tanks is a special concern. The problems associated with the storage of fuels in  
26 USTs have been due primarily to factors such as corrosion, improper installation, and  
27 overfilling. A significant number of USTs have released fuel, leading to soil and  
28 groundwater contamination. The EPA's national survey of underground motor-fuel storage  
29 tanks suggests that more than 25% of existing tank systems (i.e., tanks and their associated  
30 piping) may be leaking or are expected to leak within the next 3 to 5 years. Soil cleanup and

1 aquifer restoration will be required at tens of thousands of sites, costing from tens of  
2 thousands to several million dollars per site. In many cases, drinking-water aquifers will be  
3 unavailable for public use for decades. Individuals and communities have been forced to  
4 develop alternative water supplies. Thus, the societal costs have been, and will continue to  
5 be, extremely large, even if the actual impact on human health and on ecosystems remains  
6 small and undocumented.

7 Federal regulations (Code of Federal Regulations, 1990) have been promulgated  
8 regarding the storage and handling of fuels and chemicals. They offer state-of-the-art  
9 guidance to owners and operators of UST systems and set requirements for proper design  
10 standards, release detection, and corrective action. Over the last 5 years, actual development  
11 projects and resulting data and guidance documents have been typically assigned to the  
12 following three categories: leak prevention, leak detection, and corrective action. Although  
13 federal regulations for release detection address tanks of various sizes and contents, research  
14 to date has focused essentially on evaluating the performance of release detection systems for  
15 gasoline tanks with a capacity of 12,000 to 15,000 gal. Further research is required to  
16 determine whether existing technology can be applied to small tanks (<1,000 gal) and very  
17 large tanks (60,000 gal and above) and to tanks containing other conventional fuels such as  
18 diesel, aviation, and stationary-source combustion fuels.

19 Past experience with conventional fuels has resulted in the need to evaluate and  
20 remediate several tens of thousands of UST sites. Research has focused on gasoline-  
21 contaminated soils and aquifers, with only a modest effort to address other conventional  
22 fuels. To date, this research has included (1) evaluations of the state of the knowledge of  
23 gasoline fate and transport in soils; (2) evaluations of the state of the art of selective  
24 technologies, such as vacuum extraction and soil washing; (3) pilot and full-scale  
25 demonstration tests; and (4) preparation of site-investigation/corrective-action guidance  
26 manuals. A variety of research projects will be required to expand the arsenal of  
27 site-assessment/decision tools and cleanup technologies for gasoline-contaminated sites and to  
28 extend this arsenal to other conventional fuels, such as diesel, aviation, and stationary-source  
29 combustion fuels. Research is required to interpret such issues as the mobility of the  
30 contaminants at a site, site conditions that limit in-place cleanup, site conditions that suggest



the site is stable and not worsening, and data that show cleanup progress. In-depth studies of certain site characteristics, transport and transformation processes, and subsurface conditions, as well as of specific corrective action technologies at both bench and pilot scales and at actual sites of leaking USTs are necessary to achieve these goals.

#### **2.2.4.2 Mobile Sources**

A significant proportion of the fleet VMT is from vehicles as old as 20 years. Emissions control systems deteriorate over time, and emission rates increase. Most urban areas with excessive O<sub>3</sub> and/or CO pollution problems administer Inspection and Maintenance (I&M) programs to identify inoperative control systems requiring repair. As discussed in Section 2.2.1.1.2, however, a 1988 survey (U.S. Environmental Protection Agency, 1989f) of vehicle tampering suggested that I&M programs reduced tampering and misfueling by only about 30%. As indicated by several roadway studies of motor vehicle emissions, significant numbers of motor vehicles on U.S. roadways emit greater emissions than estimated by available models (MOBILE 4 and ARB EMFAC), especially hydrocarbons and CO (Pierson et al., 1990).

Available data suggest a need for improved procedures for identifying and repairing motor vehicles with unacceptable emissions. Enhanced I&M programs that provide a more comprehensive and accurate evaluation of the performance of emission control systems, on-board diagnostic systems that furnish the owner/operator with continuous information on the performance of the vehicle's emission control systems, and remote monitoring of emissions from vehicles on roadways are being considered for improved, more effective identification of vehicles requiring repair.

Care should also be taken to assure that the composition of emissions does not change with mileage accumulation and/or control system deterioration, presenting yet unidentified hazards from "unregulated" toxic compounds.

#### **2.2.4.3 Fuel Transport Sources**

Pollutants arising from the production and use of conventional fuels have the potential to impact aquatic ecosystems through water discharge of pollutants and accidental

1 spills/leaks, although large bodies of water can also be impacted by air deposition of  
2 particles, nitrogen, and acids. Control technology development for fuel tankers, barges, and  
3 storage tanks to reduce and contain accidental spills and leakage will reduce the entry of  
4 conventional fuels into aquatic ecosystems. Insofar as spills pose adverse risks, then cleanup  
5 technologies must be improved through research and development.

## 6 7 8 **2.3 RESEARCH NEEDS**

9 In this section, broad research objectives for each key element of risk assessment are  
10 described and priorities are assigned. The priorities across all fuels were considered with the  
11 understanding that future knowledge, technology changes, and market factors are likely to  
12 have some impact on them. One major difficulty in developing a prioritization scheme is  
13 accounting for scientific pacing. For example, in many cases, knowledge of dose response is  
14 a higher priority than knowledge of hazard identification, but hazard-identification research  
15 must proceed first to guide the dose-response work. Due to the extent of the uncertainties  
16 about fuels, the approach chosen for prioritization would, in this example, rank hazard-  
17 identification research higher than dose-response research. Each research objective is coded  
18 with one of the following prioritization phrases.

- 19
- 20 • Priority 1 for the next 2 to 4 years. This is the highest priority research  
21 over the near term. The research generally entails resolution of major  
22 issues of known concern, identification of new issues likely to be critical to  
23 risk assessment/risk reduction, crucial methods development that paces  
24 much other work, and major mandates of the CAAAs. Characterizing this  
25 work as a priority over the next "2 to 4 years" does not necessarily denote  
26 that it can be accomplished in that time frame.
  - 27
  - 28 • Priority 2 for the next 2 to 4 years. This is medium priority research over  
29 the near term. Work in this category generally entails pursuing key issues  
30 that have importance for either the exposure or effects portion of hazard  
31 identification or for evaluating key elements of risk reduction. Gaining  
32 such information will certainly be important, but is less crucial than work  
33 under Priority 1. Characterizing this work as a priority over the next  
34 "2 to 4 years" does not necessarily denote that it can be accomplished in  
35 that time frame.

- Priority 3 for the next 2 to 4 years. Although this research is of lower priority relative to other categories, it is still important to development of comprehensive baseline information for all fuels. Characterizing this work as a priority over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.
- Longer term priority. This research is essential to developing comprehensive, quantitative risk assessments and/or risk reduction approaches. However, its initiation is paced by the completion of earlier research. When major elements of the earlier research are completed, it will be possible to more definitively prioritize this category of work.

## **2.3.1 Exposure Assessment**

### **2.3.1.1 Source Characterization**

#### ***2.3.1.1.1 Stationary Source Characterization***

Although conventional petroleum-based fuels have a relatively long history of use, much remains to be learned about their emissions and discharges. Additionally, although regulatory requirements (NSPS and NPDES) have reduced emissions, VOC emissions and O<sub>3</sub>-nonattainment problems have steadily increased. Without accurate data on emissions and discharges from the recovery of crude oils and from the refining, storage, transportation, distribution, and use of conventional fuels, a factual data base will not be available to determine quantitatively the existing levels and types of emissions and discharges, to project future levels, and to provide an adequate basis for alternative fuels comparisons. Gasoline formulations will vary by type of crude as well as by season and region. The increasing use of imported crudes to offset decreased domestic production will decrease the emission and discharge levels from feedstock recovery; however, the transportation and storage problems will increase, especially in relation to spills and accidental releases. Assessment of effects from types and quantities of emissions and discharges projected for the future will be required.

#### **Research Objectives:**

1. Characterization of the quality of petroleum crudes (domestic and foreign) and of the types and levels of emissions and discharges resulting from the recovery of

crudes as well as from the production, distribution, and utilization of conventional fuels. (Priority 1 for the next 2 to 4 years.)

2. Effects of the penetration by alternative fuels on the refinery configurations and of the changes in VOCs and other stationary source multimedia emissions/discharges resulting from these changes. (Priority 2 for the next 2 to 4 years.)
3. Assessment of the potential for spills and accidental releases that may need prevention-oriented risk-reduction work, especially for releases from USTs. (Priority 1 for the next 2 to 4 years.)

#### **2.3.1.1.2 Mobile Source Characterization**

Although a great amount of knowledge about emissions from motor vehicles using conventional fuels is already available, additional research should explore the characteristics of emissions from vehicles under the operating conditions prevailing when air quality problems most frequently occur (e.g., low-temperature winter conditions and high-temperature summer conditions). Motor vehicle emissions are determined by Federal Certification, using a rather narrow "window" of operating conditions that indicate an average speed of about 20 mph, average temperature of about 70 °F, and diurnal temperature ramp of 60 to 84 °F, and most laboratory studies reported in the literature have been based on certification procedures. The literature is essentially void of compositional information for motor vehicle "running-loss" evaporative emissions. Laboratory simulations suitable for examination of running-loss emissions are currently being developed.

Conventional fuel motor vehicle technology continues to change with time. Both vehicle designs and fuel compositions are changing. The CAAAs mandate further change, as both more stringent emission regulations and fuel reformulation requirements are being promulgated. Assessment of the impact of these changes on air quality and risk to public health and welfare will require a comprehensive understanding of the characteristics of motor vehicle emissions. Three general categories of variables must be considered:

1. Vehicle-fuel technology: light-duty and heavy-duty cars, trucks, and buses; and marketed gasoline and distillate diesel fuels.
2. Operating conditions: varied average vehicle speed and engine load, varied ambient temperature, varied age (control system deterioration), and varied altitude.
3. Emission sources: tailpipe emissions, evaporative emissions (e.g., diurnal, hot soak, and running-loss), and refueling.

Assessment of the potential impact of these vehicles and fuels on O<sub>3</sub> air quality will require determination of organic emission rates and detailed species composition (hydrocarbons, aldehydes, organic acids, etc.), as well as of CO and NO<sub>x</sub> emission rates. Detailed organic compound compositions will also be needed to assess the impact of these vehicles and fuels on air concentrations of and exposure to toxics such as benzene, formaldehyde, and 1,3-butadiene. Data representative of both the motor vehicle microenvironments (parking garages, congested freeways, urban street canyons, etc.) dominating human exposure to primary emissions and the overall urban use are needed to estimate the impact on O<sub>3</sub>, CO, NO<sub>2</sub>, and particulate air quality and to assess exposure to atmospheric transformation products of the emissions. The emission rates of compounds important to climate change, such as CO<sub>2</sub>, methane, N<sub>2</sub>O, and other radiatively significant species, also need to be examined. Contrasts with alternative fuels (methanol, ethanol, CNG, etc.) will be required for all scenarios identified. Both laboratory and roadway studies should be used to develop the necessary data, assuring that the advantages of both are realized.

#### Research Objective:

1. Characterize emissions from motor vehicles designed for conventional fuels as a function of speed, ambient temperature, and mileage accumulation. Emission

levels and speciations suitable for estimating impacts on O<sub>3</sub>, NO<sub>2</sub>, CO, and particulate air quality, as well as on other factors such as global climate change and toxic compound exposure, will be provided. (Priority 1 for the next 2 to 4 years.)

### **2.3.1.2 Environmental Fate**

#### **2.3.1.2.1 Air Fate**

Gasoline vapors and exhaust gases from automobiles are extremely complex, consisting of several hundred organic compounds. These compounds, when exposed to sunlight in the atmosphere (or artificial sunlight in smog chambers), produce high levels of O<sub>3</sub> and the usual smog manifestations (reduced visibility, formaldehyde, PAN, etc.); however, their chemistry is not well understood. When dilute mixtures of auto exhaust and evaporative emissions are irradiated in smog chambers, the irradiated gases are also found to be more mutagenic than the nonirradiated reactants. The gaseous components are also more biologically active (with *Salmonella typhimurium*) than the aerosols. Further work is necessary to test the complex relationships among the VOCs, NO<sub>x</sub>, and O<sub>3</sub>. Additional work is needed to identify the compounds responsible for the high mutagenicity observed with irradiated auto exhaust.

#### **Research Objectives:**

1. Develop a mechanism that can predict all the smog manifestations produced from irradiated auto exhaust. (Priority 1 for the next 2 to 4 years.)
2. Report on the compounds responsible for the high mutagenicity observed with the irradiated exhaust gases. (Priority 1 for the next 2 to 4 years.)
3. Report on air quality predicted using airshed models showing comparisons between conventional- and alternative-fueled vehicles. (Priority 2 for the next 2 to 4 years.)

### 2.3.1.2.2 *Soil and Groundwater Fate*

Conventional fuels are complex mixtures of chemicals that migrate through the subsurface via gaseous, aqueous, and organic phases. Describing this migration requires knowledge of both partitioning dynamics and the processes controlling the transport in each of these phases. Although much is known about phase partitioning, much remains to be learned concerning the influence of media properties on the kinetics of this process. The organic-liquid phase is often very slightly miscible with water, and it is important to realize that small concentrations of the various components of the organic liquid partition into the air and water phases, even when the organic-liquid has been immobilized by capillary trapping. In effect, the organic-liquid phase of the conventional fuels acts as a continuing source of dissolved and/or vaporized organic pollutants and must be removed in order to clean up a contaminated aquifer.

The migration and capillary trapping of organic liquids from conventional fuels is dependent upon the number of fluid phases present, the physical forces exerted on the fluids, the surface chemistry, and the soil structure and heterogeneity. Understanding how these factors contribute to the migration and trapping of organic liquid pollutants is essential to understanding their behavior in the subsurface, and may in turn lead to development of improved aquifer cleanup strategies.

Current conceptual and mathematical models of the transport and fate of complex mixtures in soil and groundwater environments have not been adequately tested. Such testing is needed to help identify important research questions and to assess the utility of these models for simulating actual contaminant behavior.

#### Research Objectives:

1. Assessment of fuel and subsurface media properties which control the migration and fate of conventional fuels. (Priority 1 for the next 2 to 4 years.)
2. Evaluation of multiphase contaminant transport models. (Priority 2 for the next 2 to 4 years.)

### 2.3.1.2.3 *Surface Water Fate*

## 2.3.1.3 **Exposures**

### 2.3.1.3.1 *Human Exposures*

The impact of emissions from conventional fuels must be firmly established to provide a basis for documenting the impact of any future fuel change. Baseline measurements of exposures that result from conventional fuels are, therefore, suggested as a first requirement. In FY90, EPA will begin a modest effort to look more closely at conventional fuel emission exposures that result while driving (in-transit exposures) and the emission impact on concentrations in selected microenvironments (e.g., public and private parking garages). The selection of microenvironments was based on earlier studies, especially those of CO exposure, which reported that in-transit exposures and concentrations within garages were likely to be of greatest concern. In future years, the focus should be on obtaining a data base for the pollutants primarily emitted and for O<sub>3</sub> (a transformation byproduct of automotive emissions) and should include the following.

- (1) Measurement studies of the contribution of emissions from conventional-fueled vehicles in various exposure scenarios, at both sea-level and high-elevation locations, including in-transit exposures, exposures from service-station repair facilities, and other appropriate exposure situations. These studies should address the impact on air quality of both regulated and unregulated pollutants; the impact on transformation byproducts; and the impact on exposure, emphasizing first measurements of the compounds of interest in microenvironments thought to be most affected (i.e., personal and public garages and indoor rooms adjacent to garages or affected through direct input from air-handling systems). Later studies, if deemed necessary, would measure total human exposure by monitoring each of the routes of exposure (if possible) and validating the total exposure with applicable biomarkers of exposure (if possible). The resulting exposure distributions will become the baseline to be contrasted with those obtained from studies of alternative-fueled vehicles.



- (2) Obtaining accurate, representative activity-pattern data related to automotive-generated exposures through the Research to Improve Health Risk Assessments (RIHRA) program (Sexton and Reiter, 1989), a major effort to acquire a national time/activity-pattern data base was initiated in FY89. This effort should be patterned after the study conducted by the California Air Resources Board (CARB) in 1987 to 1988 (Robinson et al., 1989). Results from this study would provide (a) accurate information on the percentage of the population that engages in a particular activity (e.g., commuting) or spends time in selected microenvironments (e.g., parking garages), and (b) input to mathematical models used to calculate exposure profiles.
- (3) Validating the modified NEM to the extent possible through appropriate measurements and developing new models. Several prototype models currently exist that require validation and incorporation of accurate compound-specific/source-specific impacts and more accurate activity data.
- (4) Obtaining better measurements of exposures through other pathways (e.g., accidental swallowing, food/beverage, and dermal).

#### Research Objectives:

1. Exposure assessment of the identified pollutants that are primarily, if not specifically, related to use of conventional fuels, emphasizing but not limited to O<sub>3</sub>. (Priority 1 for the next 2 to 4 years.)
2. Development and application of validated human-exposure models to predict changes in exposure resulting from a choice of mobile-source fuels. (Priority 1 for the next 2 to 4 years.)

### 2.3.1.3.2 *Biota Exposures*

***Terrestrial Exposures.*** Conventional-fuel pollutants have the potential to impact terrestrial biota through atmospheric exposure. Biotic effects will depend on the pattern of exposure (e.g., rate, duration, season, and concentration), pollutant toxicity, and species sensitivity. Research should focus initially on questions regarding the pollutant deposition, exposure, and toxicity. Wet (e.g., fog) and dry (e.g., gas phase) deposition should be evaluated for importance in delivering the pollutants to vegetation. Research initially should be targeted on the South Coast Air Basin, CA and compared with the potential exposure of alternative-fuel pollutants. Environmental exposure models such as those developed as part of NAPAP and the SMCM could be used to evaluate pollutant exposure to urban, agricultural, and natural ecosystems within the South Coast Air Basin. A wind-rose model could simulate the transport of the pollutants into the surrounding areas and be combined with a Geographic Information System (GIS) framework to estimate agricultural, forest, and chaparral land area exposed to various pollutant concentrations.

#### Research Objective:

1. Exposure assessment of conventional-fuel pollutants to terrestrial ecosystems within the South Coast Air Basin, CA. (Priority 1 for the next 2 to 4 years.)

***Aquatic Exposures.*** To assess the comparative risk of different fuels, effects of fuels must be contrasted under well-defined and reasonable exposure scenarios. Both specific test cases and hypothetical generic cases should be based on reviews of past spills. The extent of the spill and the morphometry and flow of the receiving water must first be defined for reasonably typical cases. The types of organisms at risk and their microhabitats within the system of interest need to be specified, and the physical, chemical, and biological factors affecting exposure, bioavailability, and toxic response need to be characterized. The fate models discussed above can be used to compute the exposure time series expected for each organism, allowing the effects-assessment methodology discussed below to be applied to these test cases.

## Research Objective:

1. Develop example cases for fuel spills and leakages to freshwater and estuarine ecosystems, which include characterizations of system morphometry, organism types and locations, and physical/chemical properties that regulate fate and effects. Source scenarios and fate/transport models could be applied to these test cases to develop exposure time series for target organisms. (Priority 1 for the next 2 to 4 years.)

**2.3.1.4 Analytical Methodology**

Analytical methods must be developed, upgraded, and/or evaluated for measurement of source emissions, atmospheric transport and transformation, and population (human and ecosystem) exposure as necessary to support assessment of the impact of varied fuel formulations on risk to public health and welfare. Procedures suitable for certification of regulated source emissions (THC, NMHC, CO, NO<sub>x</sub>, and particles) at levels mandated by the CAAAs and for the detailed speciation necessary to support estimations of the impact on O<sub>3</sub> and toxics air quality will be required. The procedures must permit accurate and precise determination of large numbers of compounds in very complex mixtures.

Monitoring pollutants in ambient air usually requires techniques for concentrating samples. This is especially true for monitoring low concentrations of VOCs. Gas chromatography samples need to be concentrated with the use of cryogenic traps using either liquid argon or liquid oxygen. Normal GC analyses of ambient air in urban centers show many unidentified peaks, often consisting of 20 to 40% of the carbon. Greater effort is needed in the identification of these compounds; a coupling of GC/MS with infrared spectroscopy might help with the identification.

## Research Objectives:

1. Develop/upgrade/qualify analytical procedures for measuring criteria pollutant, RITG, and toxic motor vehicle emissions (e.g., 1,3-butadiene, benzene, and formaldehyde). (Priority 1 for the next 2 to 4 years.)

- 1                   • Validate classical procedures for measuring organic carbon, CO, NO<sub>x</sub>, and  
2                   CO<sub>2</sub> emissions from conventionally fueled motor vehicles at certification  
3                   emission rates (concentrations) permitted by the CAAAs; identify problems,  
4                   provide corrective actions, and/or develop new, more simplistic, lower cost  
5                   acceptable procedures.  
6  
7                   • Conduct "round robin" quality assurance evaluation of the performance of  
8                   detailed hydrocarbon chromatography for the interested user community.  
9  
10                  • Develop procedures for continuous or "real-time" measurement of selected  
11                  toxics in transient motor vehicle emissions.  
12  
13                  2.    Improve GC/MS techniques to identify compounds present in the ambient  
14                  atmosphere. (Priority 2 for the next 2 to 4 years.)  
15  
16                  3.    Develop/upgrade/evaluate ambient and microenvironmental monitoring for  
17                  measurements of toxic motor vehicle emissions (e.g., 1,3-butadiene, benzene,  
18                  and formaldehyde). (Priority 2 for the next 2 to 4 years.)  
19  
20                  4.    Develop procedures for continuous measurement of selected toxics for use in  
21                  microenvironments and in-transit monitoring. (Priority 3 for next 2 to 4 years.)  
22

## 23   **2.3.2 Effects Assessment**

### 24   **2.3.2.1 Human Health Effects**

25           In the context of EPA's alternative fuels research strategy, the primary goal of  
26   conventional fuels research is to provide a scientific basis for conducting a comparative  
27   health risk assessment of alternative fuels. The health risks of conventional fuels need to be  
28   assessed quantitatively, as a base case, so that changes resulting from the introduction of  
29   alternative fuels can be evaluated. Although the health effects of gasoline evaporative  
30   emissions and gasoline and diesel combustion emissions have been studied, the scientific data  
31   base for health assessment of these conventional fuels needs to be improved substantially in  
32   some areas. The EPA's ORD currently is assessing health risks, including cancer, from  
33   diesel emissions. This assessment will identify important data gaps and research needs for  
34   incorporation into this research strategy document at a later date (U.S. Environmental

1 Protection Agency, 1990e). The International Agency for Research on Cancer (IARC), in a  
2 recent review of the health effects of engine exhaust, identified the most urgent research  
3 needs for conventional fuels as more extensive inhalation toxicology and carcinogenicity  
4 studies of the combustion emissions from gasoline engines (IARC, 1989).

5 The research priorities identified here are based on a review of the current literature, in  
6 addition to the reviews of diesel fuel by EPA and of gasoline exhaust by IARC. The highest  
7 priorities for conventional fuels are as follows:

- 8 • chronic animal bioassays of unleaded gasoline exhaust and its  
9 transformation products (for both cancer and noncancer effects);
- 10  
11 • further evaluation of certain dosimetric and mechanistic issues for key  
12 components (i.e., benzene, 1,3-butadiene, and polycyclic organic matter of  
13 uncombusted and combusted gasoline) specifically identified in Title II of  
14 the CAAA of 1990 (provisions relating to mobile sources); and
- 15  
16 • further evaluation of certain dosimetric and mechanistic issues for diesel  
17 exhaust.

18  
19 The rationale for these priorities is identified below. Uncombusted gasoline and diesel fuel  
20 also are briefly discussed, although no priority research needs are identified, pending  
21 additional evaluation of currently available information.

#### 22 23 **2.3.2.1.2 Combusted Gasoline**

24 In contrast to the alternative fuels, a high, near-term priority is placed on a chronic  
25 bioassay for unleaded gasoline exhaust and transformation products for the following reasons:  
26 exposure to gasoline exhaust is the most common exposure associated with conventional  
27 fuels; unleaded gasoline exhaust has not been tested in a chronic bioassay; some data already  
28 exist to enable development of an adequate study design; and there is a clear need to develop  
29 an adequate base case for all future comparisons of gasoline exhaust to alternative fuels  
30 exhaust. The bioassays of unleaded gasoline exhaust should be comparable in design to  
31 existing diesel exhaust studies. In terms of the high priority placed on atmospheric  
32 transformation products, EPA studies in progress have shown that transformation of gaseous  
33 emissions from gasoline vehicles substantially increases the genotoxicity and potentially the

1 carcinogenicity of these gaseous emissions. The inhalation carcinogenicity of the whole  
2 atmospheric transformation mixture, however, has never been evaluated.

3 Because of the expense and complexity of chronic inhalation animal bioassays for  
4 unleaded gasoline exhaust and for unleaded gasoline exhaust transformation products,  
5 considerable thought and preliminary evaluation of various study designs should occur.  
6 Screening vehicle classes and operating conditions, using in vitro assays and shorter-term  
7 in vivo assays, would be a major part of such a preliminary evaluation. Because of the  
8 major contribution to air pollution made by older vehicles, these so-called "superemitters"  
9 should be included in this evaluation. Evaluation of atmospheric transformation products  
10 should be conducted concurrently, using UV irradiation of the whole combustion mixture in  
11 order to simulate atmospheric conditions that produce transformation. As part of the chronic  
12 bioassays, evaluation of dosimetry is necessary to interpret results, to facilitate comparison of  
13 the results to similar results from other fuels, and to extrapolate the results to humans. Also,  
14 pending the outcome of the bioassays, mechanistic studies are likely to be needed to fully  
15 interpret the findings.

16 While cancer is the primary focus of the proposed chronic bioassays, noncancer  
17 endpoints also need to be evaluated in the same studies. Past experiences with fuels and  
18 their combustion products suggests that there is a potential for respiratory system effects to  
19 occur, including effects on the pulmonary immune system. Use of additional "satellite"  
20 animal groups for specialized evaluations of respiratory system effects (e.g., pulmonary  
21 function, lung morphology host-resistance models) should be considered. Any observed  
22 respiratory system effects will need to be evaluated in terms of the known health effects of the  
23 NAAQS pollutants, as compared to the effects of the whole mixture(s).

#### 24 25 ***2.3.2.1.3 Uncombusted Gasoline***

26 In terms of the carcinogenic potential of gasoline vapors, the current research strategy  
27 proposes that no additional health research be conducted on uncombusted gasoline vapors  
28 until after recent data have been reviewed and incorporated into a risk assessment.

29 In particular, an epidemiological study of gasoline vapor exposures has recently been  
30 completed by the American Petroleum Institute and considerable mechanistic information on

the relevance of the animal bioassay data to human carcinogenesis has been developed by the Chemical Industry Institute of Toxicology and others. Based on the findings of this proposed review, additional research needs can be developed and incorporated into the current research strategy document, if warranted.

#### ***2.3.2.1.4 Key Components of Uncombusted and Combusted Gasoline***

While the highest research priority for conventional fuels is placed on evaluation of the unleaded gasoline exhaust and its transformation products, additional high priority research is needed to assess key components of uncombusted and combusted gasoline specifically identified in the CAAA (e.g., benzene, 1,3-butadiene, and polycyclic organic matter [POM]). Formaldehyde is also of interest, but is discussed in the methanol chapter (Section 3.3.2.1). Increasing controls that reduce evaporative fuel losses and reformulation of gasoline are decreasing the exposures to benzene, and as a consequence are decreasing potential risks. Despite these projected decreases in exposures and risk, in a comprehensive evaluation of fuels several issues remain of interest for benzene, as well as 1,3-butadiene and POM.

For benzene, 1,3-butadiene, and POM, the primary research needs are to determine: (1) cross-species differences in dosimetry and metabolism, consequent differences in dose to target tissues, and resulting implications for human risk; (2) relationships between exposure duration, concentration, and response; and (3) mechanisms of action for carcinogenesis and resulting implications for human risk. For POM, additional research is also necessary to identify important POM components associated with conventional fuels and their combustion and transformation products, and to study these components in terms of their contribution to carcinogenic potency. This effort should employ the type of screening effort noted above (Section 2.3.2.1.2 Combusted Gasoline), using bioassay-directed fractionation to focus on POMs of interest. In the longer term, further development and validation of human biomarkers of exposure to POM should prove useful in evaluating the relevance of experimental data to environmentally exposed humans.

Additional research also is need to clarify an important noncancer effect observed in test animals. That is, 1,3-butadiene-induced gonadal atrophy has been observed in both male and female rodents at low inhaled concentrations (6 ppm for males). Subsequent to the

1 initial reports of both testicular and ovarian atrophy, relatively little additional work has been  
2 done on this topic. The implications of the observed effects for development and  
3 reproduction need to be evaluated. This effort should be tied to the appropriate  
4 pharmacokinetic and mechanistic studies necessary to interpret the findings in terms of public  
5 health risks.

#### 6 7 8 **2.3.2.1.5 Combusted Diesel Fuel**

9 Research on diesel exhaust is currently focused on using rodent inhalation studies to  
10 examine dosimetry and mechanisms of cancer induction for diesel exhaust. Some studies  
11 comparing diesel exhaust, carbon black, and titanium dioxide have been completed and  
12 others are underway. This type of research elucidates the relative roles of particulate  
13 concentrations, particle surface area, and adsorbed genotoxic organics in the induction of  
14 cancer, and is likely to impact the selection of appropriate models (and/or the development of  
15 new models) for dose-response assessment and low-dose extrapolation.

16 In addition, biomarkers have been developed to detect DNA adducts in rodents and  
17 humans exposed to diesel exhaust. Research is needed (1) to validate these biomarkers,  
18 (2) to determine the human dosimetry of diesel exhaust, and (3) to facilitate extrapolation of  
19 animal data to predicted human exposures. This type of biomarkers research, like that  
20 discussed for POM, also will be important to the risk assessment of gasoline and alternative  
21 fuels.

#### 22 23 **2.3.2.1.6 Uncombusted Diesel Fuel**

24 Little assessment of uncombusted diesel fuel has been performed. Based on more  
25 limited exposure potential (because of the more limited use of diesel fuel and its lower vapor  
26 pressure relative to gasoline), research on the uncombusted fuel is a low priority. The  
27 potential carcinogenicity of diesel fuel, relative to other fuels under consideration, could be  
28 assessed based on mutagenicity and an evaluation of the known carcinogens present.  
29 Additional uncombusted diesel fuel research is not proposed at this time pending this type of  
30 evaluation of mutagenicity and carcinogenicity.



**2.3.2.1.7 Summary**

In summary, to construct a realistic comparative risk assessment for fuels, EPA will need to have a better health data base for the conventional fuels. Basic scientific information that is necessary for risk assessment has been noted above in the context of data needs for specific chemicals or mixtures. All of these evaluations are made more difficult because of the poorly understood toxicology of complex mixtures, which constitute actual environmental exposures.

**2.3.2.1.8 Research Objectives:**

1. Conduct chronic inhalation bioassays to evaluate cancer and noncancer effects/potency of: (1) unleaded gasoline combustion emissions from a range of gasoline-powered vehicles, including those classified as "superemitters", and (2) atmospheric transformation products of unleaded gasoline. Various shorter-term studies (i.e., in vivo mutagenicity assays) should be conducted prior to the chronic inhalation bioassays to facilitate design of the chronic studies and comparisons of the newly collected data to existing data. (Priority 1 for the next 2 to 4 years.)
2. Expand the data base for benzene, 1,3-butadiene, and POM in the following areas: (1) cross-species differences in metabolism and consequent differences in dose to target tissues, (2) relationships between exposure durations, concentrations, and responses, (3) mechanisms of action in experimental models and implications for human susceptibility to chemically-induced cancer, and (4) for 1,3-butadiene only, relevance of gonadal atrophy observed in both sexes in rodents to potential reproductive and developmental effects in humans. Subsequently, biologically-based dose-response models utilizing this information should be developed. These efforts will involve integration of in vitro and in vivo data from both animals and humans. (Priority 1 for the next 2 to 4 years.)

3. Continue the exploration of the dosimetry and mechanisms of diesel exhaust carcinogenesis. (Priority 1 for the next 2 to 4 years.)
4. Validate the use of human biomarkers of exposure and dose, especially for diesel exhaust. Perform human exposure and dosimetry studies on exhaust emissions. Determine the utility of this approach for subsequent use in assessing alternative fuel combustion emissions. (Priority 2 for the next 2 to 4 years.)

#### **2.3.2.2 Ecosystems Effects**

The main goal of the conventional-fuels research is to provide data to complete comparative ecological risk assessments with alternative fuels. Providing guidance to policy makers as fuel switching occurs is also important. This section briefly describes the terrestrial and aquatic (freshwater and marine) research needed to complete the assessments. The research is progressive in nature, with one research project providing information and leading to the next. Preliminary assessments will identify conventional-fuel pollutants of concern and ecosystem components and biota at risk. If information in the literature is weak, research projects are proposed to strengthen the data base. Also, proposed research projects will be ranked according to scientific prioritization and the need for comparisons with alternative fuels.

##### ***2.3.2.2.1 Terrestrial Ecosystem Effects***

Conventional-fuel pollutants produced from evaporative emissions and fuel combustion have the potential to impact terrestrial ecosystems through atmospheric gaseous and wet/fog exposures. The existing literature should be used to assess the hazards posed to terrestrial biota and ecosystems; however, several research projects are proposed and may be carried out, if needed, to provide a data base to complete comparisons with alternative fuels. One research area to be emphasized is plant exposures to O<sub>3</sub> and air toxics due to changes in mobile emissions associated with alternative fuels. Exposure-response experiments should expose plants to conventional-fuel pollutants individually and in binary combinations with O<sub>3</sub>.

Initially, two trees and two crops should be treated to various exposure regimens in plant chambers to develop exposure-response relationships for plant process functions such as photosynthesis, yield, growth, and seed production.

Research should then progress to sophisticated mesocosm studies. First, experiments are needed to evaluate pollutant partitioning within the soil-plant-air continuum and effects on an array of biota. Then, to evaluate the interactions of possible global climate change and pollutant effects, pollutant partitioning and plant effects should be studied in response to altering temperature and water stress. Last, plants should be exposed to the complete combustion products of conventional fuels (gasoline and diesel) after irradiation, to allow an evaluation of the effects of the pollutant/transformation products on plant growth and development.

The final study proposed is a field project in which biomarkers (e.g., abnormal enzyme activity) and other ecological endpoints should be used to monitor the effects of pollutants on vegetation within urban, agricultural, and natural ecosystems. Research should be conducted only to provide information currently not in the literature.

#### Research Objectives:

1. Evaluate the responses of plants to O<sub>3</sub> exposures at various concentrations and in binary combinations with conventional-fuel pollutants to assess the sensitivity of plant process functions. (Priority 1 for the next 2 to 4 years.)
2. Evaluate the effects of conventional-fuel pollutants within plant mesocosms with altered temperature and water stress. (Priority 3 for the next 2 to 4 years.)
3. Evaluate the effects of conventional-fuel tailpipe-emission/transformation products on plant growth and development at various exposure scenarios. (Longer term priority.)

4. Evaluate the use of biomarkers to monitor the effects of conventional-fuel pollutants on vegetation. (Longer term priority.)

#### **2.3.2.2.2 Aquatic Ecosystem Effects**

**Fresh Water Effects.** As explained in Section 2.2, adequate prediction of the toxicity of different fuels and fuel fractions is needed to make reasonable statements about risks due to fuel spills and leakages. Toxicity tests on diesel fuel and, especially, gasoline are currently inadequate for assessing toxicity from exposures in the water column. A major research goal is, therefore, to improve toxicity test methods for conventional fuels and to conduct further testing to increase knowledge of fuel toxicity.

Gasoline toxicity tests using both gasoline emulsions and various dissolved fractions need to be conducted on selected freshwater organisms. The fractionation and the nature of the test material must be specified in cooperation with projects on exposure assessment of spills, so the toxicity results can be appropriately applied to situations in which the composition of the fuel released to the environment is changing. Study of the kinetics of toxicity will enable prediction of responses to transient exposure; analyses based on the time course of effects or the accumulation of toxicants (Mancini, 1983; Van Hoogen and Opperhuizen, 1988) will be used. The correlation of toxicity with chemical properties of gasoline constituents may be a possible means to characterize fuel toxicity based on its chemical composition. As justified by preliminary exposure assessment and hazard identification, additional effects data should be gathered on mixtures representative of urban waters contaminated by fuels and fuel transformation products via multiple pathways (i.e., spills, leakage, effluents, deposition, and runoff).

Laboratory tests should also be conducted on benthic organisms using fuel-contaminated sediments; due to the longer duration of sediment contamination, these tests should place more emphasis on chronic toxicity. Tests with laboratory microcosms are needed to address effects of fuels on a variety of planktonic species and on community-level endpoints, and to evaluate the importance of interactions between organisms in regulating response to fuels.

Even with toxicity to individual organisms and microcosms characterized, the question of how real systems respond to fuel spills will still remain. In order to test exposure and

1 effects assessment methods and to evaluate system level effects that may not be addressed by  
2 laboratory testing, an experimental set of aquatic ecosystems (enclosed littoral zones of a  
3 natural pond or whole artificial experimental ponds) need to be subjected to simulated spills  
4 of gasoline of various amounts, and immediate and delayed direct toxic effects, indirect  
5 effects on organisms, and recovery need to be documented in these systems.

6  
7 Research Objectives:

- 8
- 9 1. Evaluate the toxic effects of gasoline and its fractions on selected freshwater  
10 aquatic organisms and develop dose-response models suitable for application to  
11 fuel-spill and discharge exposure assessments. (Priority 1 for the next  
12 2 to 4 years.)
  - 13  
14 2. Test the effects of a simulated gasoline spill on an experimental freshwater  
15 aquatic ecosystem to evaluate assessment techniques and empirical determination  
16 of system effects. (Priority 1 for the next 2 to 4 years.)
- 17

18 ***Marine Effects.*** Many years and considerable sums of money have been spent studying  
19 the effects of petroleum on marine systems. Most of this work has focused on fuel oils and  
20 crude oil. Less research has been conducted on gasolines.

21 Although a considerable amount is known about the toxicity of petroleum compounds to  
22 various marine organisms, a full understanding of the impact of these fuels on marine  
23 ecosystems is lacking. Fuel releases to the marine environment occur as large volume  
24 catastrophic spills and as chronic discharges; therefore, both acute and chronic toxicity  
25 experiments should be conducted. Because most of the work done to date has involved acute  
26 toxicity studies, chronic effects research is most needed. Mesocosm experiments would  
27 enable a better understanding of the community-level effects of these mixtures and the  
28 resiliency of marine ecosystems to petroleum insult. This would require testing a variety of  
29 community types using integrative system measurements, such as oxygen consumption and  
30 nutrient fluxes, to assess the state and health of these systems. Also, due to the likely

transient nature of the exposures, kinetic-based toxicity models need to be developed to provide better predictions of the effects of fuels on marine systems.

#### Research Objectives:

1. Develop information on the toxicity of various conventional fuels (especially gasolines) to selected marine organisms. (Priority 1 for the next 2 to 4 years.)
2. Determine the effects of conventional fuels on the structure and function of marine mesocosm communities via mesocosm or controlled field spills. (Priority 1 for the next 2 to 4 years.)

### **2.3.3 Global Warming**

The research described on source characterization, environmental fate in ambient air, and risk reduction/control technology will result in identification of changes in RITGs due to the manufacture and combustion of conventional fuels. It is not repeated here.

#### Research Objective:

1. Identify and characterize RITGs affected by conventional fuel production and use. This information will be used as input to global climate models being developed and applied under the global climate research program. (Priority 1 for the next 2 to 4 years.)

### **2.3.4 Risk Prevention/Mitigation**

#### **2.3.4.1 Stationary Sources**

The effectiveness of existing prevention and control technologies and practices for stationary sources of VOCs must be assessed. Based on this evaluation, development of designs and operational information is necessary to optimize existing stationary-source controls, especially for gasoline storage, distribution, and marketing. Guidance is needed to

1 develop new or improved control systems, designs, and operating procedures to minimize  
2 emissions/discharges from the recovery of feedstocks as well as from production,  
3 transportation, distribution, and use of conventional fuels. Carbon-based controls are  
4 especially important for hydrocarbon recovery. Federal regulations regarding storage and  
5 handling of fuels and chemicals have been promulgated; however, research is still needed to  
6 optimize methodologies, equipment, standards, and guidance, both for release detection and  
7 monitoring and for site investigation and assessment where leaks are suspected.

8       Underground storage tank remediation activities have increased markedly since  
9 implementation of the September 1988 EPA technical regulations for leak detection and  
10 cleanup. State-reported data indicate that tens of thousands of costly UST site investigations  
11 and cleanups are currently underway and that this number will sharply increase in the next  
12 2 to 4 years as new sites are identified. New and improved technologies have potential for  
13 reducing the time and total cost of remediation at these sites without sacrificing quality;  
14 however, these technologies are seen as risky investments, and states require more oversight  
15 and approval for their application. Increased research is required to raise the confidence  
16 level associated with using these technologies and to enable cheaper, quicker, and higher  
17 quality cleanups. Five major UST research areas to be addressed are:

- 18  
19       1.     Improved site assessment—to make cost-effective, on-site determinations of  
20               conditions would contribute to more timely and appropriate actions at sites;  
21
- 22       2.     Expedited design and installation of remediation hardware—remediations could  
23               begin more rapidly if general design criteria were available for referral when  
24               overseeing remediations;  
25
- 26       3.     Decreased cleanup time through improved contaminant removal—previous  
27               research indicates that contaminants can be more efficiently removed at a lower  
28               total cost than conventional techniques; a greater number of improved technology  
29               options is required;  
30

4. Cheaper treatment alternatives for UST remediation-site waste streams—improved techniques are required to ensure that remediations that improve groundwater quality do not sacrifice air quality or do not bankrupt the UST owner or state budget;
5. Confirming site cleanup—research is required to better determine when a remediation should be terminated and what the continued threat to groundwater may be from contamination remaining at closed sites.

In addition to these five areas, leak detection research will be conducted for both small USTs (<1,000 gal) and large USTs (60,000 gal and more) and for USTs containing other conventional fuels such as diesel, aviation, and stationary-source combustion fuels.

#### Research Objectives:

1. Development of control technology design and operational information to optimize existing stationary-source controls, especially for emissions for conventional fuel storage, distribution, and marketing. (Priority 1 for the next 2 to 4 years.)
2. Development of guidance on new or improved control systems, design methods, and operating procedures, to minimize stationary source emissions and discharges. (Priority 1 for the next 2 to 4 years.)
3. Cooperative development (i.e., with industry) of new or improved control systems to maximize emission/discharge reduction from the production, storage, transportation, and marketing of conventional fuels. (Priority 1 for the next 2 to 4 years.)



4. Reduction of the occurrence and severity of releases by development of user-oriented accidental release reference manuals/guidelines for the prevention of accidental releases of conventional fuels from storage, production, transportation, and marketing. (Priority 2 for the next 2 to 4 years.)
5. Development of new commercial products to enable real-time determination of UST site conditions in preparation for site remediation. Research should proceed from concept development to field testing of the new measurement techniques. Prototype measurement methods and devices need to be developed. (Priority 1 for the next 2 to 4 years.)
6. Development of new commercial products and engineering processes to achieve complete site remediation more quickly by improving contaminant removal both in situ and aboveground. Research should proceed from concept development to field testing of products and processes; prototype designs and methods need to be developed. (Priority 1 for the next 2 to 4 years.)
7. Development of criteria and testing protocols for detecting leaks in small USTs (<1,000 gal) and in very large USTs (60,000 gal and more) containing gasoline as well as other conventional fuels. (Priority 1 for the next 2 to 4 years.)
8. Development of new commercial products for more rapid design and installation of UST remediation hardware. Immediate research should focus on (a) vacuum enhanced free product recovery, (b) design of recovery trenches, (c) hydraulic containment of dissolved contamination, (d) soil washing, (e) low-temperature thermal desorption, and (f) enhanced bioremediation techniques. (Priority 2 for the next 2 to 4 years.)
9. Development of cost-effective new commercial products and methods to confirm the progress and completion of UST remediations. Research should proceed

from concept development to field testing of monitoring techniques; prototype methods need to be developed. (Priority 2 for the next 2 to 4 years.)

10. Development of new, cost-effective commercial products and engineering processes to carry out UST remediations that do not simply transfer the contaminants from one media to another. Research should focus on the development of new technologies for treating hydrocarbon vapors and aqueous waste streams generated by UST remediation. Research should proceed from concept development to field testing; prototype designs and methods need to be developed. (Priority 3 for the next 2 to 4 years.)

#### **2.3.4.2 Mobile Sources**

The performance of motor vehicle emissions control systems needs to be monitored as a function of consumer mileage accumulation. Attention should be directed to the impact of CAAA programs that are designed to improve the long-term performance of "in use" vehicle emissions control systems (e.g., enhanced I&M, on-board diagnostics, and remote-sensing systems for identification of malfunctioning vehicles). The focus of this effort should be O<sub>3</sub>-precursor emissions and CO.

##### **Research Objective:**

1. Assess the effectiveness of motor vehicle emissions control as a function of consumer mileage accumulation. (Priority 1 for the next 2 to 4 years.)

#### **2.3.4.3 Fuel Transport Sources**

Significant efforts have been made to reduce the potential for major oil spills and to improve clean-ups when prevention fails. However, continued analysis of the efficacy of prevention methods is needed as is further investigation of the best approaches to clean-up of spills.

Research Objective:

1. Assess mitigation options to reduce the impact of conventional-fuel spills on sensitive aquatic systems. (Priority 2 for the next 2 to 4 years.)

## 3.0 METHANOL

### 3.1 RISK ASSESSMENT RESEARCH FRAMEWORK

Of the potential alternatives for replacing petroleum distillate fuels in the United States, methanol has received the greatest attention, due primarily to reduced engine emissions, current economics, and projected near-term production capacities. To assess the potential impacts of transition to methanol fuel, an understanding of emissions, atmospheric chemistry, target population exposures, health/ecosystem effects, and possibilities for risk reduction/control is required. Though methane is projected to be the primary near-term feedstock for methanol manufacture and is an important global warming gas, the impact of increased methanol production on methane emissions has not been well quantified. The following discussions address these issues and identify future research needs.

Methanol has been frequently discussed as an alternative to conventional petroleum fuels in this country, and steps have already been taken in California and elsewhere to introduce methanol fuels for motor vehicles. Neat methanol (M100 or 100% methanol) as well as mixtures of methanol and gasoline (e.g., M85, or 85% methanol, 15% gasoline) fall under the heading of methanol fuels. In the near term, flexible-fuel vehicles, designed for mixtures of unleaded gasoline and M85, will be in use. In the future, dedicated vehicles designed for M100 will also likely come into use. Although methanol is a well-known chemical, its use as a fuel raises many questions for which answers may be unavailable or only partly available.

During recent years, the U.S. motor vehicle and petroleum industries have given significant attention to methanol as an alternative to conventional gasoline and diesel fuels. For example, the Air Pollution Research Advisory Committee of the Coordinating Research Council (sponsoring members are the American Petroleum Institute and the Motor Vehicle Manufacturers Association) has recommended that methanol research receive the highest priority ranking for all new projects in the 1990 to 1992 period (Coordinating Research Council, 1989; American Petroleum Institute, 1988; Society of Automotive Engineers, 1988).

1        This chapter first highlights some key points of information and research issues about  
2        methanol fuels in the format of a risk assessment. This Risk Assessment Research  
3        Framework section takes the Introduction to Risk Assessment Framework for Fuels  
4        (Section 1.4) as its point of departure, focusing on only those facets of the generic  
5        framework that are specific to methanol fuels. The risk assessment framework section is  
6        followed by a more extensive discussion of background and rationale (Section 3.2), which is  
7        intended to provide guidance and support for key research needs, rather than serve as a  
8        complete review of the literature. A discussion of research needed to provide the foundation  
9        for a quantitative risk assessment of these fuels follows (Section 3.3).

### 11        **3.1.1 Exposure Assessment**

#### 12        **3.1.1.1 Source Characterization**

##### 13        ***3.1.1.1.1 Emissions from Feedstock and Fuel Production, Storage, and Distribution***

14        ***Feedstocks.*** The foremost near-term feedstock option for production of methanol is  
15        natural gas, emissions of which are important to global climate impacts. Natural gas  
16        extraction/recovery emissions and discharges have been identified in a limited manner but  
17        need to be quantified for each step of the process, from the drilling of the well and well  
18        production to the gathering of the raw gas at nearby field processing points for removal of  
19        hydrogen sulfide, other contaminants, and natural gas liquids. The emissions of concern are  
20        radiatively important trace gases (RITGs), especially methane and carbon dioxide (CO<sub>2</sub>), and  
21        hydrogen sulfide (H<sub>2</sub>S) from venting operations, sulfur dioxide (SO<sub>2</sub>) and RITGs from  
22        flaring, methane loss during the gathering, and RITGs and some volatile organic compounds  
23        (VOCs) from recovery of the liquids. The fate of extraordinarily large quantities of CO<sub>2</sub>  
24        present in the extracted methane before processing needs to be determined.

25        The extent of changes in natural gas production must be estimated as a function of  
26        growth in methanol use. If natural gas production were to be greatly expanded, other  
27        environmental impacts associated with exploration, extraction, and pipeline systems would  
28        need to be assessed. Such impacts would include disturbances of wildlife habitats, soil  
29        resources, and land surfaces.

1       **Production.** Production technologies for generation of methanol would differ widely if  
2 feedstock material other than methane were used, and, thus, would differ in the types and  
3 degrees of their potential hazards. Aside from methanol itself, methane releases are likely to  
4 be the primary concern from natural gas-based methanol production. Other RITG emissions  
5 would be related to the energy requirements of the particular production technology. Waste  
6 catalyst disposal would also be a major concern.

7       Facilities for producing methanol may generate effluents that can enter lakes, rivers, or  
8 estuaries. These releases would be regulated under existing programs (e.g., NPDES) such  
9 that the risk to ecosystems should be acceptably low, but the level and cost of treatment  
10 needed to satisfy these regulations have not been determined and, therefore, need to be  
11 researched. The existing concern about the capability of current controls to control  
12 effectively emissions of conventional fuels is further compounded by the introduction of  
13 methanol into the fuel systems. The impact of methanol on existing transportation,  
14 distribution, and storage system controls, where its use could affect control system  
15 effectiveness and result in increased emissions, needs to be evaluated.

16  
17       **Storage and Distribution.** Leakages and spills, especially large accidental releases, of  
18 methanol fuels from distribution and storage systems to terrestrial and aquatic ecosystems  
19 could pose a significant hazard to fresh water, soil, ground water, and marine systems. The  
20 probability and extent of such releases from pipelines, tankers, storage tanks, and other  
21 systems may possibly be estimated from past experience with other fuels. In head spaces of  
22 storage vessels, methanol equilibrium concentration is within its flammability limits; if  
23 ignited, it could rupture the vessel and result in major releases and fires. A catastrophic  
24 release hazard assessment is needed to identify specific areas of concern that may need  
25 prevention-oriented risk reduction work. This is especially true in the distribution and  
26 handling facilities, where industrial prevention and control approaches are not widely  
27 practiced and technical expertise is the weakest. The greater corrosivity of methanol fuels  
28 compared to gasoline and diesel fuels implies potentially greater risk of leakage, particularly  
29 from underground storage tanks (USTs). The compatibility of fabrication materials and the  
30 internal corrosion and reactive potential with methanol must be compared to the data

1 available on conventional fuels and must be examined in comparison to both current and  
2 future designs of UST systems (tanks and piping). Research must also identify the threat  
3 posed by fuel leaks and spills to ecosystems and approaches for mitigating such occurrences.

#### 5 **3.1.1.1.2 Emissions Related to Fuel Use**

6 **Stationary Source Emissions.** Though emissions of hydrocarbons, carbon monoxide  
7 (CO), CO<sub>2</sub>, and oxides of nitrogen (NO<sub>x</sub>) resulting from combustion of methanol in boilers,  
8 internal combustion engines, and turbine engines appear to be relatively low, this must be  
9 confirmed. Source characterization profiles for aldehyde emissions for certain sources  
10 utilizing methanol where exposure will be important (e.g., stationary internal combustion  
11 [IC] engines and other nonhighway vehicles) are not known and need to be evaluated.

12  
13 **Mobile Source Emissions.** Several motor vehicle categories are being developed for  
14 methanol fuel, and each is distinguished by engine design, fuel specification, and emissions  
15 characteristics. Spark-ignition Otto-cycle engines (used primarily in passenger cars and light-  
16 duty trucks) are being designed for M100, M85, and flexible fuels (any mixture of methanol  
17 and gasoline). Compression-ignition diesel engines (used primarily in heavy-duty trucks and  
18 buses) are also being designed for methanol with an ignition improver. Research should be  
19 directed to the category of motor vehicle most responsible for the air quality problem of  
20 concern (e.g., light-duty passenger cars and trucks for ozone [O<sub>3</sub>] and CO air quality and all  
21 categories of vehicles for particulate and nitrogen dioxide [NO<sub>2</sub>] air quality).

22 Flexible-fuel motor vehicle emission rates and compositions vary significantly with the  
23 percentage of methanol in the fuel. Volatility varies with the percentage of methanol, and  
24 the relative contribution of exhaust and evaporative emission sources varies with fuel  
25 volatility (along with ambient temperature, vehicle average speed, etc.). With methanol fuel,  
26 O<sub>3</sub> benefit can potentially be derived from both reduction in the rate of organic emissions and  
27 changes in the composition of the emissions to mixtures of lower photochemical reactivity.  
28 The EPA currently estimates that tailpipe organic carbon-emission rates (g/mi) from M100  
29 vehicles will be similar to those from advanced gasoline vehicles; however, evaporative  
30 (diurnal, hot soak, running-loss) and refueling emission rates (g/mi) from M100 vehicles will

1 be less than 20% of those from advanced gasoline vehicles (using 9 psi Reid Vapor Pressure  
2 [RVP] gasoline). Total organic carbon emission rates from M100 vehicles are projected to  
3 be about 30% of those from advanced gasoline vehicles. The organic carbon from M100  
4 vehicles is estimated to be about 16% nonmethane hydrocarbon (NMHC), 81% methanol,  
5 and 3% formaldehyde; from advanced gasoline vehicles, it is about 99% NMHC and 1%  
6 formaldehyde.

7 The impact of methanol fuel on emissions of CO and NO<sub>x</sub> depends on engine design.  
8 Methanol engines designed for operation at near-stoichiometric air:fuel ratios yield reductions  
9 in NO<sub>x</sub>, but provide little improvement in CO emissions relative to gasoline; those designed  
10 for fuel-lean combustion reduce CO emissions, but provide little improvement in NO<sub>x</sub>  
11 emissions relative to gasoline (with closed-loop three-way catalyst control technology).

12 Most efforts to speciate organics from methanol-fuel vehicles have been directed toward  
13 providing data for O<sub>3</sub> impact analysis; however, toxic emissions could also be substantially  
14 impacted. Preliminary data indicate that the emission rates of toxics such as benzene and  
15 1,3-butadiene are reduced relative to gasoline by using methanol fuels. Given that engine-out  
16 formaldehyde emissions are elevated by methanol fuel, control of these emissions is  
17 important to environmental impact. The durability of formaldehyde emission control over  
18 mileage-accumulation ranges typical of U.S. fleets (on the order of 100,000 miles) is largely  
19 unknown, especially if the catalyst formulations and calibrations (cold start light-off) used are  
20 different from conventional gasoline technology. Little is known about the emission rates of  
21 other potentially important compounds such as methyl nitrite and formic acid.

22 Heavy-duty methanol-fuel engines generally produce lower particulate and NO<sub>x</sub>  
23 emissions than comparable diesel-fuel engines; however, emissions of methanol,  
24 formaldehyde, and CO from methanol-fuel engines are elevated and will require an oxidation  
25 catalyst for control. Again, emission rates of unregulated compounds such as methyl nitrite  
26 and formic acid need to be evaluated for heavy-duty methanol engines.

27 Tailpipe CO<sub>2</sub> emissions from advanced technology methanol-fuel motor vehicles are  
28 expected to be somewhat lower than from conventional gasoline and diesel vehicles  
29 (estimated at about 80% of conventional vehicles emissions), but the overall CO<sub>2</sub> burden will  
30 depend strongly on the feedstock and production of the fuel.



1 Almost all of this information was developed using laboratory simulations of motor  
2 vehicles operating under conditions defined by EPA for emissions certification (i.e.,  
3 19.6 mph average speed, 70 °F average temperature, 60 to 84 °F diurnal ramp). Experience  
4 with gasoline vehicles suggests significant sensitivity of emission rates and composition to  
5 operating variables. Knowledge of methanol vehicle emissions must be expanded to include  
6 conditions associated with air quality problems (e.g., high-temperature summer periods when  
7 O<sub>3</sub> violations are more common and low-temperature winter periods when CO violations are  
8 more common).

### 10 **3.1.1.2 Environmental Fate**

#### 11 **3.1.1.2.1 Air Fate**

12 An important consideration for introduction of methanol fuels is impact on O<sub>3</sub>. Less  
13 O<sub>3</sub> production would be expected from fuels and associated emissions that have lower  
14 photochemical reactivity than conventional gasoline and diesel fuels. In a complex way,  
15 photochemical reactivity depends on variables such as initial and boundary conditions  
16 (VOC/NO<sub>x</sub> ratio, precursor concentrations, etc.), meteorological conditions, emission rates,  
17 and photochemical mechanisms. Data suggest that the O<sub>3</sub> benefit of methanol fuel is less at  
18 high VOC/NO<sub>x</sub> ratios than at low ratios, and because of relatively high formaldehyde  
19 reactivity, it depends significantly on control of elevated engine-out formaldehyde emissions.  
20 Efforts to provide a better understanding of the variation of urban and rural VOC/NO<sub>x</sub> ratios  
21 must be undertaken. The potential impact of methanol fuels on O<sub>3</sub> would also depend upon  
22 the significance of motor vehicle emissions to local precursor inventories (which vary from  
23 city to city). Recent studies predict modest O<sub>3</sub> reductions in most cities, assuming  
24 "equivalent carbon" emission rates (i.e., the organic composition is varied, but the carbon-  
25 emission rate does not change). If the carbon-emission rates for methanol-fuel vehicles were  
26 reduced relative to vehicles using conventional fuels, O<sub>3</sub> reduction would be greater.  
27 Preliminary estimates suggest reduced carbon-emission rates with optimized M85 and M100  
28 vehicles (e.g., 70% reductions are projected with M100 fuels primarily from evaporative  
29 emissions). Experience with fleet vehicles will be necessary to validate these estimates.

1 Most of the emphasis of modeling studies has been on peak O<sub>3</sub> concentrations;  
2 however, emphasis should also be placed on the impact of methanol substitution on integrated  
3 average O<sub>3</sub> concentrations. Further, the accuracy of available models for predicting multiday  
4 episodal O<sub>3</sub> is largely unknown, because smog chamber data cannot be used to validate  
5 models (wall effects become very important with multiday irradiations). Multiday episodes  
6 may not show significant improvements on O<sub>3</sub> formation in all areas. The automotive  
7 contributions to O<sub>3</sub> precursors vary from city to city; the VOC/NO<sub>x</sub> ratio varies similarly.  
8 As the VOC/NO<sub>x</sub> ratio increases, changes in VOC reactivity have less influence on  
9 O<sub>3</sub> production.

10 Methanol is removed from the troposphere largely through its reaction with hydroxyl  
11 (OH) radicals and through wet deposition. The atmospheric lifetime, if removed by reaction  
12 with OH radicals, is about 17 days. Because methanol is fully water soluble, it should be  
13 readily removed from the atmosphere by aqueous aerosols, resulting in an atmospheric  
14 lifetime much shorter than 17 days and probably closer to 5 days.

15 The primary product of the reaction of methanol with OH radicals is formaldehyde.  
16 Formaldehyde and formic acid may also be produced by the reaction of dissolved methanol  
17 in aerosols, because sunlight acting on aqueous aerosols produces oxidants such as OH,  
18 O<sub>2</sub> (<sup>1</sup>Δg), and XO<sub>2</sub> radicals. Dimethyl and monomethyl sulfate (DMS and MMS,  
19 respectively) have been observed downwind of power plants, presumably as products of the  
20 reaction of organics with SO<sub>2</sub> on aerosols. A recent study has shown that DMS is not  
21 produced in the gas phase when methanol and SO<sub>2</sub> co-exist; however, this study did not  
22 investigate possible heterogenous reactions on aerosol surfaces. If methanol emissions  
23 increase, perhaps more organic sulfates such as DMS and MMS will be produced.  
24 Peroxyacetyl nitrate production is expected to decrease with the use of methanol.

25 Although formaldehyde motor vehicle emissions are expected to increase with methanol  
26 fuels, especially during cold-start operation, formaldehyde from secondary atmospheric  
27 processes may decrease with methanol fuels relative to gasoline fuels, depending upon  
28 precursor concentrations, reaction rates, and emission control devices. The net result could  
29 be lower ambient formaldehyde concentrations. Initial (morning) concentrations are more

1 important to daily peak O<sub>3</sub> levels, however, and the initial concentrations will be more  
2 sensitive to tailpipe emissions.

3 All possible reactants and products in the photooxidation of methanol-gasoline blends  
4 must be monitored to understand fully the impact of methanol substitution on risks to health  
5 and the environment. The chemistry of transformation products other than O<sub>3</sub> (e.g.,  
6 mutagenic chemicals) must be studied, and appropriate model improvements must be  
7 implemented.

#### 8 9 ***3.1.1.2.2 Soil and Groundwater Fate***

10 To determine whether methanol-contaminated ground water presents a potentially  
11 significant source of human and ecosystem exposure, the transport and fate of methanol in  
12 soil and ground water need to be understood. The rate of transport will depend upon the  
13 hydraulic properties of the soil and the changes in these properties resulting from the  
14 introduction of methanol. These changes are expected to be relatively small in most soils  
15 and aquifers, but they may be significant in soils containing substantial quantities of smectite  
16 minerals.

17 The extent to which groundwater quality may be impacted by methanol is strongly  
18 dependent upon the rate at which it is attenuated by microbial degradation. At low  
19 concentrations, methanol is known to readily biodegrade in soils; however, at high  
20 concentrations it may be toxic to microbial populations. An understanding of the dynamics  
21 of methanol transport, the relationship between methanol concentration and biodegradation,  
22 and the effect of methanol on the microbial ecology of the soil column is, therefore,  
23 important. To assess the impact of methanol fuels on groundwater quality, each of these  
24 issues requires additional research.

25 When the soil/groundwater matrix contains other organic contaminants, high  
26 concentrations of methanol could mobilize these compounds and result in increased potential  
27 for human or ecological exposure. For nonpolar (hydrophobic) chemicals, this solubilization  
28 or mobilization could be quantified under equilibrium conditions; however, the dynamics or  
29 kinetics of this process are dependent upon characteristics of the medium and are less well

1 understood. Similar considerations apply to surface freshwater and marine aqueous-sediment  
2 systems.

### 3 4 **3.1.1.2.3 Surface Water Fate**

5 Methanol spills in freshwater and near-coastal estuaries are likely to present significant  
6 hazards to aquatic life forms in both direct and indirect ways. Direct toxicity to exposed  
7 populations will be important if exposure levels to methanol are sufficiently high.  
8 Accordingly, the most important fate processes regarding direct toxicity are those that  
9 determine near-field concentration gradients. Because of methanol's properties, spills should  
10 readily mix with water and dissolve quickly; volatilization will be important, especially in the  
11 immediate area.

12 Perhaps the major impact of spills is the indirect effect of oxygen depletion that results  
13 from biodegradation of the methanol. In brief, methanol will degrade rapidly (unless  
14 microbial toxicity occurs) and deplete the dissolved oxygen. Simultaneously, reaeration will  
15 proceed to replenish the dissolved oxygen. The spatial extent and the duration of the  
16 dissolved-oxygen depletion will depend upon the reaeration rate, the microbial degradation  
17 rate, and the rate of methanol removal by volatilization. The influence of mixing and  
18 advective transport on the methanol concentration will also be important. The real extent of  
19 and degree of oxygen depletion will have a direct bearing on the severity of acute effects  
20 such as marine fish kills. The phenomena may occur in both marine and freshwater.

21 Priority research for the fate of methanol in fresh water and estuaries should therefore  
22 include investigation of the rate of biological degradation; toxic thresholds for such  
23 degradation; reaeration within spill areas; and the mixing, advection, and volatilization of the  
24 spilled compound. Finally, transformation products need to be identified and their fates need  
25 to be investigated for potential additional effects.

### 26 27 **3.1.1.3 Exposures**

#### 28 **3.1.1.3.1 Human Exposure Assessment**

29 Using computer models, the EPA Office of Mobile Sources has estimated methanol  
30 concentrations for various vehicle and traffic scenarios under both typical and severe

(unfavorable) operating conditions. Likely locations of increased concentrations include street canyons, roadway tunnels, expressways, and personal as well as public parking garages. Model predictions have indicated that maximum methanol exposures are expected in personal garages, with short-term peak exposures as high as  $650 \text{ mg/m}^3$  (approximately 500 ppm). In contrast, predicted maximum in-traffic concentrations of methanol are expected to be considerably lower (5 to  $6 \text{ mg/m}^3$  [4 ppm]). Formaldehyde concentrations as high as  $16.3 \text{ mg/m}^3$  (12 ppm) have also been estimated under certain conditions in personal garages. Although these model estimates are preliminary and involve many uncertainties and untested assumptions, the results highlight the importance of the personal garage as a microenvironment likely to be of great concern for pollutant exposures related to methanol fuel use. In addition, emissions occurring within a personal garage may contribute to indoor air-quality problems via door openings or air-exchange systems, but these aspects have not been modeled.

The exposure research must be coordinated with ongoing research. For example, the California Energy Commission has a research program underway that includes measuring levels of pollutants in a garage with methanol vehicles. Additional EPA research will be initiated, based on analyses of these efforts. Total methanol exposures need to be evaluated, including exposures within vehicles during normal operation and exposures during refueling and in service station repair facilities. The potential for exposure through noninhalation routes (e.g., accidental ingestion, contaminated food or water, and dermal absorption from spills) also must be assessed to evaluate research needs. Further, the contribution of endogenous methanol arising from certain dietary items needs to be considered.

Characterization of ambient  $\text{O}_3$  patterns and trends has been the responsibility of the EPA Office of Air Quality Planning and Standards. Their national and regional analyses are contained in annual reports, such as the National Air Quality and Emissions Trends Report (U.S. Environmental Protection Agency, 1990d). These reports indicate that occurrences above the standard 1-h level of 0.12 ppm are common, especially in some years during the summer months throughout the country, with maximums of approximately 0.2 ppm. Less is known about ambient levels of formaldehyde and methanol. Based on a research monitoring network located in five urban areas, 24-h formaldehyde levels were uniformly below

0.05 ppm. In contrast, indoor levels, especially in new mobile homes, have been observed to be a factor of 10 higher than the outdoor ambient levels. Ambient methanol levels are generally considered to be very low (i.e., 0.001 to 0.002 ppm).

After research on groundwater transport and fate provides more information on the potential for drinking water exposure, a preliminary exposure estimate is indicated. If exposures appear to be significant, then a full exposure assessment is warranted.

#### ***3.1.1.3.2 Biota Exposure Assessment***

The biota of terrestrial and aquatic ecosystems will potentially be exposed to pollutants derived from fugitive emissions during methanol fuel manufacture, transportation, storage, and vehicle refueling, and through fuel combustion. Air quality changes resulting from the production and use of methanol fuels may impact biota through exposures to methanol and formaldehyde. Airborne pollutant gaseous exposure and deposition represents the greatest potential threat to terrestrial ecosystems, whereas accidental spills/leakage would have the greatest impact on aquatic ecosystems. Such exposures could be acute or chronic, frequent or infrequent, high level or low level, and widespread or confined. Scenario modeling efforts (e.g., models from the National Acid Precipitation Assessment Program [NAPAP] and EPA's National Center for Intermedia Transport Research) will need to be applied to determine whether significant ecosystem exposures resulting from switching to methanol fuel are likely to occur or to pose any threat to biota.

The Spatial Multimedia Compartmental Model (SMCM) can be used to predict pollutant concentration and mass fraction in air, soil, water, and sediment through time. A geographic information system (GIS) framework can provide pollutant exposures to various terrestrial ecosystems. Exposure data can provide guidance to develop exposure-response studies for hazard identification of the pollutants at realistic ambient concentrations.

As explained in the generic fuel risk assessment in the introductory chapter, exposure assessments for aquatic ecosystems involve integration of efforts on source characterization and environmental fate with information on the populations of organisms at risk. The resulting exposure information will be used in effects assessments, as discussed below. For acute exposures from methanol fuel spills, this will involve (1) identifying example

1 ecosystems at risk, (2) computing an exposure time series appropriate to the habitat and  
2 behavior of the various organisms, and (3) obtaining other exposure/environmental  
3 information needed for kinetic-based effects models. For chronic exposures from more  
4 continuous releases and from atmospheric deposition (for which more rudimentary risk  
5 assessments initially will be done), ecosystems at risk will still need to be identified, but only  
6 average, general exposures will be needed to compare with effects concentrations from  
7 chronic toxicity assessment tests.

#### 9 **3.1.1.4 Analytical Methodology**

10 Analytical methodologies for measuring source emissions, for monitoring the ambient  
11 air transport and transformation of these emissions, and for monitoring the exposure of target  
12 populations (human and ecosystem) to the pollutants of interest, are prerequisites for  
13 determining the relative impacts of varied motor fuels on risk to public health and welfare.

14 Source emissions characterization requires accurate, precise analytical procedures for  
15 certification of regulated emissions (total hydrocarbons [THC], CO, NO<sub>x</sub>, CO<sub>2</sub>, and  
16 particles) and for comprehensive speciation of unregulated emissions. With methanol fuels,  
17 certification of organic emissions is more complex than simple determination of THC, as  
18 with conventional fuels. Measurements of methanol and formaldehyde, in addition to THC,  
19 are required. Regulations are based on the emission rate of total organic carbon (the sum of  
20 hydrocarbon, methanol, and formaldehyde). Current recommended practice requires  
21 chromatographic measurement of methanol and formaldehyde, along with classical THC  
22 flame-ionization detection (FID). The FID measurement is corrected for response to  
23 methanol (there is no response to formaldehyde) to obtain THC concentrations. As with  
24 conventional fuel vehicles, the CAAAs further require that methane emission rates be  
25 measured with methanol-fuel vehicles to permit determination of the NMHC emission rates  
26 by difference with THC. Improved, less costly, and less complicated procedures are needed  
27 for emissions certification. A number of compounds, in addition to those currently  
28 regulated, are of interest with methanol fuels. Formic acid, methyl nitrite, nitrous oxide  
29 (N<sub>2</sub>O), benzene, and 1,3-butadiene are examples. Detailed emissions speciation is necessary  
30 for comparison of the O<sub>3</sub> and toxics air quality impact of methanol fuels with conventional fuels.

1 Many of the same techniques employed for conventional fuels to monitor ambient  
2 transport and transformation will be applicable to methanol; however, special consideration is  
3 needed for the analyses of methyl alcohol by gas chromatography (GC), because this  
4 compound shows considerable tailing. Also, development of methodology for the analyses of  
5 dimethyl sulfate (DMS) may be necessary. Techniques used for DMS analyses have included  
6 capillary GC (using flame photometric detectors), GC-MS, ion chromatography, and Fourier  
7 transform infrared spectrometry (FTIR). One or more of the techniques should be tested to  
8 measure low ppb levels of DMS. Techniques for measuring formaldehyde are troubled by  
9 the simultaneous presence of O<sub>3</sub>.

10 Ambient air monitoring and microenvironmental monitoring will require methods  
11 development for the measurement of methanol and formaldehyde. In addition, personal  
12 monitors for these pollutants will be required if population exposure studies are undertaken in  
13 later years.

### 14 15 **3.1.2 Effects Assessment**

#### 16 **3.1.2.1 Human Health Effects**

17 As discussed under mobile source characterization, M85 is likely to have a far greater  
18 market penetration than M100; thus, the need to understand the toxicity of M85 is greater at  
19 present. Although the health effects of M85 will be some combination of the effects of  
20 M100 and gasoline, simple assumptions of additivity in proportion to the percentages of the  
21 mixture are unlikely to be valid. For example, both gasoline and methanol can influence  
22 metabolic processes and other aspects of pharmacokinetics, thereby resulting in potentiation  
23 of the effects of other chemicals. Also, the chemistry of the combustion mixture and  
24 atmospheric transformation mixtures of M100, M85, and gasoline will be different. Thus,  
25 although health effects information on M100 and gasoline will be very useful in guiding  
26 research decisions on M85, such research must be conducted on M85 itself because  
27 predictions based on gasoline and M100 individually would have unacceptable levels of  
28 uncertainty.

29 The discussion to follow centers on neat methanol (M100) and combustion mixtures of  
30 M85. Neat methanol is of immediate interest because it will be present in emissions of M85



1 and the available qualitative data indicate reasons for significant concern. Also, it is more  
2 cost-effective to wait until formulation of M85 is more stable before initiating health research  
3 on M85, whether as evaporative or combustion emissions. No substantial research on  
4 combustion emissions of M100 is proposed unless M100 is predicted to have significant  
5 market penetration. Use of methanol fuels will result in altered levels of other pollutants  
6 (e.g., O<sub>3</sub>, benzene, formaldehyde). Ozone and benzene are discussed under conventional  
7 fuels; formaldehyde is discussed here. There is also a question regarding the formation of  
8 DMS as a carcinogenic transformation product, but no health research on DMS is proposed  
9 until atmospheric chemistry studies and a preliminary risk assessment warrant such research.  
10

#### 11 ***3.1.2.1.1 Individual Pollutants—Methanol and Formaldehyde***

12 Methanol has been identified as a potential health hazard that requires further targeted  
13 dose-response and exposure assessment. The highest priorities for assessment are  
14 pharmacokinetics, developmental effects, reproductive deficiencies resulting from decreased  
15 gonadal function, and potential gradual loss of visual acuity associated with chronic  
16 exposure. Folate deficient individuals, who may represent a population at enhanced risk to  
17 methanol toxicity, are special concerns, especially since pregnant women have a relatively  
18 high level of folate deficiency.

19 The EPA has already begun confirming and extending research on the reproductive and  
20 developmental effects of methanol using acute and subchronic exposures. Various studies  
21 administered by the Health Effects Institute are devoted to neurobehavioral effects,  
22 pharmacokinetics, and developmental effects of methanol. General Motors is also  
23 investigating the health effects of methanol, especially in folate-deficient animal models.  
24 Future research will need to focus on dose-response assessment, key extrapolation issues  
25 such as high-to-low dose extrapolation, the effects of repetitive and chronic exposures, and  
26 the reversibility of observed effects.

27 Pharmacokinetic and dosimetric data for methanol (as well as formaldehyde) are  
28 important to the identification of the toxic agent and the location of toxic action. Such  
29 information is also necessary to improve the following extrapolations: animal-to-human,  
30 noninhalation-to-inhalation, high-to-low dose, and across various exposure durations.

1 Substantial information on this topic exists for formaldehyde; however, both experimental  
2 and modeling work is required for methanol that, in conjunction with tissue sensitivity data,  
3 will allow a more complete utilization of existing data and selection of the most metabolically  
4 appropriate test species for comparative risk assessment of fuels.

5 In addition to the direct effects of fuel and fuel-related mixtures, interactive toxicity  
6 should be considered. Data in the literature and from ongoing research at EPA indicate  
7 significantly increased toxicity of common solvents in animals exposed to high concentrations  
8 of methanol or ethanol. Dose-response investigations to determine the potential for  
9 interactive toxicity at environmentally relevant concentrations are needed. Elucidation of the  
10 mechanism(s) through which nonadditive toxicity is exerted will assist animal-to-human  
11 extrapolations.

#### 13 **3.1.2.1.2 Mixtures**

14 The evaporative, combustion, and transformation products of M85 are complex  
15 mixtures and, as a consequence, dictate a somewhat different approach relative to methanol  
16 itself (i.e., evaluation of mixtures). In contrast to the fuel vapors, respiratory, immunotoxic,  
17 and carcinogenic endpoints are currently the greatest concerns for combustion and  
18 atmospheric transformation products. Based on very limited information, the scenarios of  
19 greatest interest appear to be potential carcinogenic effects of ambient-air exposure and  
20 potential noncancer effects of microenvironmental exposure. Noncancer ambient-air effects  
21 can be evaluated through assessing the impacts of alterations in levels of O<sub>3</sub>, NO<sub>2</sub>, and CO  
22 discovered through research programs on exposure assessment. However, comparisons of  
23 cancer risks to those of conventional fuels will require research. Microenvironmental  
24 increases in formaldehyde and methanol, in mixture with other common combustion  
25 emissions, will require research evaluation. The approaches to assessing carcinogenic and  
26 noncarcinogenic risks for these mixtures are discussed below.

27 Identifying and assessing cancer risks posed by all the individual components of the  
28 mixtures would not be feasible; however, using a battery of in vitro and short-term in vivo  
29 assays, the carcinogenic potential of methanol combustion and transformation mixtures  
30 relative to the other fuel-related mixtures can be estimated. The need for in vivo chronic

1 cancer bioassays thus can be defined. Only those mixtures that appear to be more potent  
2 than conventional fuel-related mixtures should be assessed in this detail.

3 In general, the evaluation of possible noncancer effects associated with combustion and  
4 transformation mixtures must await further atmospheric chemistry and exposure evaluations  
5 of M85 formulations. Because of the difficulty in assessing noncancer effects of mixtures,  
6 exposure assessments to determine potential changes in known toxic components (e.g.,  
7 O<sub>3</sub>, NO<sub>2</sub>, CO, PAN, and formaldehyde) as well as the formation of new or less well studied  
8 compounds are crucial. Application of animal toxicology screening methods would provide  
9 guidance for the need of and design of more intense examinations. The initial focus would  
10 be on acute exposures to combustion emissions and evaporative emissions to estimate  
11 microenvironmental effects and subchronic exposures to combustion emissions transformed  
12 photochemically to estimate ambient-air effects. Major endpoints would include those for the  
13 respiratory, immune, reproductive, and nervous systems, as well as developmental effects.  
14 Due to the key components of these mixtures (e.g., methanol and formaldehyde in the acute  
15 studies and O<sub>3</sub>, NO<sub>2</sub>, methanol, and formaldehyde in the subchronic studies), it is quite  
16 likely that follow-up research would be needed to develop adequate hazard identification  
17 information, but such research cannot be defined without more information from screening-  
18 level studies. More advanced exposure-response studies may be indicated from the hazard  
19 identification.

20 Field studies could also be planned; possible targets of interest would be a city before  
21 and after fuel switching or cohorts with personal-garage exposures to gasoline, diesel, or  
22 alternative fuels. The full range of exposures (high-level short-duration to low-level chronic)  
23 and outcomes might be considered. This approach could be conducted in conjunction with  
24 epidemiologic studies (considering both cancer and noncancer effects). A careful evaluation  
25 of the design and power of the study as well as of laboratory data currently being collected  
26 will be necessary before a decision can be made about the feasibility of a field study.

### 3.1.2.2 Ecosystem Effects

#### 3.1.2.2.1 Terrestrial Ecosystem Effects

The biological and ecological effects of methanol fuel air pollutants (e.g., methanol and formaldehyde) have not been extensively studied, particularly in relation to likely ambient exposure levels or in binary combination with other pollutants such as O<sub>3</sub>. Laboratory investigations of a few plant species show that methanol, formaldehyde, and other air toxics (e.g., formic acid) associated with methanol fuels may inhibit root and leaf growth, seedling development, and/or seed germination. The effects of these chemicals on wildlife may vary from irritation of the eyes, mucous membranes, and respiratory tract to possible changes in behavioral patterns, depending upon concentration and exposure duration. Chronic, sublethal exposures, as will likely occur with vegetation, may decrease plant productivity, reduce reproduction potential, and alter the competitive advantage of sensitive species within the plant community.

Given the lack of information on vegetal effects of methanol-fuel pollutants, hazard identification research on plants is needed for assessment purposes. The need for wildlife research will be based upon the results of the animal research described previously. Exposure-deposition studies are required to document pollutant exposure patterns to plants. Exposure-response research is needed to identify the sensitivity of plant species to formaldehyde, methanol, and formic acid individually and in combination and also in combination with O<sub>3</sub>. Microcosm/mesocosm studies would be beneficial in identifying the environmental fate and biota effects of methanol fuel pollutants and the potential for bioaccumulation. A biomonitoring study would document the impact of methanol-fuel pollutants on crops and trees as the fuel gains importance in urban areas such as Los Angeles or New York.

#### 3.1.2.2.2 Aquatic Ecosystem Effects

On the basis of water concentrations, methanol is much less toxic than the mixture of components in gasoline and diesel fuel; however, methanol is more readily dissolved in aqueous solutions, and its toxicity is exerted more quickly compared to gasoline or diesel fuels. These factors make any comparative assessment dependent on the time course of the

1 spillage and on the fate of the fuel within the system of concern. Further, this indicates a  
2 need for additional evaluation of the effects of time-variable exposures of freshwater and  
3 marine organisms to methanol and methanol blends. Toxicity models that account for the  
4 toxicokinetics of methanol must be developed to allow predictions of the effects of variable  
5 environmental concentrations on aquatic organisms at risk. Releases of methanol to aquatic  
6 systems could have direct toxic effects on individual organisms or community functions.  
7 Unlike high concentrations, low concentrations may not directly kill organisms, but they  
8 could affect the reproductive process or specific, sensitive life stages of populations.

9 Aquatic systems could also be impacted by secondary effects of methanol releases,  
10 which could be related to the presence of methanol metabolites that are toxic to these  
11 organisms. In addition, the biodegradation of large amounts of methanol could cause organic  
12 enrichment of aquatic systems, which, depending upon the circulation conditions of the area,  
13 could lead to oxygen depletion with toxic consequences to a wide range of populations and  
14 communities over many trophic levels. Also, toxic compounds already present in aquatic  
15 sediments could be mobilized by methanol releases. Research on the fate of methanol in  
16 aquatic systems is needed to guide studies on such potential aquatic effects.

### 18 **3.1.3 Risk Prevention/Mitigation**

#### 19 **3.1.3.1 Stationary Sources**

20 Control technology assessment and research and development on controls need to  
21 include a definition of applicability of existing control systems, the best control technology,  
22 enhancement of the effectiveness of existing controls, and development of new innovative  
23 controls for maximum risk reduction in problem areas. After assessing the adequacy of  
24 existing prevention and control technologies and practices for stationary sources of emissions  
25 related to methanol fuel production and use, the following specific information/data  
26 deficiencies need to be addressed.

27 Guidance is needed to develop new or improved control systems, design methods, and  
28 operating procedures that would minimize emissions/discharges from the recovery of  
29 feedstocks as well as from production, transportation, distribution, and use of methanol.

1 Specifically, control options for aldehydes from sources using methanol where exposure may  
2 be important, including nonhighway use and stationary IC engines, require evaluation.

3 User-oriented accidental-release reference manuals/guidelines for prevention of  
4 accidental releases of methanol from storage, production, transportation, and marketing need  
5 to be developed. Specific consideration should be given to the corrosiveness and the vapor-  
6 space flammability potential of methanol.

7 The overall global hydrocarbon system relative to production of methanol from natural  
8 gas needs analysis. The best strategies for minimizing methane efficiency losses and leaks  
9 need to be identified. For example, should methane be converted to methanol outside of the  
10 United States and be shipped to the United States, or alternatively, should natural gas be  
11 shipped to the United States and be converted in U.S. refineries? An accelerated research  
12 effort on the use of waste CO<sub>2</sub> for methanol production, such as developing technology for a  
13 man-made carbon cycle to use waste CO<sub>2</sub> and solar energy to produce methanol should be  
14 conducted.

15 Because methanol fuels may be more corrosive than gasoline and diesel fuels, the  
16 increased potential for leaks from USTs must be recognized. Given the physical and  
17 chemical differences between these fuels, existing technologies for detecting leaks from USTs  
18 must be assessed to determine if modifications are required for application to methanol fuels.  
19 Guidance documents on site investigations (where leaks are suspected) are based on our  
20 understanding of the fate and transport of gasoline in the soil/groundwater environment.  
21 Guidance documents on soil cleanup and aquifer restoration are based primarily on the  
22 properties of, and experience with, gasoline. A switch to methanol, which has somewhat  
23 different properties, will require revisiting, revising, and expanding upon this work. Certain  
24 soil cleanup technologies that may have somewhat limited applicability to gasoline-  
25 contaminated soils may be applicable to methanol-contaminated soils. Leak prevention  
26 standards and protocols that may be suitable for gasoline and fuel oil may be quite unsuitable  
27 for methanol.

### 3.1.3.2 Mobile Sources

A better understanding of the durability of emission control systems in methanol-fuel vehicles and of the impact of control system deterioration on emissions composition is required, especially for in-use fleets. For example, clarification on whether the formaldehyde fraction of methanol vehicle exhaust will increase with catalyst deterioration is needed. If formaldehyde emission rates are observed to increase beyond acceptable levels, then new, more durable catalyst formulations will need to be developed.

### 3.1.3.3 Fuel Transport Sources

Control technology development for fuel tankers, barges, and pipe lines to reduce and contain accidental spills and leakage will reduce the entry of methanol fuels into aquatic ecosystems; however, accidents are inevitable. Insofar as spills pose a significant adverse risk, cleanup technologies must be improved through research.

## 3.2 BACKGROUND AND RATIONALE

### 3.2.1 Exposure Assessment

#### 3.2.1.1 Source Characterization

##### 3.2.1.1.1 Stationary Source Characterization

In 1991, 4.3 million tons of methanol were synthesized (Reisch, 1992). About 45% of methanol produced was used as solvents and in producing other chemicals (except formaldehyde), 40% was used in producing formaldehyde, and 14% was fuel-related (Anonymous, 1992). Although petroleum and coal feedstocks are used in some commercial production of methanol, the major feedstock, by far, is natural gas (methane). Unless the price of natural gas (relative to petroleum) increases significantly or availability is limited, methane is expected to be the primary feedstock material indefinitely (Faith et al., 1965; American Petroleum Institute, 1988). Tennessee-Eastman, however, recently stated that its coal gasification synthesis of methanol/acetic anhydride was more cost effective than petroleum-based synthesis (Anonymous, 1988). As suggested by this illustration, future

1 technological development is likely to influence the use of feedstocks, which will, in turn,  
2 affect emissions and subsequent potential impacts.

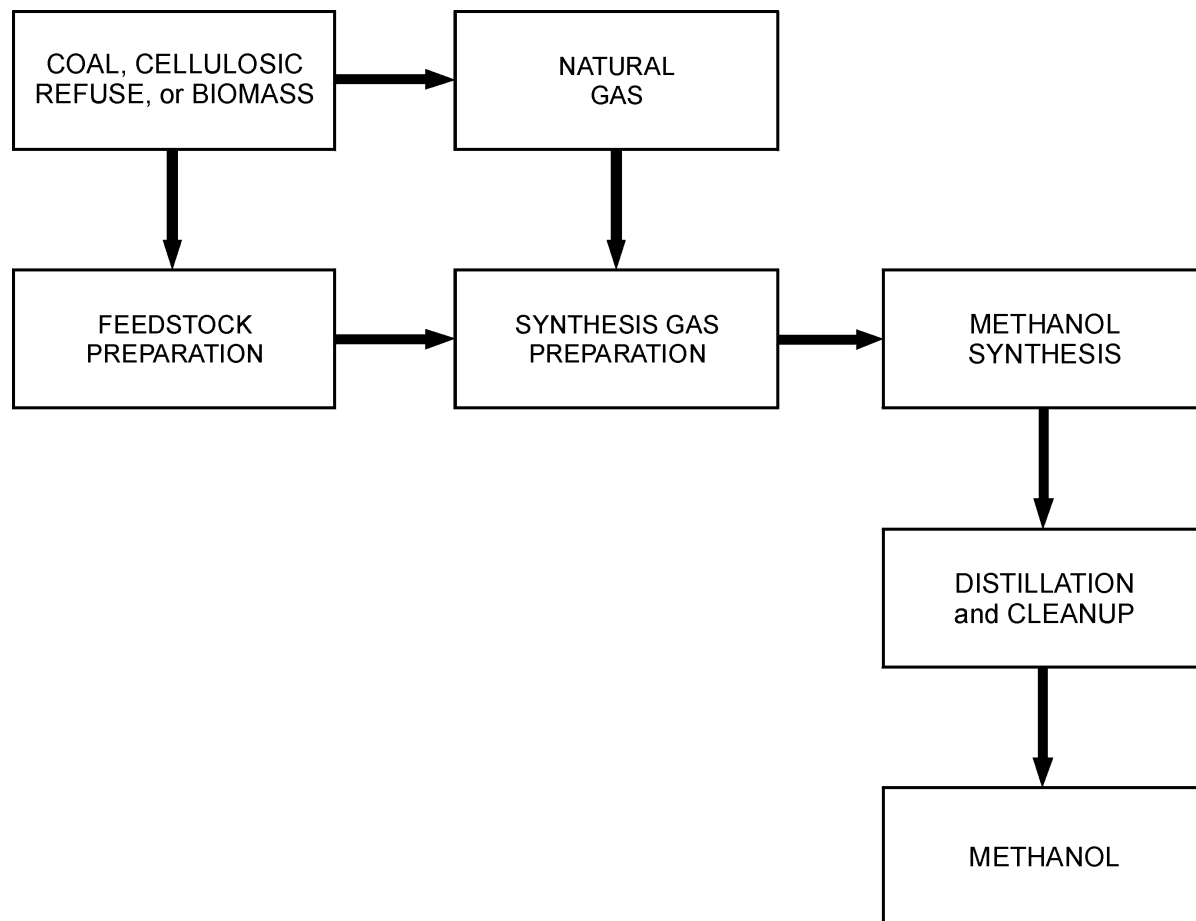
3  
4 **Processes.** Methanol is presently produced by catalytic reaction of a synthesis gas  
5 composed of CO and hydrogen. The synthesis gas can be made from natural gas, petroleum,  
6 coal, oil shale, or biomass feedstocks. Production processes are well defined, except for  
7 combined reforming and "fluid bed" emerging technologies.

8 Methanol is produced from methane by initially converting methane into CO and  
9 hydrogen, and then reacting these gases. Figure 3-1 illustrates the overall production process  
10 for synthesis of methanol (American Petroleum Institute, 1988). The gasification of coal  
11 with proper purification will produce a sulfur-free synthesis gas that can be used for  
12 synthesis of methanol or other products. Figure 3-2 provides a diagram of different  
13 processes and their products that could be produced utilizing a coal derived sulfur-free  
14 synthesis gas feedstock (U.S. Environmental Protection Agency, 1983b). If the required  
15 amount of hydrogen is insufficient, hydrogen is formed by the water-gas shift reaction  
16 (reaction of CO with water to form hydrogen and CO<sub>2</sub>). Petroleum feedstock could also be  
17 used to produce a synthesis gas; however, additional process steps may be required to crack  
18 the higher hydrocarbon molecules. For coal as a feedstock, the basic reaction of carbon  
19 (coal) with steam in a gasification process forms the synthesis gas.

20 The primary concerns are the sources and levels of emissions and discharges that will  
21 result from the storage, transfer, and distribution of natural gas (feedstock) and methanol,  
22 compared to gasoline. Although many of these discharges have been quantified, or  
23 qualitatively identified to various degrees, data to develop risk, health, or potential ecological  
24 impacts are not now available.

25  
26 **Cost of Production.** The cost of producing methanol from natural gas will depend  
27 upon cost of the natural gas, capital investment, and operations. The extent of future use of  
28 methanol in the United States and worldwide will be strongly influenced by cost of  
29 production. The following discussion is not exhaustive, but is provided to give some  
30 perspective on this important aspect. Table 3-1 shows the cost of producing methanol from



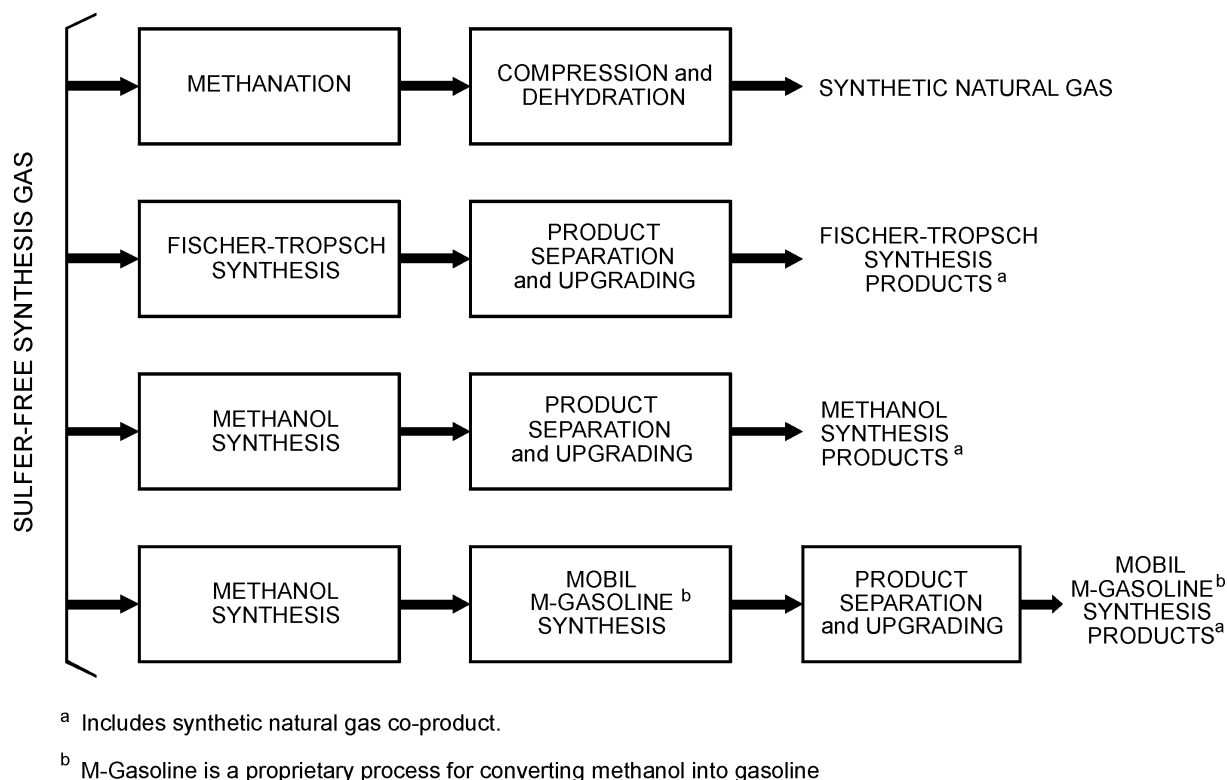


**Figure 3-1. Methanol production process—simplified diagram.**

Source: American Petroleum Institute (1988).

methane at foreign sites (U.S. Environmental Protection Agency, 1989a). The range from low to high would include plants in the United States. Table 3-2 presents costs for producing methanol from coal, with cost expressed as dollars per million BTUs (Brown et al., 1982). These are plant production costs and range from \$0.23 to \$0.51 per gallon. The numbers are engineering estimates and do not include all costs of transporting the fuel to market.

Presently, the well-head cost of natural gas is about \$1.71 per million BTUs and is forecasted to rise to around \$1.90 in 1990. The effects that gas price deregulation will have on the price, however, are unknown.



**Figure 3-2. Simplified flow diagram for conversion of synthesis gas to synthetic natural gas or liquid fuels.**

Source: U.S. Environmental Protection Agency (1983b).

**Emissions.** The emission of organics, other than alcohols, from methane-derived methanol would be extremely low. The release of methanol and any contaminant higher alcohols from vents and fugitive emissions would be the major concern. This concern is based on the toxicity of methanol and its significant solubility in water. Although synthesis of methanol from methane is an established technology, quantification of chemical types and magnitudes of emissions is needed at all steps (i.e., from gas production through the manufacture of methanol). Data are available, but they must be assembled and analyzed. Although methanol is presently transported by rail or truck, the large-scale use of methanol as a motor fuel would likely require pipeline movement and a widespread distribution/marketing system. Figure 3-3 shows a typical gasoline distribution system. The

**TABLE 3-1. COSTS OF FUEL METHANOL DELIVERED TO THE UNITED STATES (CENTS/GAL)**

|                       | Trinidad | Middle East | Australia | Canada | U.S. Gulf | Alaska |
|-----------------------|----------|-------------|-----------|--------|-----------|--------|
| Natural Gas           | 5-10     | 5-10        | 5-10      | 5-10   | 5-10      | 5-10   |
| Nongas Operating      | 5.9      | 7.1         | 9.1       | 5.4    | 5.6       | 9.4    |
| Capital Recovery Cost | 13.9     | 15.3        | 21.6      | 13.0   | 12.4      | 21.1   |
| Total Production Cost | 25-30    | 27-32       | 36-40     | 28-43+ | 33-53+    | 33-40  |
| Transport Cost        | 5.0      | 5.0         | 4.0       | 8.0    | 0.0       | 8.0    |
| Total Delivered       | 30-35    | 32-35       | 40-45     | 36-51+ | 33-53+    | 41-48  |

Source: U.S. Environmental Protection Agency (1989a).

incompatibility between methanol and materials presently used for fuel movement would necessitate the modification or replacement of existing systems. The information base on potential sources of methanol emissions and their potential severity is limited and requires further development. This undertaking would, in turn, identify areas in which data must be obtained to understand the impact of these emissions.

Organic emissions from coal-based methanol production would depend upon the type of coal conversion system utilized. Entrained-bed gasifiers, such as the Texaco type, produce very few organic substances. Fixed-bed gasifiers, such as the Lurgi used at Great Plains, produce significant quantities of organics, oils, and tars. Table 3-3 shows the diverse types of species that are produced (U.S. Environmental Protection Agency, 1983a). The types and quantities will vary, depending upon the coal used, the process configuration, and the process conditions. Long-range research must quantify these emissions. The fracturing of coal normally produces significant quantities of organics, especially aromatic compounds.

Primary sources of CO emissions will be the combustion of fuel for power and steam and the production of the synthesis gas and methanol. Because CO is a primary reactant, high efficiencies of operations would result in very low emissions. The production of

**TABLE 3-2. SUMMARY OF ECONOMIC RESULTS<sup>a</sup> OF METHANOL CO-PRODUCTION AND TEXACO-BASED GASIFICATION COMBINED CYCLE PLANTS**

|   | Conventional Texaco<br>GCC Power<br>Plant with<br>No Methanol<br>Production | High-Efficiency<br>Oxygen-Blown<br>Texaco GCC<br>(EPRI AP-1624) | Coal-Fired<br>Steam Plant<br>FGD-Subcritical<br>EXTC-79 | Texaco GCC<br>Plant with<br>Once-Through<br>Methanol<br>Co-production<br>2400/1000/1000 | Dedicated<br>Coal to<br>Methanol<br>(EPRI AP-1962)<br>B2 |
|---|---|---|---|---|--|
| CAPACITY FACTOR, %  | 70  | 70  | 70  | 90  | 90   |
| <u>PRODUCTION AT DESIGN CAPACITY</u>  |   |   |   |   |  |
| Net system power, MW  | 1,106.52  | 1,095.75  | 987.18  | 810.34  | 0  |
| Overall plant heat rate, BTU/kWh  | 9,214   | 9,404   | 89,981  | N.A.  | N.A.   |
| Methanol produced, tons/day   | 0   | 0   | 0   | 2,283.4   | 10,927   |
| Overall system efficiency coal power and<br>methanol, % of coal<br>higher heating value | 37.0  | 36.29   | 34.19   | 45.5  | 57.88  |
| TOTAL CAPITAL REQUIRED <sup>b</sup> , \$/kW   | 1,077   | 1,009   | 1,030   | N.A.  | N.A.   |
| \$FOEB <sup>c</sup> /day  | N.A.  | N.A.  | N.A.  | 32,165  | 41,666   |
| <u>COST OF ELECTRICITY</u>  |   |   |   |   |  |
| First year, mills/kWh   | 47.36   | 45.45   | 52.66   | 39.85   | N.A.   |
| Last year, mills/kWh  | 23.30   | 23.24   | 26.41   | 22.08   | N.A.   |
| Levelized, mills/kWh <sup>d</sup>   | 33.14   | 32.23   | 365.1   | 29.11   | N.A.   |
| <u>COST OF METHANOL</u>   |   |   |   |   |  |
| First year, \$ per 10 <sup>6</sup> BTU  | N.A.  | N.A.  | N.A.  | 5.58  | 7.87   |
| Last year, \$ per 10 <sup>6</sup> BTU   | N.A.  | N.A.  | N.A.  | 3.55  | 7.87   |
| Levelized, \$ per 10 <sup>6</sup> BTU   | N.A.  | N.A.  | N.A.  | 4.32  | 7.87   |

<sup>a</sup>The dedicated coal-to-methanol plant economics have been based on regulated company ownership. All other cases employ regulated utility financing.

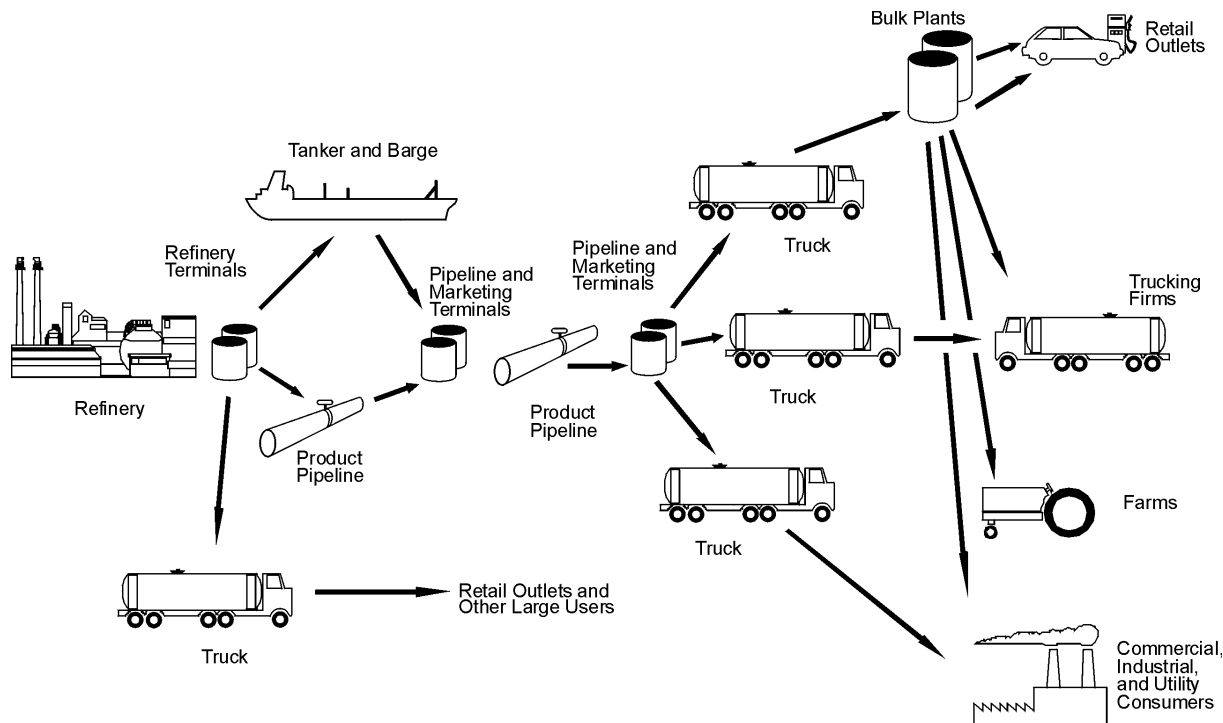
<sup>b</sup>Mid-1980 basis.

<sup>c</sup>FOEB = Barrels of distillate fuel oil ( $5.85 \times 10^6$  BTU/BBL) with high heating value equivalent to methanol produced.

<sup>d</sup>Levelized cost = Average cost at constant mid-1980 dollars.

Key: GCC = Gasification Combined Cycle; EPRI = Electric Power Research Institute; FGD = Fuel-gas desulfurization.

Source: Brown et al. (1982).



**Figure 3-3. Typical gasoline distribution system.**

Source: American Petroleum Institute (1988).

methanol from nonmethane fossil-fuel feedstocks would increase emissions of CO<sub>2</sub>. Sources of NO<sub>x</sub> are related to combustion activities (i.e., boilers, heaters, and incinerators) and have been fairly well documented.

Sources and types of air toxics would follow the trend for other organics. As an emission from all feedstocks except coal and petroleum, methanol would be the air toxic of primary concern.

Extraction of natural gas (methane) worldwide results in substantial emissions (e.g., waste gases and leaks). Methane is a key global climate gas; that is, it is an RITG and its concentration in the atmosphere has increased rapidly in recent decades. The United States

**TABLE 3-3. MATERIAL FLOW FROM A LURGI-TYPE GASIFIER**

| Stream Name       | Raw Lurgi Gas<br>(kg/h) | Lurgi Syn G<br>(kg/h) | AGR Off Gases<br>(kg/h) |
|-------------------|-------------------------|-----------------------|-------------------------|
| Hydrogen          | 15,238                  | 15,192                | 46                      |
| Oxygen            | 1,248                   |                       | 1,248                   |
| Nitrogen/argon    | 2,268                   | 2,212                 | 56                      |
| Carbon monoxide   | 78,568                  | 76,972                | 1,568                   |
| Carbon dioxide    | 252,252                 | 26,664                | 217,976                 |
| Methane           | 33,200                  | 32,272                | 864                     |
| Ethane            | 2,790                   | 1,200                 | 1,590                   |
| Ethylene          | 364                     | 154                   | 210                     |
| Propane           | 660                     | 4                     | 660                     |
| Propylene         | 546                     |                       | 546                     |
| Butane            | 429                     |                       | 383                     |
| Butylenes         | 728                     |                       | 644                     |
| Other aliphatics  | 920                     |                       | 96                      |
| Benzene           | 757                     |                       | 41                      |
| Toluene           | 216                     |                       | 3                       |
| Other aromatics   |                         |                       | 399                     |
| Hydrogen sulfide  | 2,788                   |                       | 2,751                   |
| Carbonyl sulfide  | 66                      |                       | 66                      |
| Methyl mercaptan  | 346                     |                       | 317                     |
| Ethyl mercaptan   | 143                     |                       | 93                      |
| Other mercaptans  | 30                      |                       |                         |
| Hydrogen cyanide  | 32                      |                       | 219                     |
| Ammonia           | 2,055                   |                       |                         |
| Hydrogen chloride | 14                      |                       |                         |
| Water             | 293,634                 |                       |                         |
| Particles         | 494                     |                       |                         |
| Tars              | 5,710                   |                       |                         |
| Oils              | 6,181                   |                       |                         |
| Phenol            | 1,371                   |                       |                         |
| Fatty acids       | 605                     |                       |                         |
| Others            | 2,387                   |                       |                         |
| Total             | 706,040                 | 154,670               | 229,776                 |

Source: U.S. Environmental Protection Agency (1983a).

1 uses about 20 trillion cubic feet of natural gas a year, which is moved almost totally via  
2 pipeline. Losses of methane from production, pipelines, and distribution are quite uncertain  
3 and may be as high as 2 to 5% (DeLuchi et al., 1987). The extraction of coal is also a  
4 source of methane emissions that may have been underestimated in the past. Quantification  
5 of these methane emissions is needed.

6  
7 ***Discharges.*** Methanol would be the main effluent discharge to water when methane is  
8 used as the feedstock. Because of the solubility of methanol in water, uncontrolled  
9 discharges could have an impact on surface and ground waters. A thorough evaluation of the  
10 types of organic and inorganic pollutants that are increased when coal-based systems are used  
11 to produce methanol is needed. The main waste discharges to land would be spent catalysts  
12 and ash-type materials from coal-based systems.

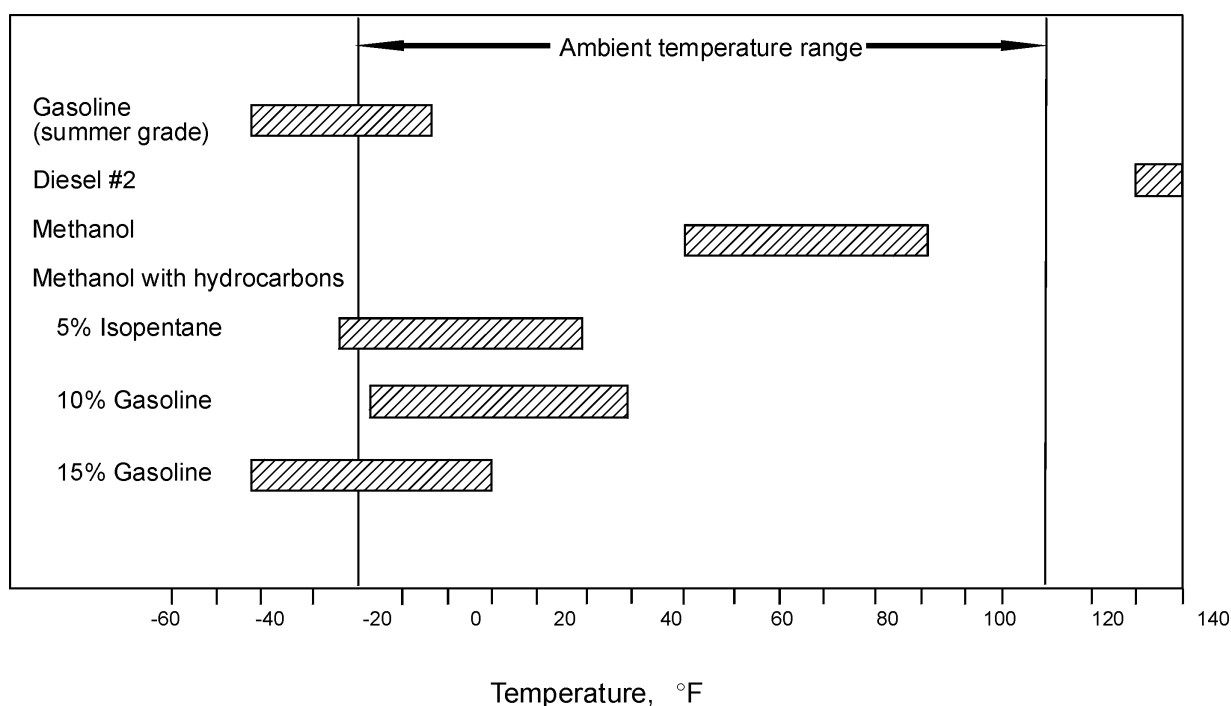
13  
14 ***Accidental Releases.*** Accidental release of methanol is a major concern because of its  
15 flammability and lack of visible flame when burned; fires started by such release would be  
16 difficult to detect. The flammability of methanol, however, is lower than that of gasoline  
17 (Machiele, 1989). Figure 3-4 gives a comparison of vapor-space flammability between  
18 various methanol liquid fuels and gasoline/diesel fuels. In head spaces of storage vessels,  
19 methanol equilibrium concentration is within its flammability limits; if ignited, it could  
20 rupture the vessel and result in major releases and fires.

21 The Toxic-Release Inventory of 1989 (U.S. Environmental Protection Agency, 1989c)  
22 showed that methanol was the eighth largest of the SARA Section 313 chemicals released in  
23 1987, with 98,019 tons of methanol being released to the air; 12,455 tons released to surface  
24 waters; 46,256 tons released to public sewage; 7,351 tons released to land; 9,791 tons  
25 released to underground injection; and 35,901 tons released to off-site transfers (U.S.  
26 Environmental Protection Agency, 1989c).

### 27 28 ***3.2.1.1.2 Mobile Source Characterization***

29 A conventional gasoline engine requires few modifications for operation with methanol;  
30 however, development of a methanol-fuel engine that can attain the superior theoretical

| PROPERTY  | METHANOL | ETHANOL | GASOLINE |
|---|----------|---------|----------|
| Flash point, °F   | 52       | 55      | -45      |
| Autoignition temperature, °F                            | 867      | 793     | 495      |
| Flammability limits, volume percent                     | 6-36     | 4.3-19  | 1.4-7.6  |
| Vapor pressure at 70 °F, psi                            | 1.9      | 0.8     | 4.8      |
| Vapor pressure at 100 °F, psi                           | 4.6      | 2.3     | 8-15     |
| Concentration in saturated air at 68 °F, volume percent | 13       | 5.4     | 25-50    |



**Figure 3-4. Vapor space flammability limits for liquid fuels (hatched areas).**

Source: U.S. Environmental Protection Agency (1983f).

1 expectations of good performance with low environmental degradation represents a greater  
 2 challenge. As has been the case with conventional-fuel engines, an optimized methanol  
 3 engine will not evolve quickly. For this reason, a distinction between two types of methanol  
 4 vehicles (i.e., current-technology vehicles and advanced-technology vehicles) is helpful. The  
 5 two vehicle families are expected to be different in engine design, fuel specification, and  
 6 emissions. Current-technology methanol-fuel passenger cars and light-duty trucks are



1 designed to use M85 fuel. Advanced-technology vehicles would be optimized for M100 fuel.  
2 The type of methanol fuel to be used is important, because it strongly influences the  
3 emissions. The gasoline component of M85 influences both tailpipe and evaporative  
4 emissions (U.S. Environmental Protection Agency, 1989a; Williams et al., 1990; Gabele,  
5 1990; California Air Resources Board, 1989; Horn and Hoekman, 1989). Additionally, a  
6 family of flexible-fuel vehicles likely will be marketed during the transition period when  
7 methanol production and distribution facilities are expanding. These vehicles will be  
8 compatible with gasoline, methanol, and any mixture of the two fuels.

9 Table 3-4 provides recent EPA estimates of the relative organic emission strengths for  
10 light-duty gasoline, optimized M85, and M100 motor vehicles; and Table 3-5 provides the  
11 compositional characteristics of these emissions. The methanol data are based on experience  
12 with a limited number of prototypes. The characteristics of emissions from flexible-fuel  
13 motor vehicles will vary significantly with the fuel composition (fraction of methanol). The  
14 volatility of the blend varies from M0 to M100, according to Figure 3-5, and the relative  
15 contribution of exhaust and evaporative sources will vary with fuel volatility. Table 3-6  
16 provides illustrative data. The flexible-fuel evaporative data in Table 3-6 include only  
17 diurnal and hot-soak emissions, whereas the evaporative data in Table 3-4 include diurnal,  
18 hot-soak, running-loss, and refueling emissions.

19 The impact of methanol fuel on emissions of CO and NO<sub>x</sub> relative to conventional fuels  
20 depends on engine design. Methanol engines designed to be operated at near-stoichiometric  
21 air:fuel ratios reduce NO<sub>x</sub> emissions, but provide little improvement in CO emissions relative  
22 to gasoline; and those designed for fuel-lean combustion reduce CO emissions, but provide  
23 little improvement in NO<sub>x</sub> emissions relative to gasoline (DeLuchi et al., 1988). Methanol  
24 engines produce less NO<sub>x</sub> than gasoline engines at a given air/fuel ratio and compression  
25 ratio because of methanol's lower flame temperature, high latent heat of vaporization, and  
26 fast flame speed; however, dedicated methanol engines likely will be operated at higher  
27 compression ratios and leaner (higher) air/fuel ratios than gasoline engines. The higher  
28 compression ratios will increase temperature and pressure and, thus, NO<sub>x</sub> formation, and the  
29 lean air/fuel ratios will preclude conventional stoichiometric three-way catalyst NO<sub>x</sub> control.

**TABLE 3-4. VEHICULAR EMISSION RATES**

| Fuel/Species             | Exhaust (g/mi) | Evap. (g/mi) | Total C <sup>a</sup> (mole/mi) | Fractional C |
|--------------------------|----------------|--------------|--------------------------------|--------------|
| <b>Current Gasoline</b>  |                |              |                                |              |
| NMHC <sup>b</sup>        | 0.700          | 1.030        | 0.12246                        | 0.998        |
| Formaldehyde             | 0.007          |              | 0.00023                        | 0.002        |
| Total                    | 0.707          | 1.030        | 0.12269                        | 1.000        |
| <b>Proposed Gasoline</b> |                |              |                                |              |
| NMHC                     | 0.530          | 0.410        | 0.06686                        | 0.998        |
| Formaldehyde             | 0.005          |              | 0.00016                        | 0.002        |
| Total                    | 0.535          | 0.410        | 0.06702                        | 1.000        |
| <b>Optimized M85</b>     |                |              |                                |              |
| NMHC                     | 0.150          | 0.160        | 0.02200                        | 0.472        |
| Methanol                 | 0.500          | 0.250        | 0.02341                        | 0.503        |
| Formaldehyde             | 0.035          |              | 0.00117                        | 0.025        |
| Total                    | 0.685          | 0.410        | 0.04658                        | 1.000        |
| <b>Optimized M100</b>    |                |              |                                |              |
| NMHC                     | 0.050          |              | 0.00360                        | 0.164        |
| Methanol                 | 0.500          | 0.072        | 0.01785                        | 0.813        |
| Formaldehyde             | 0.015          |              | 0.00050                        | 0.023        |
| Total                    | 0.565          | 0.072        | 0.02195                        | 1.000        |

<sup>a</sup>The average molecular weight per mole carbon (C) in exhaust and evaporative NMHC emissions are assumed to be 13.88 and 14.30, respectively.

<sup>b</sup>NMHC = Nonmethane hydrocarbons

Source: U.S. Environmental Protection Agency (1989a).

1 Less is known about unregulated emissions. Efforts to examine the composition of organic  
2 emissions from methanol-fuel motor vehicles have begun, with emphasis on providing the  
3 speciation necessary to estimate the potential impact on urban O<sub>3</sub> (Gabele, 1990; Williams  
4 et al., 1990; California Air Resources Board, 1989; Wright et al., 1989). These preliminary  
5 data indicate that the emission rates of toxics such as benzene and 1,3-butadiene are reduced  
6 by using methanol fuels relative to gasoline. Most hydrocarbon emissions associated with  
7 uncombusted gasoline and selected combustion products of gasoline will be reduced as the  
8 gasoline fraction of the fuel is decreased. Less is known about unregulated emissions such as

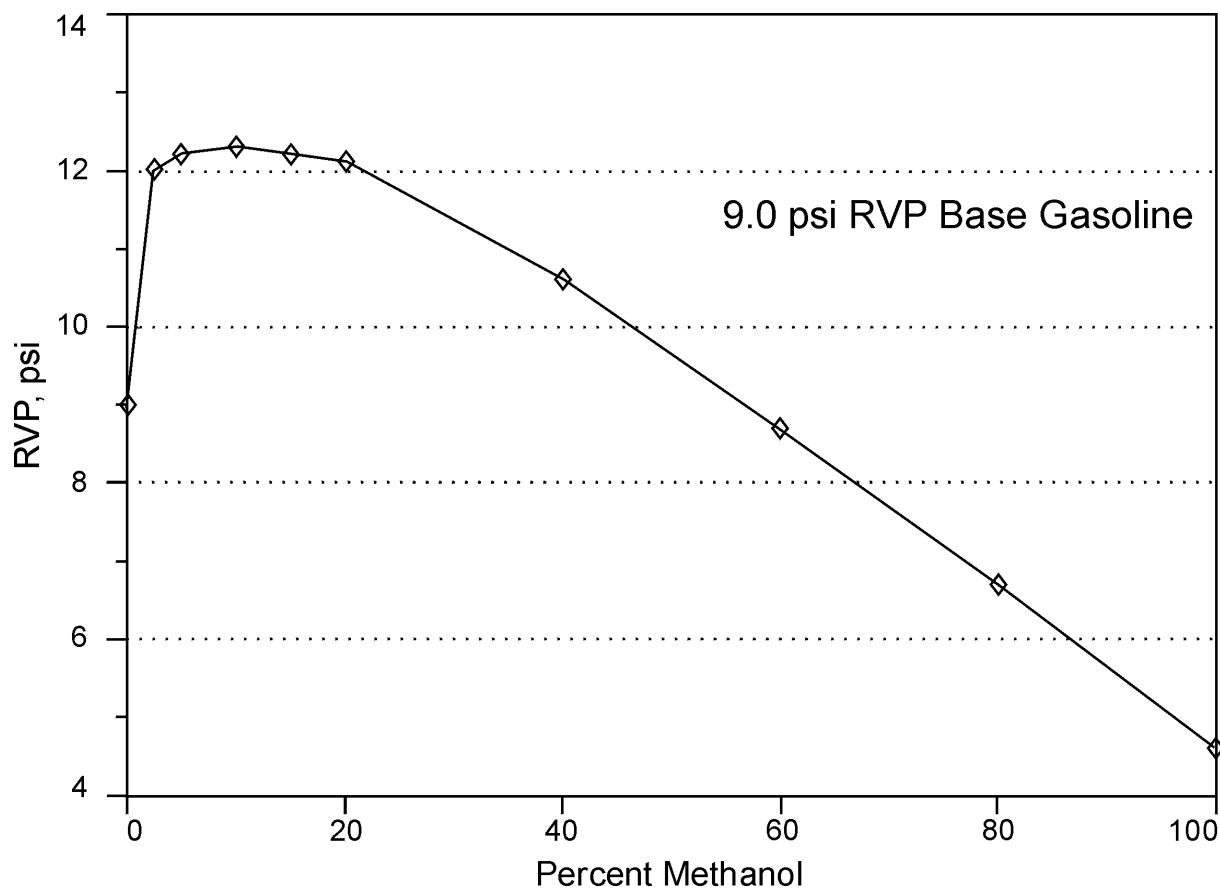
**TABLE 3-5. DISTRIBUTION OF NONMETHANE ORGANIC CARBON EMISSIONS  
BY ORGANIC COMPOUND CLASSES**

| Class <sup>a</sup> | Vehicle Type           |                             |                                  |                                   |                            |                            |                             |
|--------------------|------------------------|-----------------------------|----------------------------------|-----------------------------------|----------------------------|----------------------------|-----------------------------|
|                    | Current<br>M0<br>Fleet | Prototype<br>M0<br>Vehicles | Variable-<br>Fuel M85<br>Vehicle | Variable-<br>Fuel M100<br>Vehicle | Improved<br>M85<br>Vehicle | Ultimate<br>M85<br>Vehicle | Ultimate<br>M100<br>Vehicle |
| ALK4               | 0.222                  | 0.196                       | 0.091                            | 0.007                             | 0.091                      | 0.091                      | 0.007                       |
| ALK7               | 0.240                  | 0.262                       | 0.063                            | 0.007                             | 0.063                      | 0.063                      | 0.007                       |
| ETHE               | 0.040                  | 0.047                       | 0.027                            | 0.003                             | 0.027                      | 0.027                      | 0.003                       |
| PRPE               | 0.012                  | 0.052                       | 0.017                            | 0.003                             | 0.017                      | 0.017                      | 0.003                       |
| TBUT               | 0.055                  | 0.014                       | 0.004                            | 0.001                             | 0.004                      | 0.004                      | 0.001                       |
| TOLU               | 0.080                  | 0.184                       | 0.040                            | 0.005                             | 0.040                      | 0.040                      | 0.005                       |
| XYLE               | 0.111                  | 0.030                       | 0.010                            | 0.001                             | 0.010                      | 0.010                      | 0.001                       |
| TMBZ               | 0.055                  | 0.002                       | 0.002                            | 0.000                             | 0.002                      | 0.002                      | 0.000                       |
| HCHO               | 0.004                  | 0.009                       | 0.076                            | 0.045                             | 0.040                      | 0.010                      | 0.010                       |
| ALD2               | 0.002                  | 0.002                       | 0.001                            | 0.000                             | 0.001                      | 0.001                      | 0.000                       |
| MEOH               | 0.000                  | 0.000                       | 0.585                            | 0.914                             | 0.651                      | 0.681                      | 0.949                       |
| NR                 | 0.090                  | 0.106                       | 0.023                            | 0.008                             | 0.023                      | 0.023                      | 0.008                       |
| CH4                | 0.089                  | 0.096                       | 0.061                            | 0.006                             | 0.061                      | 0.061                      | 0.006                       |

<sup>a</sup>Classes from Lurmann et al. (1987).

Source: Dunker (1989).

formic acid and methyl nitrite. Engine-out formaldehyde emissions are elevated by methanol fuel (Horn and Hoekman, 1989), so control of these emissions is particularly important to environmental impact. The durability of formaldehyde emission controls should be monitored over mileage-accumulation ranges typical of U.S. fleets (to 100,000 miles), especially if catalyst formulations and calibrations (cold start light-off) that are different from conventional gasoline technology should emerge. The promulgated certification practice controls total organic carbon emissions (methanol, hydrocarbon, and formaldehyde, collectively), and associated in-use surveillance/recall programs will also monitor these emissions (Federal Register, 1989a). Research should monitor both organic-mass emission-rate changes and compositional changes with mileage accumulation.



**Figure 3-5. Vapor pressure of methanol-gasoline blends.**

Source: Black (1991b).

1 Emissions from conventional gasoline and diesel engines vary significantly with  
 2 operating variables such as ambient temperature, vehicle average speed, altitude, and fuel  
 3 volatility. The EPA model MOBILE 4 is generally used to estimate changes in fleet average  
 4 emission rates as a function of these and other variables (U.S. Environmental Protection  
 5 Agency, 1989b). The sensitivity of emissions from methanol-fuel vehicles to such operating  
 6 variables has not been studied adequately to define the algorithms necessary for including this  
 7 vehicle category in MOBILE 4. For example, at 74 °F, the model predicts that evaporative  
 8 hydrocarbon emissions (diurnal, hot soak, running-loss, and refueling) constituted about 37%  
 9 of total 1985 fleet average NMHC emissions at 9.0 psi RVP gasoline volatility, and 53% at

**TABLE 3-6. COMPOSITION OF EXHAUST AND EVAPORATIVE EMISSIONS  
FROM VARIABLE-FUEL VEHICLE<sup>a</sup>**

| Component   | M0   |      | M15  |      | M50  |      | M85  |      | M100 |      |
|---|------|------|------|------|------|------|------|------|------|------|
|   | Exh  | Evap | Exh  | Evap | Exh  | Evap | Exh  | Evap | Exh  | Evap |
| Methanol  | 1.2  | 0    | 38.2 | 51.7 | 106  | 66.8 | 215  | 84.9 | 761  | 108  |
| Formaldehyde  | 7.2  | 0    | 11.1 | 0    | 16.8 | 0    | 36.7 | 0    | 40.2 | 0    |
| Acetaldehyde  | 2.2  | 0    | 2.1  | 0    | 1.6  | 0    | 0.46 | 0    | 0.08 | 0    |
| Total hydrocarbon                                   | 229  | 122  | 210  | 99.8 | 172  | 67.0 | 50.6 | 25.0 | 9.4  | 7.6  |
| <u>Individual Hydrocarbons as Carbon % of Total</u> |      |      |      |      |      |      |      |      |      |      |
| <u>Hydrocarbon</u>                                  |      |      |      |      |      |      |      |      |      |      |
| Methane   | 15.8 | 0    | 7.5  | 0    | 11.9 | 0    | 26.8 | 0    | 25.5 | 0    |
| Ethane  | 3.4  | 0    | 1.2  | 0    | 1.2  | 0    | 0    | 0    | 3.0  | 0    |
| Ethylene  | 6.1  | 0    | 7.0  | 0    | 7.0  | 0    | 10.0 | 0    | 7.8  | 0    |
| Acetylene   | 1.3  | 0    | 3.5  | 0    | 2.3  | 0    | 5.8  | 0    | 20.6 | 0    |
| Propylene   | 4.7  | 0    | 4.8  | 0    | 4.5  | 0    | 4.9  | 0    | 8.1  | 0    |
| Propyne   | 0.4  | 0    | 0    | 0    | 0.1  | 0    | 3.0  | 0    | 9.5  | 0    |
| Isobutylene   | 3.7  | 0    | 3.6  | 0    | 3.5  | 0    | 3.2  | 0    | 3.3  | 0    |
| Isobutane   | 0.6  | 9.0  | 1.1  | 2.2  | 0.2  | 1.3  | 0.2  | 1.7  | 0    | 0    |
| 1,3-Butadiene                                       | 0.4  | 0    | 0.6  | 0    | 0.6  | 0    | 0.7  | 0    | 3.3  | 0    |
| Butane  | 2.3  | 43.4 | 8.3  | 10.4 | 2.8  | 7.7  | 1.6  | 43.6 | 0    | 15.4 |
| Isopentane  | 3.5  | 4.8  | 9.5  | 8.8  | 3.8  | 10.9 | 4.4  | 11.4 | 0    | 18.0 |
| Pentane   | 2.9  | 2.6  | 3.2  | 4.4  | 2.6  | 5.0  | 2.4  | 4.5  | 0    | 2.2  |
| Isohexane   | 1.5  | 1.0  | 1.1  | 1.9  | 1.3  | 2.1  | 1.4  | 2.3  | 1.4  | 5.0  |
| Hexane  | 0.9  | 0.8  | 0.8  | 1.6  | 1.1  | 2.0  | 0.6  | 0.6  | 2.2  | 0    |
| Benzene   | 4.2  | 0.9  | 4.0  | 1.8  | 4.6  | 2.0  | 4.0  | 1.7  | 9.5  | 0.8  |
| 2 Methylhexane                                      | 4.1  | 3.5  | 4.3  | 5.4  | 4.3  | 4.9  | 2.4  | 4.0  | 0    | 9.0  |
| Isoctane  | 9.2  | 5.6  | 9.2  | 8.8  | 9.4  | 10.4 | 6.8  | 6.2  | 0    | 8.7  |
| 2,3,4-Trimethylpetane                               | 1.5  | 1.4  | 1.5  | 2.3  | 1.8  | 3.0  | 1.1  | 1.8  | 0    | 5.3  |
| Toluene   | 14.7 | 13.0 | 13.7 | 27.0 | 14.4 | 27.6 | 10.0 | 13.8 | 0    | 26.8 |
| % of total hydrocarbons listed here                 | 81   | 86   | 85   | 75   | 77   | 77   | 89   | 92   | 94   | 91   |

<sup>a</sup> All results expressed in mg/mi for standard tests, except as noted.

Source: Williams et al. (1990).

1 11.5 psi RVP gasoline volatility (20 mph, low altitude). At 94 °F, the percentages are 49%  
2 and 63%, respectively. Similar characterization of evaporative emissions with methanol fuels  
3 has not been completed.

4 Methanol is also a potential alternative fuel for heavy-duty buses. Heavy-duty methanol  
5 engines generally emit less particulate matter (PM) and NO<sub>x</sub> than comparable diesel engines.  
6 But emissions of methanol, formaldehyde, and CO are elevated and will require an oxidation  
7 catalyst for control (Alson et al., 1989; Eberhard et al., 1989; Ullman et al., 1986). Less is  
8 known about the emission rates of unregulated compounds (e.g., methyl nitrite and formic  
9 acid) from methanol diesel engines. As with light-duty vehicles, information on both  
10 regulated and nonregulated emissions as a function of fuel type, average vehicle speed,  
11 vehicle age, and ambient temperature will be required to predict air quality impact and health  
12 and welfare effects.

13 Tailpipe CO<sub>2</sub> emissions from advanced-technology methanol-fuel motor vehicles are  
14 expected to be somewhat lower than conventional gasoline and diesel vehicle emissions  
15 (about 80% of conventional vehicle emissions), but the overall CO<sub>2</sub> burden will depend  
16 strongly on the feedstock used for production of the fuel. Relative to a petroleum base,  
17 estimates range from about -100% change per mile with biomass feedstock (assumes entire  
18 process runs on biofuels and nonfossil electricity) to about +100% with coal feedstock  
19 (DeLuchi et al., 1987).

20 The potential environmental impact of methanol transportation fuels can be understood  
21 only with expanded efforts to characterize both regulated and unregulated emissions resulting  
22 from advancing technologies.

### 24 **3.2.1.2 Environmental Fate**

#### 25 **3.2.1.2.1 Air Fate**

26 The release of methanol into the atmosphere can form O<sub>3</sub> when photooxidized by  
27 sunlight in the presence of NO<sub>x</sub>. Its reactivity or ability to form O<sub>3</sub>, however, is less than  
28 most of the VOCs from gasoline. Methanol is removed from the troposphere largely through  
29 its reaction with hydroxyl OH radicals and through wet deposition. The atmospheric  
30 lifetime, if removed by reaction with OH radicals, is about 17 days (Atkinson, 1985).

Henry's Law constant is  $220 \text{ mol L}^{-1} \text{ atm}^{-1}$ , which makes methanol fully soluble (Gaffney et al., 1987). It, therefore, should be removed from the atmosphere by aqueous aerosols, which would result in an atmospheric lifetime much shorter than 17 days, probably closer to 5 days. The primary product of the reaction of methanol with OH radicals is formaldehyde. Formaldehyde and formic acid may also be produced by the reaction of dissolved methanol in aerosols, because sunlight acting on aqueous aerosols produces oxidants such as OH,  $\text{O}_2(^1\Delta\text{g})$ , and  $\text{XO}_2$  radicals (Faust and Hoigne, 1990). Monomethyl sulfate (MMS) and DMS have been observed downwind of power plants, ostensibly a product of the reaction of organics with  $\text{SO}_2$  on aerosols (Hansen et al., 1986). A recent study has shown that DMS is not produced in the gas phase when methanol and  $\text{SO}_3$  coexist (Japar et al., 1989). This study, however, did not investigate possible heterogenous reactions on aerosol surfaces. If methanol emissions increase, perhaps more organic sulfates (DMS and MMS) will be produced. Peroxyacetyl nitrate production is expected to decrease with the use of methanol.

The reactivity of the exhaust gas mixture from methanol-powered vehicles is expected to be lower than that from gasoline-powered vehicles, even though the formaldehyde emission levels can be relatively high during cold starts. The net atmospheric formaldehyde burden will also be affected by secondary chemical processes that produce formaldehyde. Methanol substitution should decrease ambient levels of formaldehyde since most (approximately 80%) of the daytime concentration is a result of photochemical reactions (Keating, 1989). Precursor concentrations and reaction rates of methanol fuels relative to those of gasoline fuels will determine the extent of the decrease.

The state of California has recently estimated the relative  $\text{O}_3$ -forming potential of M85 fuel vehicle emissions to be about 36% of that of conventional unleaded gasoline fuel vehicle emissions (California Air Resources Board, 1991). This estimate was based on comparison of  $\text{g O}_3/\text{g}$  nonmethane organic gas emissions for these fuel categories using Carter's maximum incremental reactivities. The benefit of lower reactivity with methanol fuel, however, depends upon the initial formaldehyde concentration. The benefits obtained from the use of methanol fuel decreased with increasing formaldehyde levels (Jeffries et al., 1985; Carter et al., 1986). The  $\text{VOC}/\text{NO}_x$  ratio was also considered important; as the ratio increased, the benefits from methanol substitution decreased (Dunker, 1990). This was also

1 observed for multiday irradiations in one smog chamber study (Carter et al., 1986). No  
2 improvements in final O<sub>3</sub> levels were observed after 2- or 3-day irradiations (Carter et al.,  
3 1986). The ability of a smog chamber to duplicate the changes and conditions of an actual  
4 atmosphere, however, limits the applicability of these results. The walls of smog chambers  
5 become important sinks for reactant pollutants, which are then reemitted on the second and  
6 third days.

7       These experimental data are contrasted by modeling studies (Russell et al., 1989;  
8 Russell and Harris, 1988; Harris et al., 1988) that showed beneficial results from methanol  
9 substitution, not only for the first day of a stagnation period but throughout a multiday  
10 episode. These investigators modeled the South Coast Air Basin and found a 16% decrease  
11 in peak O<sub>3</sub> with M100 substitution. Similar results were obtained with M85 (8% decrease in  
12 O<sub>3</sub>). Some of the benefits predicted, however, may be due, at least in part, to peculiarities  
13 of the model (Keating, 1989). Because the model is dated, it should be further documented  
14 and reviewed. A modeling study was also recently done by Sillman and Samson (1989) for  
15 the Detroit-Port Huron area. These results indicate that the use of methanol (M100)  
16 improved urban O<sub>3</sub> by about 5%. An M85 mixture showed no improvement. Methanol had  
17 almost no impact on rural O<sub>3</sub> formation.

18       An earlier modeling study by Whitten et al. (1986) found that benefits from the use of  
19 methanol as an automotive fuel are dependent upon a number of factors, including, as stated  
20 above, the amount of formaldehyde emitted, the amount of VOC the methanol displaced, and  
21 the amount of carryover for the second day. These modeling studies suggest that not all  
22 cities will show the same benefits when methanol is substituted for gasoline; however, most  
23 studies did show some benefit with all scenarios tested. Methyl nitrite has also been  
24 observed as an exhaust product (Jonsson and Bertilsson, 1982), but another investigator  
25 concluded that this compound can be formed artifactually upon sample storage (Smith, 1985).  
26 Nitrites are especially important in the formation of photochemical smog, because they  
27 photodissociate in the presence of sunlight to produce OH radicals, thereby propagating  
28 chemical reactions in the atmosphere.



### 3.2.1.2.2 *Soil and Groundwater Fate*

Methanol would be susceptible to introduction into the subsurface environment through essentially the same pathways as petroleum-based fuels (i.e., transportation or storage/transfer leaks, spills, or catastrophic release). Once in the subsurface, however, the transport and fate of methanol and gasoline would be substantially different. This disparity in behavior is primarily due to the solubility of methanol and the resulting physical and chemical properties of the solution phase.

Because methanol is completely miscible with water, eventually it will mix with percolating water or groundwater and move as a single liquid phase. The dynamics of this mixing process will be dependent upon the physical and hydraulic properties of the porous medium and the related amounts of the methanol and water available for transport. In the absence of volatilization, dissolution will be complete, with the total methanol source being incorporated into the soil/groundwater. When at or near the soil surface, however, methanol can be susceptible to rapid volatilization dependent on surface temperatures and winds that can reduce the quantity available for leaching toward the groundwater. The extent of volatile losses or gas-phase transport, both at the surface and deeper in the soil profile, also will be a function of soil characteristics such as air and water permeability. Theoretical functional relationships between these properties and volatilization, which are needed to predict the vapor transport of methanol in the subsurface, are known, but operational experience and field data and testing are limited.

The rate of movement of the liquid- or aqueous-phase methanol through the subsurface will be controlled by advection and sorption. Liquid chromatography theory and experience, as well as limited experimental data with soil (Wood et al., 1990), suggest that methanol will move rapidly through the subsurface with little or no interaction (sorption) with the solid matrix. The rate of movement will thus depend only upon the head (volume of methanol or methanol-water) and the physical and hydraulic properties of the porous media (and on the extent to which these properties are altered by exposure to methanol). The effect of methanol, as a neat solution or in mixtures with water, on the hydraulic properties of soils and aquifers is poorly understood. Appropriate laboratory and field studies are needed to parameterized groundwater threat/exposure models.

1        Because of its mobility, methanol would exhibit a high potential for groundwater  
2        contamination, unless attenuated by volatilization and subsurface chemical or microbial  
3        processes. If methanol is present in high concentrations, microbial transformations would  
4        not be expected to occur because methanol would act as a sterilant. Conversely, when  
5        methanol is present at low concentrations, microbial activity could be stimulated and  
6        significant attenuation could occur. The conditions under which degradation of methanol  
7        would occur are not well quantified over the wide concentration ranges and over relatively  
8        large and poised Eh ranges found in soil-groundwater systems. Such degradation kinetics are  
9        also a major research need if realistic groundwater threats are to be evaluated.

10       Because methanol is more mobile than gasoline, it could exhibit a greater potential for  
11       groundwater contamination; however, additional information concerning biodegradation and  
12       floating, miscible NAPL dissolution and transport in soils and aquifers are required to make  
13       an objective comparison of these fuels. On the other hand, because it is miscible with water,  
14       does not interact significantly with the solid matrix, and biodegrades at low concentrations,  
15       methanol would be easier to remove from contaminated aquifers.

16       When petroleum-based products are present in a predominantly methanol fuel, as with  
17       M85, attention must be focused on the effects of methanol on the mobility and fate of other  
18       hydrocarbon constituents. Methanol is known to increase significantly the mobility of  
19       nonpolar organic compounds (Rao et al., 1985; Nkedi-Kizza et al., 1987; Wood et al.,  
20       1990), but little information is available on the biotransformation of specific organics in the  
21       presence of mixed methanol-water systems. Field evaluations of both the transport and  
22       transformation of hydrocarbons in methanol-water mixtures are needed.

#### 23 24       ***3.2.1.2.3 Surface Water Fate***

25       As a neat replacement fuel or as a major blend component, methanol would be  
26       introduced into surface water systems in a manner that is essentially similar to  
27       petroleum-based products and is subject to most of the same physical transport and biotic and  
28       abiotic transformation processes. The most important probable sources are (1) the  
29       continuous, small inputs from boats (due to spills and fuel transfers) and the releases of  
30       untreated or improperly treated methanol from production facilities or storage/transfer

1 systems (drips); and (2) catastrophic, pulse releases from tankers, barges, or tank farms on  
2 shore. The first category of continuous-release sources is believed to be manageable, based  
3 on existing fate and transport/exposure methods and kinetics data. Other than accounting for  
4 dissolved oxygen utilization during biological oxidation of the methanol, no significant  
5 impacts would be anticipated.

6 The second source category (i.e., pulsatile releases) is likely to have major aquatic  
7 ecosystem impacts, but adequate information on source intensity, duration, and probability  
8 for either fresh surface water systems or marine embayments/estuaries is lacking.  
9 Nevertheless, large volumes of fuel products are routinely transported through marine  
10 ecosystems. A switch to the widespread use of alternative fuels such as methanol will mean  
11 changes in the types of products transported through coastal waters, which will inevitably  
12 result in the release of different compounds to these waters. Recent oil spills in Alaska,  
13 Rhode Island, Delaware, and Texas serve as reminders that large accidental fuel releases to  
14 marine systems occur. Adequate descriptions of the pulsed mixing-dispersion-dissolution  
15 process for the floating methanol-water binary system (relating to stream, river, lake, and  
16 estuarine hydrology) are not available. Moreover, quantitative descriptions of the  
17 volatilization of methanol from a pulsed system over a wide range of concentrations and  
18 turbulence have not been field-evaluated. Finally, proper accounting for biological  
19 degradation lag/inhibition, degradation kinetics, and reaeration/oxygen availability cannot be  
20 made for such a wide range of methanol concentrations until additional transformation  
21 research has been completed for fresh and marine surface waters. A similar situation exists  
22 for photolysis reactions. This also means that concurrent dissolved-oxygen depletion threats  
23 to fish and other aquatic organisms cannot be reliably estimated until the fate and  
24 transformation research mentioned above has been completed and incorporated into  
25 appropriate exposure and risk assessment methodologies.

### 26 27 **3.2.1.3 Exposures**

28 The pollutants associated with alternative fuels can cause effects on human health and  
29 ecosystems, but the nature and magnitude of these effects are directly dependent upon  
30 exposures. For the purpose of this document, exposures are defined as the level, pattern,

1 and duration of concentrations presented to either a human or ecosystem receptor. The  
2 internal, or delivered, dose that actually causes an effect is discussed under health and  
3 ecosystem effects. This exposure section is divided into human and biota exposures. Human  
4 exposure is subdivided into accidental, air, and drinking water. These are the principal  
5 environmental exposure routes, though food and beverages also may be major sources of  
6 human exposure. Biota exposure is subdivided into terrestrial and aquatic (freshwater and  
7 marine).

### 8 9 **3.2.1.3.1 Human Exposures**

10 ***Accidental Exposures.*** Both direct dermal and oral exposures are likely to occur.  
11 Accidental oral exposure due to fuel siphoning or to children's ingestion of fuels is a  
12 substantial concern. Each year about 52,000 children receive accidental exposures to  
13 gasoline (Litovitz, 1988). Ingesting 12 mL of M85 can be lethal to a 10-kg 1-year-old child,  
14 and smaller amounts can be quite toxic to children. This incidence is expected to be lower  
15 with methanol, due to the likelihood of having anti-siphoning devices on methanol-fuel  
16 vehicles and less home storage since methanol is not an effective degreaser and not usable in  
17 lawn mowers. Due to the known severity of the effects, the emphasis is on estimating  
18 exposure incidence. During fueling and other transfer operations, spills to the skin can  
19 occur. The impact will be a function of absorption and toxicity, which are different for  
20 M100 and M85 fuels. The likelihood of such dermal exposure must be better quantitated.

21  
22 ***Air Exposures.*** Although exposure via air depends upon numerous factors, it primarily  
23 depends upon the association of the receptor with the pollutant (i.e., direct emissions and  
24 transformation products). Any factor that increases the number of susceptible receptors  
25 associated with the pollutant or increases the concentration and/or duration of pollutant  
26 exposure would be expected to increase the risk. Very broad sources, such as transformation  
27 products in the ambient air, would result in widespread exposures to humans and ecosystems.  
28 Even some point sources, such as personal refueling of vehicles, can result in exposure to  
29 large numbers of people. Personal and public garages would be expected to have higher  
30 pollutant levels than ambient air. Although this would not be considered widespread

1 exposure, the potential risk to individuals exposed in such situations would be higher than the  
2 risk from exposure to an ambient air situation.

3 Through its Office of Mobile Sources, EPA has conducted studies to estimate expected  
4 ambient concentrations of methanol under a wide range of vehicle and traffic conditions  
5 (Harvey et al., 1984; Gold, 1985; Moulis, 1989; Lorang, 1989). The basic approach  
6 followed in these studies was to characterize the emissions from test automobiles and  
7 compute ambient concentrations through air quality models. Concentration levels were  
8 modeled for specific microenvironments representative of typical and severe conditions. The  
9 important microenvironments for automotive exposures were identified in other studies and  
10 include street canyons, roadway tunnels, and expressways, as well as personal and public  
11 parking garages (Akland et al., 1985).

12 Table 3-7 summarizes results of these computations, which were adapted from  
13 procedures discussed in Gold (1985) and Harvey et al. (1984). The calculations show that  
14 maximal exposures are expected in garages, with an estimated "worst case" short-term  
15 methanol peak exposure of  $650 \text{ mg/m}^3$  (500 ppm) (Federal Register, 1989a). More recent  
16 evaluations indicate that this worst case estimate is too high, perhaps by a factor of 2, and  
17 should be reduced to about  $325 \text{ mg/m}^3$  (250 ppm) (Lorang, 1989). In contrast, maximum  
18 in-traffic predicted concentrations are expected to be about 5 to  $6 \text{ mg/m}^3$  (4 to 5 ppm), which  
19 would occur while traveling through a roadway tunnel. These results highlight the  
20 importance of the personal garage as the microenvironment of highest concern because (1) it  
21 represents the highest estimated concentration level, (2) the estimate is independent of the  
22 percentage of cars in the overall fleet that use methanol as a fuel, and (3) the personal garage  
23 may be a source of residential indoor exposures (Pleil et al., 1985). Other  
24 microenvironments or activities that may provide high exposures, but have not been  
25 adequately characterized, include service station refueling, service station repair facilities,  
26 in-transit exposures, and bus malls. These results are discussed in some detail elsewhere  
27 (Federal Register, 1989a; U.S. Environmental Protection Agency, 1986a; Health Effects  
28 Institute, 1987).

**TABLE 3-7. ESTIMATED AMBIENT METHANOL AND FORMALDEHYDE CONCENTRATIONS (mg/m<sup>3</sup>)<sup>a</sup> FOR SELECTED MICROENVIRONMENTS AND TRAFFIC SCENARIOS FOR METHANOL-FUEL VEHICLES**

| Scenario       | Predicted Methanol<br>(Reference <sup>b</sup> )         | Predicted Formaldehyde<br>(Reference <sup>b</sup> )     |
|----------------|---|---|
| Street Canyon  | 0.04 - 0.54 (1)<br>0.07 - 0.54 (2)<br>0.14 - 0.34 (5)   | 0.011 - 0.036 (2)<br>0.14 - 0.34 (5)<br>0.14 - 0.34 (5) |
| Roadway Tunnel | 1.0 - 5.4 (1)<br>0.75 - 5.4 (2)<br>1.4 - 3.4 (5)        | 0.104 - 0.362 (2)<br>1.4 - 3.4 (5)<br>1.4 - 3.4 (5)     |
| Expressway     | 0.005 - 0.77 (1)<br>0.006 - 0.77 (3)<br>0.01 - 0.03 (5) | 0.007 - 0.032 (2)<br>0.01 - 0.03 (5)<br>0.01 - 0.03 (5) |
| Public Garage  |   |   |
| Start          | 0.17 - 23.0 (1)   | 0.11 - 1.7 (3)  |
| End            | 0.30 - 58.0 (1)   | 0.25 - 1.0 (4)  |
| Start          | 0.72 - 23.0 (2)   | 0.077 - 0.221 (2)                                       |
| End            | 3.8 - 58.0 (2)  | 0.077 - 0.221 (2)                                       |
| Max            | 44.0 (4)  | 0.077 - 0.221 (2)                                       |
| Public Garage  |   |   |
| Start          | 29.0 - 67.0 (5)   | 0.3 - 1.7 (5)   |
| End            | 10.0 - 11.0 (5)   | 0.1 - 0.6 (5)   |
| Private Garage |   |   |
| Start          | 0.02 - 98.0 (1)   | 0.54 - 8.2 (3)  |
| End            | 10.0 - 240.0 (1)  | 0.54 - 8.2 (3)  |
| Start          | 0.02 - 98.0 (2)   | 0.5 - 16.3 (4)  |
| End            | 10.0 - 240.0 (2)  | 0.0003 - 1.03 (2)                                       |
| Max            | 650.0 (4)   | 0.0003 - 1.03 (2)                                       |
| Private Garage |   |   |
| Start          | 141.0 - 325.0 (5)                                       | 1.6 - 8.2 (5)   |
| End            | 47.0 - 54.0 (5)   | 0.5 - 3.0 (5)   |

<sup>a</sup> 1 mg/m<sup>3</sup> methanol  $\approx$  0.77 ppm; 1 mg/m<sup>3</sup> formaldehyde  $\approx$  0.74 ppm.

<sup>b</sup> KEY: (1) Gold (1985) and Harvey et al. (1984).

(2) U.S. Environmental Protection Agency (July 1986a).

(3) Moulis (1989).

(4) Federal Register (1989a).

(5) Lorang (1989).

1       The sensitivity of modeled exposure estimates to basic assumptions is important to  
2 recognize. For example, estimated exposures resulting from methanol fuel (Harvey et al.,  
3 1984; Gold, 1985) indicated that maximum methanol exposures are about 240 mg/m<sup>3</sup>  
4 (185 ppm) in private garages and that maximum in-transit exposures are about 6 mg/m<sup>3</sup>  
5 (5 ppm) while in a roadway tunnel. Using more recent emissions data, these estimates have  
6 recently been reduced by about 70 and 50%, respectively (Lorang, 1989). This underscores  
7 the need to independently verify model estimates, assumptions, and microenvironments and  
8 to obtain representative human exposure monitoring data.

9       Total human exposure studies of the impact of increased exposures to methanol,  
10 formaldehyde, and phenol are essential for understanding the impact of these pollutants on  
11 risks to human health. Private and public garages must be verified as the microenvironments  
12 in which high concentrations are likely. Other sources may also contribute to the  
13 concentrations measured within some microenvironments, which could lead to exposures  
14 higher than those listed in Table 3-7. Methanol is also available from food and beverages  
15 through consumption of fresh fruit and vegetables, and/or by drinking fruit juices and  
16 fermented beverages. This accounts for an average individual body burden of 0.5 mg/kg  
17 methanol/day (Sedivec et al., 1981). See the health effects section (Section 3.2.2.1) for  
18 further discussion of this issue. In conducting these studies, concentrations of methanol and  
19 formaldehyde, as well as of other combustion by-products, would be measured. In addition,  
20 estimates of activities and time spent in locations and/or activities associated with these high  
21 exposures would be obtained from independent data sources and combined to form the human  
22 exposure estimates. The lack of these data limits our ability to predict human exposures that  
23 will result from the use of methanol as an alternative fuel, and current exposure estimates  
24 may be no better than plus-or-minus several orders of magnitude for the maximum predicted  
25 exposures. The high degree of indoor air exposure from personal and parking garages adds  
26 to this uncertainty.

27  
28       ***Drinking Water Exposures.*** Another potential source of pollutant exposure is  
29 contaminated water supplies. Both surface water and groundwater supplies are subject to  
30 contamination by fuel products; however, experience has shown that groundwater

1 contamination problems are more difficult and more expensive to correct. Aquifer  
2 restoration, when feasible, often requires long periods of time to accomplish. Also, the  
3 quality of water from most domestic wells is poorly monitored, and exposure to low levels of  
4 contaminants from these sources could go undetected. Groundwater should, therefore, be of  
5 concern as a significant potential source of human exposure to pollutants associated with  
6 alternative fuels production and use. Additionally, agriculture crop exposure could result  
7 from the use of groundwater for irrigation.

8 Contaminant access to groundwater is normally via the vadose zone. Groundwater  
9 quality and, thus, human exposure to contaminants will be a function of pollutant mobility  
10 and attenuation in soils. To understand the impact of alternative fuels on exposure, an  
11 understanding of the relative behavior of these substances in the subsurface is necessary.  
12 Although qualitative conclusions can be drawn, our lack of knowledge on the transport of  
13 methanol in the subsurface limits our ability to predict relative human exposure that will  
14 result from the use of methanol as an alternative fuel.

#### 16 **3.2.1.3.2 Biota Exposures**

17 **Terrestrial Exposures.** Once the methanol-fuel pollutants (e.g., methanol,  
18 formaldehyde) are emitted into the atmosphere from stationary and mobile sources, they are  
19 subject to the prevailing conditions that influence their environmental fate (Schroeder and  
20 Lane, 1988). The chemical reactions that occur within the atmosphere (e.g., those producing  
21 formaldehyde or DMS) are complex and driven by processes such as OH scavenging and  
22 solar irradiation. These reactions may result in the formation of products that can be as  
23 toxic, more toxic, or less toxic to biota than the parent compounds.

24 The atmosphere is also the major pathway for the transport and deposition of the  
25 pollutants (Schroeder and Lane, 1988) from stationary and mobile sources to terrestrial  
26 ecosystem receptors—vegetation and soil (Foster, 1991). Vegetation and soil have large  
27 surface areas in contact with the atmosphere and thus are recipients to the majority of  
28 pollutant deposition. Exposure may occur via wet deposition (e.g., fog, rain, dew) and dry  
29 deposition (e.g., gases, particles). Cloud water and fog water have the potential to  
30 concentrate pollutants (Kawamura and Kaplan, 1984) and therefore represent an important



1 pathway of exposure to vegetation, more so than rain and dry deposition. The prevailing  
2 meteorological conditions and the physicochemical properties of the pollutants will dictate  
3 atmospheric residence times and pollutant deposition to the receptors (Schroeder and Lane,  
4 1988). Such exposures could be acute or chronic, frequent or infrequent, high level or low  
5 level, and local or regional. Local pollutant deposition will impact urban and agricultural  
6 ecosystems, whereas remote ecosystems will be exposed to the pollutants via long-range  
7 atmospheric transport and deposition (Moser et al., 1991). The degree of ecological impact  
8 will depend, in part, on the exposure (duration, pattern, time, and concentration) of the  
9 pollutant to the biota.

10 The environmental partitioning of pollutants within terrestrial ecosystems will dictate  
11 their potential impact on vegetation and other biota (Weinstein and Birk, 1989). For  
12 example, trace metals (e.g., lead) tend to accumulate on soil surfaces via adsorption to  
13 organic matter. Trace-metal accumulation may reduce plant growth and vigor through the  
14 disruption of nutrient uptake by the plant roots and may alter soil biota populations resulting  
15 in decreased organic matter decomposition. Gas-phase pollutants (e.g., formaldehyde) reside  
16 in the atmosphere with the potential to disrupt plant-leaf biochemical processes after  
17 absorption through the stomata or cuticle. The lipophilic nature of some pollutants (e.g.,  
18 DMS) may result in their accumulation in the waxy cuticle of leaves. The contaminants then  
19 may be passed along food chains through herbivory and predation, with the potential for  
20 biomagnification.

21 The exposure of terrestrial biota to methanol-fuel pollutants through the atmosphere is  
22 not fully understood. Pollutant deposition and exposure to biota in urban and agricultural  
23 systems are much better documented than for remote ecosystems such as forest and alpine  
24 habitats. Obviously, modeling efforts are needed to predict with statistical confidence the  
25 potential exposure of terrestrial ecosystems to the methanol-fuel pollutants. Therefore,  
26 reliable monitoring data from urban, rural, and remote locations are necessary to verify the  
27 model predictions.

28  
29 *Aquatic Exposures.* Considerations for making defensible aquatic exposure assessments  
30 for methanol fuels are similar to those discussed in the conventional fuels chapter. However,

1 these assessments will be different from those for gasoline and diesel fuel because the  
2 miscibility of methanol with water will increase dissolved concentrations and result in the  
3 dispersing of fuel more fully throughout the water column. For methanol-gasoline blends,  
4 the methanol may also alter the distribution and availability of gasoline components. Due to  
5 the potentially high concentrations of methanol in solution from large spills, the possibility of  
6 oxygen depletion must also be considered in these exposure assessments.

#### 8 **3.2.1.4 Analytical Methodology**

9 A wide range of analytical procedures is required to facilitate examination of the impact  
10 of changes in motor fuels on risk to health and the environment. The procedures can  
11 generally be categorized according to procedures for characterizing source emissions,  
12 procedures for monitoring the transport and transformation of the emissions in ambient air,  
13 and procedures for monitoring human and ecosystem exposure. Procedures both for  
14 certification of regulated emissions (THC, CO, CO<sub>2</sub>, NO<sub>x</sub>, and PM) and for comprehensive  
15 characterization of unregulated emissions are required for sources. Nondispersive infrared  
16 analyzers are commonly used to determine CO and CO<sub>2</sub>; O<sub>3</sub> chemiluminescence is used to  
17 determine NO<sub>x</sub>; and THC FID is used to determine total organic carbon. Care must be  
18 taken to assure that emissions associated with methanol fuels can be accurately determined  
19 with these classical procedures at concentrations dictated by the CAAAs. Chromatography,  
20 infrared spectroscopy, and MS are often used for detailed characterization of unregulated  
21 emissions.

22 With methanol fuels, certification of total organic emissions is complicated by the  
23 presence of significant levels of methanol and formaldehyde, in addition to normally  
24 measured THC. Procedures for measurement of methanol and formaldehyde and for  
25 compensation of the THC FID system response to methanol have been recommended,  
26 thereby permitting determination of THC (U.S. Environmental Protection Agency, 1983h;  
27 Tejada, 1986; Federal Register, 1989a). A problem has been noted with chemiluminescence  
28 NO<sub>x</sub> analysis after extended exposure of the instrumentation to emissions from methanol-fuel  
29 motor vehicles (Gabele, 1988). Erroneously high NO<sub>x</sub> concentrations are indicated, and  
30 corrective measures have been recommended. Interest in developing more simple, less costly

1 procedures than chromatography for determining methanol and formaldehyde (Gabele et al.,  
2 1988; Gabele and Cha, 1985) as well as procedures permitting continuous "real-time"  
3 measurement of methanol and formaldehyde has been expressed (Butler et al., 1985; Staab  
4 et al., 1985). Interest in measuring formic acid and methyl nitrite emissions from vehicles  
5 using methanol fuels has also been expressed (Wright et al., 1989). Assessing the impact of  
6 methanol fuel on O<sub>3</sub> and toxics air quality will require analytical procedures for determining  
7 the detailed composition of associated source organic emissions. With all measurements in  
8 source emissions, care must be taken to assure that artifactual chemistry during sampling and  
9 analysis does not bias observations.

10 Many of the same chromatographic techniques employed for ambient air hydrocarbon  
11 analysis with conventional fuels can be used with methanol fuels; however, special  
12 consideration is needed with methanol because this compound typically tails with GC  
13 analytical columns used for hydrocarbon analyses. Also, methodology may need to be  
14 developed for the analyses of DMS. Analyses techniques used for DMS analyses have  
15 included capillary GC with flame photometric detectors, GC/MS, ion chromatography, and  
16 FTIR. One or more of the techniques should be tested to measure low ppb levels of DMS.

17 Ambient air monitoring and microenvironmental monitoring will require methods  
18 development for the measurement of methanol and formaldehyde. In addition, personal  
19 monitors for these pollutants will be required if population exposure studies are undertaken in  
20 later years.

## 21 **3.2.2 Effects Assessment**

### 22 **3.2.2.1 Human Health Effects**

23 As depicted in Figure 1-2, alternative fuels could influence human health directly or  
24 indirectly by changes in air quality, water/soil quality, ecosystem integrity, and/or global  
25 warming. (Global warming is addressed in a separate global climate research planning  
26 document.) However, only direct health effects resulting from alternative fuel exposures will  
27 be explored here.

28 This Strategy focuses on the effects of inhalation exposures, because of the potential for  
29 a greater number of people to be exposed via inhalation compared to other routes.  
30

1 Ambient-air exposures are of interest because the entire U.S. population will potentially be  
2 exposed to direct emissions and their atmospheric transformation products.  
3 Microenvironments, especially garages and refueling areas, are of interest because they  
4 typically result in higher exposures to certain emissions (e.g., methanol and formaldehyde)  
5 and, therefore, may have higher health risks. Other exposure situations of potential interest  
6 exist (e.g., within vehicles in transit); however, the relative importance of various  
7 microenvironments will be determined from the results of future studies of air quality and  
8 exposures. Dermal and oral exposures associated with certain situations (e.g., accidents) are  
9 also included to a limited extent. Although the range of potential human health issues is  
10 recognized to be quite broad (e.g., health could be affected by drinking water that has  
11 become contaminated by alternative fuels), assessment of these issues awaits more  
12 information on the potential extent of such exposures.

13 Health effects are dependent upon the nature of the exposure scenario (i.e.,  
14 concentration, duration, and dose-rate) and the pollutant mixture. At present, it appears that  
15 M85 will have significantly more market penetration than M100, making risk assessment of  
16 M85 a higher priority. However, there apparently has been no published health effects  
17 research on M85. Very limited understanding can be derived from the data bases on  
18 individual components of key interest (e.g., methanol and formaldehyde) and on combustion  
19 mixtures of conventional gasoline, but such information is inadequate for quantitative health  
20 risk assessment of either M100 or M85.

21 Assessing the health risks of methanol fuels compared to gasoline will be difficult,  
22 given the complexity of the changes in direction of health effects. For example, there is  
23 likely to be some degree of reduction in health risks from O<sub>3</sub>, benzene, 1,3-butadiene, and  
24 formaldehyde (in ambient air); an increase in health risks of methanol and formaldehyde  
25 (in microenvironments); and an unknown change in the cancer and noncancer risks of  
26 combustion and evaporative emissions, with and without atmospheric transformation.

27 This background and rationale section is limited to the health effects of methanol,  
28 formaldehyde, and DMS. Other relevant information on the health effects of O<sub>3</sub>, NO<sub>2</sub>, and  
29 CO can be found in air quality criteria documents (U.S. Environmental Protection Agency,  
30 1986a, 1989g, 1990f); conventional gasoline is discussed in Section 2.2.2.1.

### 3.2.2.1.1 *Methanol*

Human exposure to methanol can result from inhalation, ingestion, or dermal contact. The distribution of methanol to tissues and organs depends on many factors, including route of entry, partition coefficients, blood flow rates, metabolic and excretion rates, and other physiological factors. The toxicity of methanol may be a function of the alcohol itself and/or its metabolites. The pharmacokinetics of methanol and these metabolites are just beginning to be understood (Black et al., 1985b; Johlin et al., 1987; Moore and Lee, 1987a,b).

Some discussions of methanol body burdens have indicated that for inhalation exposure under high exposure scenario conditions (personal garage, 150 ppm for 15 min at twice the resting ventilation rate), the added body burden of methanol would be about equivalent to that resulting from ingestion of two 12-oz diet beverages containing 555 mg aspartame/L (Health Effects Institute, 1987). (Aspartame hydrolyzes in the gastrointestinal tract, with 10% becoming free methanol [Stegink, 1984].) Although some conservative assumptions were made in estimating these body burdens, basic questions must first be answered about possible pharmacokinetic differences between routes of exposure. For example, inhaled methanol may reach the brain without first passing through the liver, which is the major organ of methanol metabolism. Bypassing the liver could result in a higher delivered dose to the brain than might otherwise occur. Thus, it is difficult at present to relate the toxicological potential of methanol body burdens resulting from different routes of exposure, even though methanol distributes readily to tissues and organs in proportion to their water content (Yant and Schrenk, 1937). A related issue concerns the identification of an appropriate biomarker(s) of exposure, especially at low levels of exposure, because the correlations of blood and urinary levels of methanol and formate with the toxic actions of methanol are not well characterized.

Methanol is cleared from the body by three routes: renal excretion, direct pulmonary excretion, and metabolism. Total body clearance rates depend on exposure concentrations. Half-times are more than 1 day for high doses and about 3 h for doses less than 0.1 g/kg (Health Effects Institute, 1987). The change in half-life is presumably due to a change from linear to nonlinear metabolism kinetics at the higher doses. At low levels, methanol disappearance follows first-order kinetics. Within the linear range, the renal, pulmonary,

1 and metabolic routes account for 0.6%, 2.5%, and 97%, respectively, of the total body  
2 clearance rate (Health Effects Institute, 1987).

3 Nonprimates and primates have long been known to differ in pathways and rates of  
4 methanol metabolism (Gilger and Potts, 1955). These differences raise the issue of an  
5 appropriate animal model. Methanol is primarily metabolized to formaldehyde by a catalase  
6 peroxidation route in rats and by an alcohol dehydrogenase (ADH) system in primates. The  
7 first metabolic product, formaldehyde, is oxidized to formic acid (formate plus hydrogen ion)  
8 so rapidly that its accumulation has not been detected in the blood. Formate is eventually  
9 converted to CO<sub>2</sub>, the rate of removal being governed primarily by the available levels of  
10 folic acid. This complex pathway is less than one-half as fast in primates as in rats. At high  
11 methanol concentrations, an accumulation of formate in primates leads to systemic toxicity  
12 and toxic effects on the optic nerve. Rodents are less sensitive to methanol toxicity of the  
13 visual system because of their greater folate/folic acid levels and hence their capacity to  
14 metabolize formate (Health Effects Institute, 1987).

15 Horton (1988) concluded that rats would be an appropriate animal model at exposures  
16 less than 1,200 ppm because the methanol blood concentrations of experimental rats and  
17 monkeys were roughly the same after 6 h at these concentrations, and the blood formate  
18 levels were not different from background (control) levels. These dosimetric similarities,  
19 however, do not imply equivalent metabolic pathways. Swine have also been recently  
20 proposed as a promising animal model because of their comparability to human folate levels  
21 and metabolic pathways (Makar et al., 1990).

22 Some values of the parameters that characterize metabolic rates, V<sub>max</sub> and the  
23 Michaelis constant, have been reported for rats and monkeys, but not for humans (Watkins  
24 et al., 1970; Palese and Tephly, 1975; McMartin et al., 1977; Däfeldecker et al., 1981;  
25 Moore and Lee, 1987a,b). For the rat, parameter values are available for the methanol  
26 (catalase), formaldehyde, and formate reactions; only the methanol (ADH) and formate rates  
27 are available for the monkey (Horton, 1988). Parameter values that are missing can be  
28 estimated by allometric scaling between species; however, the validity of this approach  
29 should be verified.

1        Although the acute neurotoxic effects of ingested methanol are relatively well-known,  
2        its effects by other routes of exposure have not been well quantified. Visual impairment is  
3        the most prominent sign of acute, high-level methanol toxicity in humans and appears to be  
4        due primarily to a toxic metabolite of methanol, formate, acting on the optic nerve or retina.  
5        Methanol-exposed rats made folate-deficient through various treatments to simulate human  
6        metabolic characteristics have shown alterations in electroretinograms and other measures of  
7        visual function (Lee, 1989; Eells, 1991). In the study by Lee (1989), such effects were seen  
8        after exposure for 90 days to methanol vapor concentrations as low as 800 ppm. Gross  
9        structural damage to various brain regions (e.g., putamen and basal ganglia) has been  
10       documented in humans by necropsy and by noninvasive imaging techniques. In addition,  
11       neurotransmitter levels appear to be affected by methanol acting directly on the hypothalamus  
12       and striatum in rats, independently of acidotic changes induced by methanol dosing  
13       (Jeganathan and Namasivayam, 1989).

14       Low-level, chronic exposure to methanol has not been studied adequately to allow firm  
15       conclusions about the potential health effects (Health Effects Institute, 1987). Although the  
16       Japanese New Energy Development Organization (NEDO) sponsored several relevant studies,  
17       including one that exposed monkeys to air concentrations of 10, 100, or 1,000 ppm methanol  
18       for periods of 7, 19, or 29 mo, a "Summary Report" (New Energy Development  
19       Organization, 1987) of this work provides only limited information. Among the more  
20       striking findings noted in the NEDO Summary Report was an increase in the occurrence of  
21       "reactive astrocytes," or astroglial cells, in various central and peripheral nerves and neural  
22       structures (e.g., hypothalamus and cerebrum) after exposure to levels as low as 100 ppm for  
23       7 mo or more.

24       An experimental study of the neurobehavioral effects of acute exposures to methanol  
25       vapor was conducted by Cook et al. (1991). Twelve young adult males were exposed to  
26        $\sim 250 \text{ mg/m}^3$  ( $\sim 192 \text{ ppm}$ ) methanol and to air alone for counterbalanced 75-min periods,  
27       with each subject serving as his own control. Most of the changes in neurobehavioral  
28       endpoints were not statistically significant. However, some significant effects and trends  
29       were noted for a cluster of variables, including latencies of certain evoked potentials,  
30       performance on a test of memory retrieval, and subjective measures of fatigue and

1 concentration. Although limitations of this study, including the small number of subjects and  
2 low statistical power of the study, make it difficult to determine conclusively whether  
3 methanol vapor at the concentration used is capable of inducing neurobehavioral effects, it  
4 does suggest the need to follow up these findings with additional research.

5 A known target of methanol is the endocrine system and, in particular, reproductive  
6 hormones. Two reports have suggested that exposure of rats to concentrations as low as the  
7 American Conference of Governmental and Industrial Hygienists (ACGIH) threshold limit  
8 value (TLV) of 200 ppm for as little as 6 h results in significant reductions in circulating  
9 testosterone levels (Cameron et al., 1984, 1985). However, a recent attempt by EPA to  
10 replicate these findings was unsuccessful (Cooper et al., 1991). Although hormone levels  
11 were altered in rats exposed for as little as 1 to 3 h to 5,000 and 10,000 ppm methanol  
12 vapor, the direction and magnitude of the effects depended on whether the subjects had been  
13 acclimated to the handling and testing conditions. Nevertheless, methanol was demonstrated  
14 to be toxic to the testes at sufficiently high acute exposure levels. These findings are  
15 supported by a preliminary report (Lee and Brady, 1991), which indicates that, although  
16 testosterone synthesis was unaffected, normal age-related degeneration of the testes  
17 (subcapsular presence of vacuoles in the germinal epithelium) was accelerated in 18-mo-old  
18 folate-deficient male rats exposed to 800 ppm methanol vapor for 20 h/day for 13 weeks.  
19 Rats that were not folate deficient did not exhibit this effect. Further work is needed to  
20 determine the effects of various exposure durations on reproductive organs and functions.  
21 Preliminary EPA research suggests that the female reproductive system in rats may be  
22 sensitive to methanol in terms of hormonal cycling. More work is needed to verify this  
23 effect and its impact on reproductive function and subsequent fetal development.

24 The developmental toxicity of methanol vapor has received scant attention. One study  
25 exposed pregnant rats for 7 h/day during Gestational Days 1 to 19 (5,000 and 10,000 ppm)  
26 or 7 to 15 (20,000 ppm) (Nelson et al., 1985a). Significant increases in the number of  
27 malformations were found at 20,000 ppm, and significant reductions in fetal weight were  
28 found at 10,000 and 20,000 ppm, with an exposure-related trend evident in the percentage of  
29 litters with abnormal fetuses. Recent efforts by EPA to confirm these findings in mice  
30 appear to have extended the lowest-observed-adverse-effect level (LOAEL) downward. In a



1 preliminary report, Rogers et al. (1991) noted significant occurrences of fetal deaths and  
2 exencephaly in offspring of pregnant mice exposed to 5,000 and 15,000 ppm methanol vapor  
3 for 7 h/day during Gestational Days 6 to 15. The effects at 5,000 ppm were confirmed when  
4 a second study replicated that condition along with an exposure level of 2,000 ppm.  
5 At 2,000 ppm, the occurrence of exencephaly was not statistically significant, but further  
6 study is needed to ascertain whether or not 2,000 ppm constitutes a no-observed-adverse-  
7 effect level (NOAEL).

8 Another study investigated postnatal neurobehavioral development in rat pups that had  
9 been exposed prenatally to methanol (Infurna and Weiss, 1986). The pregnant dams received  
10 2% solutions of methanol as drinking water for 3 days during the latter part of pregnancy.  
11 Methanol-treated groups of pups took significantly longer than controls to initiate sucking on  
12 Day 1 after birth and to locate home nest material on Day 10. These developmental  
13 neurobehavioral effects are also of interest because of their consistency with reports relating  
14 prenatal ethanol exposure to reduced sucking ability in human infants (Martin et al., 1979)  
15 and impaired olfactory associative learning in rats. More refined inhalation dose-response  
16 information is needed on the developmental toxicity of methanol.

17 Limited, but suggestive, information on relatively low-level effects of methanol on  
18 immune, cardiovascular, and hepatic functions has been reported. Like ethanol, methanol  
19 potentiates the effects of other hepatotoxicants (Cantilena et al., 1979; Cornish and Adefuin,  
20 1967; Simmons et al., 1990, 1991; Traiger and Plaa, 1971). In addition to these effects,  
21 special risk populations need to be identified and investigated. For example, folate  
22 deficiency is quite common in pregnant women and could, because of the role of the  
23 tetrahydrofolate system in metabolizing formate (McMartin et al., 1977; Johlin et al., 1987),  
24 exacerbate the effects of methanol in this population. Children are also a special risk  
25 population, particularly in view of their tendency to ingest nonpotable substances. Unless  
26 special precautionary measures are taken, substitution of methanol fuels for gasoline could  
27 result in a several-fold increase in mortalities and serious poisonings from accidental  
28 ingestions by children, based on data from the American Association of Poison Control  
29 Centers (Litovitz, 1988). To illustrate, a mere 12 mL of M85 fuel ingested by a 10-kg  
30 1-year-old child could be lethal.

### 3.2.2.1.2 Formaldehyde

Formaldehyde is a highly reactive aldehyde due to its carbonyl moiety. As a component of normal metabolism, it is involved in the biosynthesis of amino acids, lipids, and nucleotides. It is rapidly metabolized to formic acid and enters the 1-carbon pool to eventually be released as CO<sub>2</sub>. Due to its reactivity, formaldehyde can undergo diverse chemical interactions with cellular components, including alkylation reactions with nucleic acid and proteins. At environmental concentrations, this chemical reactivity and rapid rate of metabolism are thought to preclude significant uptake to sites remote from the contact site tissue (e.g., the respiratory tract for inhalation exposures).

Due to its reactivity, formaldehyde is a potent irritant of the eyes and mucous membranes in humans exposed at low concentrations (U.S. Environmental Protection Agency, 1987b). Upper respiratory (nose and throat) irritation have been documented in numerous human exposure studies to occur in the range of 0.1 to 3.0 ppm (U.S. Environmental Protection Agency, 1987b; Grindstaff et al., 1991). Exposure-response gradients for these effects have also been demonstrated (Ritchie and Lehnen, 1987; Horvath et al., 1988). Kane et al. (1979) determined the concentration associated with a 50% decrease in respiratory rate (RD<sub>50</sub>) of Swiss-Webster mice to be 3.13 ppm (95% confidence limit of 2.54 to 3.97 ppm). Buckley et al. (1984) showed minimal exfoliation, erosion, ulceration, and necrosis in the respiratory epithelium, but not the olfactory epithelium, in mice exposed to formaldehyde at the RD<sub>50</sub> for 6 h/day for 5 days. These authors predict that 0.01RD<sub>50</sub> or 0.03 ppm is the minimal sensory irritation level in humans and that 0.001RD<sub>50</sub> is the recommended highest concentration for an air standard. At higher concentrations, the upper airway irritation becomes severe. Sensory and irritant thresholds, based on a larger data base of all age groups in normal subjects and individuals with respiratory tract symptoms need to be established (Consensus Workshop on Formaldehyde, 1984).

Lower airway irritation, as characterized by cough, wheezing, and chest tightness, has been reported in humans exposed to higher ranges of formaldehyde (5 to 30 ppm) (Consensus Workshop on Formaldehyde, 1984). Exposures between 50 and 100 ppm cause serious injury such as pulmonary edema, inflammation, pneumonitis, and pneumonia. Prevalences

1 of cough and sputum production or chest symptoms (tightness and pain) also increase in  
2 populations exposed at levels of formaldehyde below 1 ppm (Broder et al., 1988a,b,c;  
3 Horvath et al., 1988). Pulmonary function investigations have not been performed with  
4 prescribed protocols or reported consistently across studies, but some have indicated transient  
5 or acute effects on ventilation mechanics (U.S. Environmental Protection Agency, 1987b;  
6 Grindstaff et al., 1991). Chronic ventilation impairment as an outcome has not been  
7 adequately addressed in any investigations.

8        Formaldehyde is definitely a primary dermal sensitizing agent, inducing allergic contact  
9 dermatitis (Type IV) and probably immunologic contact urticaria (probably Type I)  
10 (Consensus Workshop on Formaldehyde, 1984). The evidence for allergic airway responses  
11 to inhaled formaldehyde is less extensive and the potential for low-to-moderate formaldehyde  
12 exposures to cause sensitization remains equivocal. Sufficiently well-controlled scientific  
13 studies are not available to definitively establish the development of respiratory tract allergy  
14 to formaldehyde gas per se. The majority of the existing studies were designed as  
15 prevalence studies. The interpretation of findings is uncertain due to questions about quality  
16 of the environmental exposure measurements, the nature of the test materials, the methods of  
17 testing, definition of symptomatology, lack of testing for specific versus nonspecific  
18 sensitivity, and lack of unexposed comparison or control groups (Consensus Workshop on  
19 Formaldehyde, 1984; Grindstaff et al., 1991). Formaldehyde-induced asthma has been  
20 documented with bronchoprovocation tests in dialysis nurses exposed to high levels of  
21 formaldehyde (Hendrick, 1983), but another study of 13 patients with a history suggestive of  
22 asthma induced by formaldehyde found no evidence of bronchospasm in response to  
23 formaldehyde levels as high as 3 ppm (Frigas et al., 1984). Cohen et al. (1989) reported  
24 respiratory distress syndrome in an individual exposed to phenol-formaldehyde resin, but the  
25 other agents in the resin preclude isolating formaldehyde as the causative agent. Brooks  
26 et al. (1985) also noted reactive airway dysfunction syndrome and exposure to formaldehyde.  
27 Thrasher et al. (1988) observed elevated immunoglobulin G, immunoglobulin E, and  
28 immunoglobulin M antibodies to formaldehyde human serum albumin in six cases with  
29 previous occupational formaldehyde exposure, although consistent elevations were not  
30 observed and the lack of exposure characterization again precludes definitive causality.

1           It is also not known whether or not there are susceptible groups to inhalant sensitization  
2 to formaldehyde. Conceivably, asthmatics might be more sensitive to the irritant action of  
3 formaldehyde (Consensus Workshop on Formaldehyde, 1984). Green et al. (1987),  
4 however, showed no differences between asthmatics and nonasthmatics in the statistically  
5 significantly increased reporting of upper respiratory symptoms (nose, throat, and eye  
6 irritation) from exposure to 3 ppm formaldehyde for 1 h during mild or heavy exercise.  
7 Nonasthmatics showed small but consistent decrements in forced expiratory volume (at 1 and  
8 3 s) and forced vital capacity (FVC), whereas no decrements were observed among  
9 asthmatics. Green et al. (1987) posed the hypothesis that asthmatics may have an increased  
10 mucus-producing capabilities that alter the amount of formaldehyde available for irritation.  
11 Uba et al. (1989) observed that burning and watering eyes were statistically significantly  
12 reported more frequently by medical students exposed to formaldehyde who were asthmatic  
13 than by healthy students similarly exposed. Lower airway irritation (cough, chest symptoms,  
14 and dyspnea) and pulmonary function were not different between asthmatics and  
15 nonasthmatics in this study.

16           Other noncancer endpoints recently investigated for formaldehyde include  
17 immunotoxicity and neurotoxicity. With respect to the immunotoxicity data, Grindstaff et al.  
18 (1991) conclude, "these newer studies have failed to overcome problems related to showing  
19 that formaldehyde was the causal agent, determining if the observed effects are representative  
20 of large population groups, and understanding of the potential health consequences of  
21 immune stimulation." Reports in the literature have linked formaldehyde with a number of  
22 behavioral and physiological effects such as thirst, dizziness, apathy, inability to concentrate,  
23 and sleep disturbances (U.S. Environmental Protection Agency, 1987b). Only one report  
24 published since that review, Kilburn et al. (1987), attempted to assess neurologic function,  
25 but interpretation of the negative results of the study is limited by deficits in its experimental  
26 design, including lack of a control group, lack of control on selection bias, and limited  
27 exposure characterization (Grindstaff et al., 1991). The Consensus Workshop on  
28 Formaldehyde (1984) felt that formaldehyde posed little, if any, risk as a potential human  
29 teratogen. The Workshop also noted that no adequate reproductive or developmental studies  
30 existed using inhalation exposures and that studies to investigate the possible differences in

1 the kinetics and metabolism of formaldehyde with differing routes of exposure in laboratory  
2 animals would help to evaluate if these endpoints were of concern.

3 The reactivity properties of formaldehyde are also likely to contribute to its  
4 carcinogenicity potential. The current EPA carcinogenicity assessment for lifetime exposure  
5 on the Integrated Risk Information System (IRIS, 1991) classifies formaldehyde as B1, a  
6 probable human carcinogen, based on limited evidence in humans and sufficient evidence in  
7 laboratory animals. Based upon the induction of nasal squamous-cell carcinoma in male rats  
8 in the Kerns et al. (1983) study described below, the EPA has developed an inhalation slope  
9 factor of  $4.5 \times 10^{-2}$  per mg/kg/day. This results in an upper bound cancer unit risk of  
10  $1.3 \times 10^{-5}$  per  $\mu\text{g}/\text{m}^3$ . Additional animal data regarding the carcinogenicity of formaldehyde  
11 became available during the 1988 to 1990 period. The EPA is in the process of evaluating  
12 the newer data and will likely recommend a modified unit risk value for inhalation exposure,  
13 once the assessment is completed in 1992. The discussion to follow describes several of the  
14 cancer bioassays as well as research on mechanisms likely to be involved in the responses.  
15 At least 28 relevant epidemiologic studies have been conducted. Among these, two cohort  
16 studies (Blair et al., 1986, 1987; Stayner et al., 1988) and one case-control study (Vaughan  
17 et al., 1986a,b) were well-conducted and specifically designed to detect small to moderate  
18 increases in formaldehyde-associated human risks. Blair et al. (1986, 1987) studied workers  
19 exposed to formaldehyde largely through resin formation and observed significant excesses in  
20 lung and nasopharyngeal cancer deaths. Despite a lack of significant trends with increasing  
21 concentration or cumulative formaldehyde exposure, lung cancer mortality was significantly  
22 elevated in analyses with or without a 20-year latency allowance. No explicit control was  
23 made for smoking status, however. Stayner et al. (1988) reported statistically significant  
24 excesses in mortality from buccal cavity tumors among formaldehyde-exposed garment  
25 workers. Vaughan et al. (1986a,b) controlled for smoking and alcohol consumption and  
26 examined occupational and residential exposures. This study showed a significant association  
27 between nasopharyngeal tumors and having lived 10 or more years in a mobile home.  
28 No exposure measurements were available. Although there is considerable evidence for  
29 increased cancer risk in the above studies, EPA has categorized the human evidence for  
30 carcinogenicity of formaldehyde as "limited", primarily owing to possible exposures to other

agents. Newer studies support these data but do not provide definitive evidence for a causal association between formaldehyde and human cancer due to limited ability to detect small to moderate increases in risk (Grindstaff et al., 1991). Three studies carried out in Scandinavia (Edling et al., 1988; Holmstrom et al., 1989; Boysen et al., 1990) on individuals occupationally exposed to formaldehyde at the time of study showed higher scores of histological abnormalities (metaplasia and mild dysplasia) in the nasal mucosa of these workers compared to a small group of workers not occupationally exposed.

The IARC reviewed essentially the same literature as that evaluated on the IRIS and concluded there was "limited" evidence of carcinogenicity to humans, defined as "a positive association has been observed between exposure to the agent and cancer for which a causal interpretation is considered credible, but chance, bias or confounding could not be ruled out with reasonable confidence" (International Agency for Research on Cancer, 1987). The International Agency for Research on Cancer (1987) believed the evidence was strongest for cancers of the nose and nasopharynx because exposure-response relationships had been observed in several studies. This group also noted an excess in lung cancer in several studies, but that exposure-response gradients were not consistently demonstrated across all studies. The excesses in mortality from leukemia and brain cancer were primarily limited to occupations with formalin exposure, but IARC believed that factors other than formaldehyde might have increased the risk for these cancers, a view shared by the Consensus Workshop on Formaldehyde (1984).

The Universities Associated for Research Education in Pathology (UAREP) reviewed the same body of literature and commented only on the determination of causality. The UAREP concluded that a causal relationship has not been established for cancer at any site and noted that if such a causal relationship exists, the excess risk must be small (Universities Associated for Research Education in Pathology, 1988).

Important issues for the epidemiologic data, particularly in view of experimental data in monkeys (described below) showing no evidence of formaldehyde DNA-protein adducts or of cellular proliferation in the maxillary sinuses or lungs, is the relevance of grouping cancer of the nasal cavity with that of the nasal sinuses for classification purposes by the International Classification of Diseases. Questions pertaining to exposure characterization and dosimetry

are also important because some studies suggest that nasopharyngeal and sinonasal cavity risks may be enhanced with simultaneous exposure to particles or wood dust (Blair et al., 1987; Olsen et al., 1984).

Carcinogenicity for the nasal epithelium has been investigated in Syrian Golden Hamsters (Dalbey, 1982) and in three strains of rats: Fisher 344 (F344) (Kerns et al., 1983; Tobe et al., 1985), Sprague-Dawley (Albert et al., 1982; Sellakumar et al., 1985), and Wistar (Feron et al., 1988; Woutersen et al., 1989); C575L/6 × C3HF1 mice (Kerns et al., 1983). The principal evidence indicating that formaldehyde is carcinogenic derives from the inhalation studies in F344 rats and C575L/6 × C3HF1 mice conducted by the Chemical Industry Institute of Toxicology (CIIT) in which groups of rats and mice (120/sex/group) were exposed whole-body to 0, 2.0, 5.6 and 14.3 ppm of formaldehyde for 6 h/day, 5 days/week for 24 mo (Kerns et al., 1983). Squamous-cell carcinomas of the nasal cavity were observed in 44% of the rats (51/117 males and 52/115 females) exposed to 14.3 ppm and in 0.9% of the rats (1/119 male and 1/116 female) exposed to 5.6 ppm. Tumor incidences were much less in mice, 0.9%, and occurred only at the highest (14.3 ppm) concentration. Chang et al. (1983) showed that the differences in observed incidences between rats and mice may have been due to differences in dosimetry between the species. Mice are more sensitive to the sensory irritant effects of formaldehyde and, in response, reduce their minute volumes to a greater extent than do rats. Thus, at the 14.3 ppm concentration, mice actually inhaled approximately only half as much formaldehyde as did the rats.

It is not known whether differences in dosimetry or species sensitivity accounts for the lack of carcinogenicity observed in the 88 male Syrian hamsters exposed to 10 ppm formaldehyde for 5 h/day, 5 days/week for their lifetime by Dalbey (1982). No respiratory cancers were detected, although the study is also limited because only two microscopic sections of the nose were examined for each animal.

Another study in F344 rats completed at CIIT (Monticello, 1990) supports the results of the 1983 study, in that nasal tumors were found with formaldehyde exposures to 10 and 15 ppm. At 0, 0.7, 2 and 6 ppm, no tumors were observed (Monticello, 1990). Other than that fewer animals were allotted to exposure groups in this study, the reasons for the

1 difference in results at 6 ppm compared to those in Kerns et al. (1983) are unclear  
2 (Grindstaff et al., 1991). Tobe et al. (1985) exposed groups of male F344 rats to 0, 0.3,  
3 2.0, and 15 ppm of formaldehyde vapor for 6 h/day, 5 days/week for 28 mo and also  
4 observed squamous-cell carcinomas only at the high exposure concentration.

5 Albert et al. (1982) and Sellakumar et al. (1985) showed significant incidences of  
6 squamous-cell carcinomas of the nasal cavity in Sprague-Dawley rats exposed to 15 ppm  
7 formaldehyde for 6 h/day, 5 days/week for life. Feron et al. (1988) showed a low incidence  
8 (4.5%) nasal tumors in Wistar rats exposed to 20 ppm for 6 h/day, 5 days/week for  
9 13 weeks and held for observation for up to 117 weeks, indicating a carcinogenic potential of  
10 formaldehyde after short-term exposure to high concentrations.

11 That formaldehyde-induced nasal tumors were found mainly at exposure concentrations  
12 that also induced severe degenerative, hyperplastic, and metaplastic changes in the nasal  
13 epithelium suggested that increased cytotoxicity and cell proliferation may play a role in the  
14 induction of nasal cancer by formaldehyde. To study the significance of cytotoxicity to the  
15 nasal mucosa to induction of nasal tumors by formaldehyde in rats, Woutersen et al. (1989)  
16 conducted a long-term inhalation study in which male Wistar rats with either damaged  
17 (bilateral intranasal electrocoagulation) or undamaged nasal mucosa were exposed to 0.1,  
18 1.0, or 10 ppm formaldehyde for 6 h/day, 5 days/week for 28 mo. The results showed that  
19 compound-related rhinitis and hyperplasia developed in rats with either damaged or  
20 undamaged tissue exposed to 10 ppm, but the incidence of these lesions was greater in the  
21 rats with damaged noses. Exposure to 10 ppm of formaldehyde for 28 mo produced a  
22 significant incidence of nasal squamous-cell carcinomas in rats with damaged noses but not in  
23 rats with intact tissues. No compound-related nasal neoplasms or cytotoxic effects were  
24 observed at the other concentrations in rats with either damaged or undamaged tissues.  
25 Preliminary results of an ongoing chronic study in F344 rats (Monticello and Morgan, 1990)  
26 lend some support to the hypothesis that cell proliferation may play an important role in  
27 formaldehyde-induced nasal carcinogenesis because there appears to be a correlation between  
28 sustained cell proliferation and tumor induction. Statistically significant elevations in cell  
29 proliferation and inflammation scores have been confined to the high concentration groups  
30 (10 and 15 ppm), as were tumors, through the 16-mo analysis of this 2-year study. There



1 does not appear to be site-specificity with respect to proliferation and tumor induction,  
2 however, as the maxilloturbinate is a region with high proliferation and no tumor induction.

3 Other studies have also been directed at investigating other possible mechanisms of  
4 action of formaldehyde. Morgan et al. (1986) reexamined the histologic sections from the  
5 nasal passages of the tumor-bearing rats in the Kerns et al. (1983) study and found that the  
6 majority of the squamous-cell carcinomas occurred on the lateral side of the anterior portion  
7 of the nasoturbinate and adjacent lateral wall (57%) or the midventral nasal septum (26%).  
8 About 10% were on the dorsal septum and the roof of the dorsal meatus. Only one  
9 squamous-cell carcinoma was found on the medial aspect of the maxilloturbinate, a region  
10 expected to have a high "delivered dose" due to airflow patterns influencing regional  
11 deposition. Because inflammation and sustained cell proliferation, but not tumors, occurred  
12 in this latter region, the authors postulate that local tissue sensitivity may be an important  
13 factor in addition to regional exposure.

14 Swenberg et al. (1983) used a <sup>3</sup>H-thymidine labeling technique to index cell  
15 proliferation in rats and mice exposed to 0.5, 2, 6 and 15 ppm formaldehyde for 6 h/day for  
16 3 to 5 days. A 10- to 20-fold increase, as compared with controls, was found in the labeling  
17 index (defined as the proportion of cells in a given population that are in the process of DNA  
18 replication) in the nasal epithelium of rats at both 2 and 18 h after exposure to 6 or 15 ppm  
19 of formaldehyde, but only slight increases in rats exposed to 2 or 0.5 ppm. In mice, this  
20 index of increased cell proliferation was evident only at 15 ppm and was much lower than in  
21 rats. Zwart et al. (1988) studied the effects of low concentrations on cell proliferation.  
22 Wistar rats were exposed to 0, 0.3, 1, and 3 ppm for 6 h/day, for 3 days or for 5 h/day for  
23 13 weeks. This study showed an initial (at 3 days) high proliferation rate in the primary site  
24 of tumors in the other investigations in the 1 and 3 ppm exposed rats. The dose-response  
25 was log-linear with about a 10-fold increase in proliferation from the 1 to 3 ppm group.  
26 After 13 weeks of exposure, the cell turnover rate in this region tended to be slightly lower  
27 than in controls. In the anterior region, an increase in proliferation was seen at both time  
28 points. Cell proliferation in rats exposed to 0.3 and 1 ppm was not different from controls.  
29 Together, these studies indicate that a significant increase in cell proliferation occurred at the  
30 higher concentrations with a marked species difference. In rats, the proliferation increase

1 lacks site specificity with respect to observed areas of tumor induction, and it appears to be  
2 transient.

3 Both in vitro and in vivo studies (Morgan et al., 1983, 1986) have shown a clear  
4 concentration-dependent effect of formaldehyde on the mucociliary apparatus of rats.  
5 At 15 ppm, there was significant inhibition of mucociliary activity, whereas only slight  
6 effects were noted at 2 or 6 ppm. This range appears to correspond to the range where  
7 dose-responses in nasal mucosa cytotoxicity and carcinogenicity were observed (Grindstaff  
8 et al., 1991). It has, therefore, also been postulated that the mucus layer may serve as a  
9 protective trap that removes much inhaled formaldehyde at low concentrations, whereas at  
10 high concentrations, the clearance is inhibited, the layer becomes saturated, and a greater  
11 amount of formaldehyde reaches the underlying epithelium. Concentration-by-time  
12 ( $C \times T$  or "dose-rate") studies of Wilmer et al. (1989) and Feron et al. (1988) have also  
13 recently indicated that concentration is of greater importance than duration of exposure in  
14 eliciting toxic responses and that the exposure regimen (intermittent vs. continuous also has  
15 an influence).

16 The kinetics of covalent binding of inhaled formaldehyde to DNA in the respiratory  
17 tract of F344 rats has been the focus of extensive research at CIIT (Casanova-Schmitz et al.,  
18 1984; Casanova and Heck, 1987; Casanova et al., 1989, in press) as a possibly important  
19 factor in the carcinogenic mechanism. Together, these studies have shown that formaldehyde  
20 forms DNA-protein cross-links (DPX) under in vivo conditions and that the rate of DPX  
21 formation is more closely related to the intracellular (delivered) concentration of  
22 formaldehyde than to the administered concentration. The DPX have been demonstrated in  
23 rat nasal tissues exposed to formaldehyde at 0.3, 0.7, 2, 6, and 10 ppm for 6 h, in a  
24 nonlinear relationship to formaldehyde exposure concentration. Based on these data, a model  
25 has been developed that takes into account the influx of labeled formaldehyde ( $^3\text{H}$ - and  
26  $^{14}\text{C}$ -formaldehyde used experimentally) into the nasal mucosa cells; the oxidative metabolism  
27 of intracellular formaldehyde; and the elimination of formaldehyde by other routes, including  
28 diffusion and other metabolic transformations.

29 More recent efforts have expanded some of the above approaches to investigate the  
30 effects of formaldehyde in the nasal tissues of rhesus monkeys as a species more closely

1 related to humans in terms of nasal anatomy, physiology, and biochemistry (Casanova et al.,  
2 in press; Monticello and Morgan, 1989). Monkeys were exposed head-only to  
3 <sup>14</sup>C-formaldehyde at concentrations of 0.7, 2, and 6 ppm for 6 h. The DPX were  
4 demonstrated in the nasal mucosa at concentrations  $\geq 0.7$  ppm. Low, but statistically  
5 significant, concentrations of DPX were detected in the larynx/trachea/carina and major  
6 intrapulmonary airways at 2 ppm. No DPX were detected in the maxillary sinuses or lung at  
7 any concentration. The pattern of DPX in the monkey nasal mucosa could be predicted by a  
8 simple pharmacokinetic model that took into account the local tissue concentration of  
9 formaldehyde, the extraction ratio, and the total quantity of DNA per tissue sample. The  
10 formation of DPX and the characteristics of nasal lesions induced by formaldehyde  
11 (Monticello, 1989) in monkeys demonstrate qualitative similarities between this species and  
12 rats. More importantly, monkeys and rats also have significant quantitative similarities  
13 (i.e., DPX in the monkey can be semiquantitatively predicted from those in the rat by  
14 adjusting for differences in minute volume and quantity of DNA). The formation of DPX  
15 was shown to be as much as an order of magnitude lower than that in rats and thus this  
16 modeling has major implications for extrapolation to human risk estimates from the  
17 laboratory animal data (Casanova et al., in press). That no DPX or lesions were  
18 demonstrated in the maxillary sinuses is also important to the evaluation of risk from  
19 epidemiologic studies because they use classifications of the combined tumors of the sinus  
20 with those of the nasal cavity when assessing human risks.

21 Expansion of these acute modeling efforts to incorporate longer term data is critical to  
22 ascertain the relevant mechanisms of formaldehyde carcinogenicity in order to diminish  
23 uncertainties in human risk assessments. Because formaldehyde is both DNA reactive and a  
24 potent cytotoxicant, integration of the mechanisms discussed above would best be taken into  
25 account by a biologically based approach. In particular, it appears that preneoplastic changes  
26 in the nasal passages must be distinguished from other noncancerous, adaptive changes.  
27 Measurement of the extent and duration of site-specific cell proliferation must be done in  
28 conjunction with elucidation of the biochemical and molecular alterations that influence the  
29 susceptibility of these sites to the carcinogenic activity of formaldehyde.

### 3.2.2.1.3 *Dimethyl Sulfate*

The human carcinogenicity data are inadequate for assessing cancer risk from exposure to DMS. Druckrey et al. (1966) reported four cases of bronchial carcinoma in a group of 7 to 11 workers occupationally exposed to DMS. Although occasional DMS intoxication was noted in all the workers, additional information regarding the exposures are not available. The International Agency for Research on Cancer (1979) reviewed an unpublished epidemiologic study by S. Pell. Among workers exposed occupationally to DMS (number unspecified), six cancer deaths were reported compared with an expected mortality of 2.4. Respiratory tract cancer was responsible for three of the deaths (1.02 expected). Neither the increased incidence of respiratory tract cancer nor the increased rate of cancer at all sites was statistically significant.

Both injection and inhalation of DMS resulted in the induction of tumors in experimental animals. Druckrey et al. (1970) exposed 27 and 20 BD rats to 10 or 3 ppm DMS vapor, respectively, for 1 h/day, 5 days/week for 130 days. One rat in the high dose group and two in the low dose group developed nervous system tumors. Although no concurrent control group was reported, the results are considered to be significant because these types of tumors are very rare in BD rats. Additional tumors included three squamous-cell carcinomas of the nasal epithelium and a lymphosarcoma in the high dose group and one squamous-cell carcinoma in the low dose group. Schloegel and Bannasch (1970) reported tumors in the lungs, thorax, and nasal passages of hamsters, rats, and mice exposed to 0.5 or 2.0 ppm DMS vapor. The significance of these results, however, is uncertain because control data were not reported, nor were tumor incidences tabulated by species or dose.

Injection of 8 and 16 mg/kg/week DMS for approximately 1 year resulted in injection-site sarcomas in 7/11 surviving low-dose rats and 4/6 high-dose rats plus 1 hepatic carcinoma in a low-dose rat (Druckrey et al., 1966). A single subcutaneous injection of 50 mg/kg induced injection site tumors in 7/15 rats (Druckrey et al., 1970). In the same study, a single intravenous injection of 20 mg/kg DMS in BD rats on Day 15 of gestation induced malignant tumors in 7/59 offspring.

Despite the poor quality of the studies, because of the high response rates and the induction of rare tumor types, the data are considered to be "sufficient" to indicate

1 carcinogenicity in test animals. Based upon sufficient evidence for cancer in animals and  
2 inadequate data in humans, DMS was considered by the EPA to best fit into  
3 weight-of-evidence category B2 and is therefore considered to be a probable human  
4 carcinogen. The International Agency for Research on Cancer (1979) has classified DMS  
5 into category 2A and thus also considers it to be a probable human carcinogen.

6 A quantitative estimate of cancer potency from either oral or inhalation exposure is not  
7 available at this time.

### 8 9 **3.2.2.2 Ecosystem Effects**

#### 10 ***3.2.2.2.1 Terrestrial Ecosystem Effects-Atmospheric Exposures***

11 Releases of methanol and its combustion products into the atmosphere from production,  
12 storage, transportation, and vehicle exhaust may pose a threat to ecosystems (Weinstein and  
13 Birk, 1989). The use of methanol as a replacement fuel within the alternative fuels program  
14 may increase the atmospheric load of this alcohol. Also, the atmospheric concentrations of  
15 other toxic chemicals (e.g., formaldehyde, formic acid) may increase or decrease, depending  
16 on emissions and vehicle control technology. In addition, exposures to atmospheric  
17 transformation products such as O<sub>3</sub> and formaldehyde are expected to change. Within the  
18 methanol ecosystem effects assessment, comparisons need to be made with conventional  
19 gasoline and diesel fuel combustion products (e.g., CO, CO<sub>2</sub>, NO<sub>x</sub>, VOCs, and PM) and  
20 transformation products (e.g., O<sub>3</sub> and PAN) to evaluate which fuel poses the greatest hazard  
21 to terrestrial ecosystems.

22 As in the case of conventional fuels, the degree of ecological impact of methanol and  
23 its combustion and transformation products will depend upon (1) emission patterns and  
24 concentrations, (2) pollution deposition patterns and exposure to organisms, and  
25 (3) sensitivity of the biota (Weinstein and Birk, 1989). Each item represents an area that  
26 requires investigation by specific research projects for a methanol ecological risk assessment.

27 The effects of some of the conventional-fuel pollutants (e.g., PM, SO<sub>x</sub>, NO<sub>x</sub>, O<sub>3</sub>) on  
28 terrestrial biota are documented in the various Air Quality Criteria Documents (e.g., U.S.  
29 Environmental Protection Agency, 1982a,b; 1986a) and other literature (e.g., Smith, 1990;  
30 Newman and Schreiber, 1988). However, the potential ecological impacts of methanol-fuel

1 pollutants (e.g., methanol, formaldehyde, formic acid) are not known. Laboratory  
2 investigations of a few plant species show that methanol, formaldehyde, and formic acid may  
3 inhibit root and leaf growth, seedling development, and/or seed germination (Table 3-8).  
4 The effects of these chemicals on animals may vary from mucous membrane and respiratory  
5 tract irritation to behavioral changes, depending upon the concentration and exposure  
6 duration (Newman and Schreiber, 1988). A complete analysis of the impact of these  
7 chemicals on plants and animals cannot be ascertained from the literature because of limited  
8 references, unreliable data, and insufficient concentrations/exposure scenarios; therefore,  
9 research must be conducted to fill these information gaps.

10 Ecological perturbations caused by methanol-fuel pollutant deposition on terrestrial  
11 ecosystems may have ramifications through all levels of biological organization, depending  
12 on the duration and severity of pollutant exposure and organism sensitivity (see Figure 2-9).  
13 Although the adverse impacts of air pollution effects on ecosystems cannot be specified in  
14 detail, as biota react differently to air pollution stress, the following generalized events may  
15 be observed and apply similarly to plants and animals even though differences in the pathway  
16 of exposure exist (Bormann, 1985): (1) disruption of biochemical or physiological processes;  
17 (2) reduction in growth, reproduction, and abundance of sensitive individuals or populations;  
18 and (3) changes in the composition, structure, and function of communities and ecosystems.  
19 The impacts of air pollution on vegetation is better documented than for wildlife or soil  
20 biota.

21 Vegetation and soil are receptors of wet and dry pollutant deposition because of the  
22 large surface areas exposed to the atmosphere (Foster, 1991). Pollutants enter into plants  
23 through the leaves or roots, depending on the site of deposition, physicochemical properties  
24 of the contaminants, and plant morphology. Biochemical processes are the first site of action  
25 within the plant (Foster, 1991). If enzymatic degradation detoxifies the pollutant, then no  
26 injury will occur. However, if the pollutant or its metabolites are not rendered harmless,  
27 then alterations in plant metabolism may result in foliar injury, altered carbohydrate and  
28 nutrient allocation, and reduced growth and reproductive capability. The degree of impact to  
29 the plant will depend on the pollutant toxicity, exposure pattern, and plant sensitivity. Acute  
30 exposures usually cause observable morphological damage within the short term, such as

**TABLE 3-8. SUMMARY OF METHANOL, FORMALDEHYDE, AND FORMIC ACID POTENTIAL EFFECTS ON PLANTS<sup>a</sup> AND FISH<sup>b,c</sup>**

| Species             | Exposure                    | Effects <sup>d</sup>                   |
|---------------------|-----------------------------|--|
| <b>Methanol</b>     |                             |  |
| Soybean             | 1,900 ppm, liquid, 98 h     | Root dry mass decrease                 |
| Lupine              | 1,000 ppm, liquid, 24 h     | Root dry mass decrease                 |
| Impatiens           | 1,000,000 ppm, liquid, 24 h | Pollen grain germination decrease      |
| Cotton              | 25 ppm, liquid, 5 h         | Fruit ethylene increase                |
| Wheat               | 1,900 ppm, liquid, 7 days   | Leaf cell size decrease                |
| Sunflower           | 100 ppm, liquid, 24 h       | Seedling root injury                   |
| Pea                 | 100 ppm, liquid, 24 h       | Seedling root size increase            |
| Plantago            | 0.006 ppm, gas, ---         | Shoot dry mass decrease                |
| Plantago            | 0.009 ppm, gas, ---         | Shoot dry mass decrease                |
| White clover        | 0.006 ppm, gas, ---         | Shoot dry mass decrease                |
| White clover        | 0.009 ppm, gas, ---         | Shoot dry mass decrease                |
| Rye grass           | 0.006 ppm, gas, ---         | Shoot dry mass decrease                |
| Rye grass           | 0.009 ppm, gas, ---         | Shoot dry mass decrease                |
| Rainbow trout       | 8,000 ppm, liquid, 48 h     | TLm                                    |
| Rainbow trout       | 13,680 ppm, liquid, 96 h    | LC <sub>50</sub>                       |
| Creek chub          | 8,000 ppm, liquid, 24 h     | LD <sub>0</sub>                        |
| Creek chub          | 17,000 ppm, liquid, 24 h    | LD <sub>100</sub>                      |
| <b>Formaldehyde</b> |                             |  |
| Oat                 | 682,000 ppm, 10 days        | Seed germination decrease              |
| Oat                 | 692,000 ppm, 10 days        | Mature plant, seed production increase |
| Bean                | 0.4-1 mg/plant, liquid      | Shoot dry mass decrease                |
| Rainbow trout       | 118 ppm, liquid, 96 h       | LC <sub>50</sub>                       |
| Lake trout          | 100 ppm, liquid, 96 h       | LC <sub>50</sub>                       |
| Atlantic salmon     | 173 ppm, liquid, 96 h       | LC <sub>50</sub>                       |
| Rainbow trout       | 118 ppm, liquid, 96 h       | LC <sub>50</sub>                       |
| Black bullhead      | 62 ppm, liquid, 96 h        | LC <sub>50</sub>                       |
| Channel catfish     | 66 ppm, liquid, 96 h        | LC <sub>50</sub>                       |
| <b>Formic Acid</b>  |                             |  |
| Wheat               | 46 ppm, liquid, 7 days      | Seedling root size decrease            |
| Wheat               | 184 ppm, liquid, 7 days     | Seedling root size decrease            |
| Wheat               | 460 ppm, liquid, 7 days     | Seedling root cell size decrease       |

<sup>a</sup>Source: PHYTOTOX data base (Royce et al., 1984).<sup>b</sup>Source: Verschueren (1983).<sup>c</sup>Effects on other animals are described in the Health Effects section.<sup>d</sup>LD<sub>50</sub> = Lethal dose for 50% of the subjects, LD<sub>100</sub> = lethal dose for 100%, LC = lethal concentration, TLm = Median threshold limit.

1 leaf lesions, stunted growth, or even death. However, plant damage resulting from acute  
2 exposures are limited in time and space because of control technology mandated by  
3 legislation.

4       Chronic, sublethal pollutant exposures to vegetation are much more common and  
5 widespread than acute exposures (Moser et al., 1991). Sublethal exposures may not induce  
6 observable morphological damage, but altered biochemical processes may decrease plant  
7 vigor and productivity, alter phenology, or reduce reproductive potential. Altered  
8 physiological process may render the plant more susceptible to insect damage, disease, and  
9 other natural stressors. Decreased reproduction will impact populations through the loss of  
10 new recruitments to the plant community. With continual exposure, sensitive plant  
11 populations may decrease in numbers, allowing tolerant species to become dominant. Thus,  
12 shifts in plant community structure and composition could result in decreased biological  
13 diversity and altered ecosystem functions.

14       Pollutant deposition to soils will affect soil biota (Shafer, 1985). Possible soil biota  
15 responses may include species mortality, gene pool alterations, population shifts, alteration of  
16 species competition, changes in nutrient cycle, and effects to plant roots. Such changes may  
17 indirectly impact vegetation growth and development. The effects of pollutant deposition to  
18 soil are not very well documented in the literature.

19       Methanol-fuel pollutants may have the potential to affect animals/wildlife through  
20 inhalation, dermal contact, and food and water consumption (Newman and Schreiber, 1988;  
21 Schreiber, 1985). The direct effects on animals may vary from mucous membrane and  
22 respiratory irritation to alterations in activity patterns, depending upon exposure duration and  
23 concentrations. Indirect effects may reduce competitive ability, foraging behavior, or  
24 predator escape mechanisms. Reduced plant cover and habitat quality will result in animals  
25 being more susceptible to predation and disease. Adequate birthing sites may be reduced  
26 because of changes in vegetation architecture. Many of the conventional-fuel pollutants  
27 should have low bioaccumulation potential, with the obvious exception of lead. Trophic  
28 transfer of these toxic chemicals may occur by animal consumption of contaminated forage  
29 and water.



#### 3.2.2.2.2 *Landscape and Watershed Alterations from Methanol Production*

In addition to the above ecological issues, the environmental impact of methanol production from fossil fuels and biomass is also a concern. As noted in the discussion of feedstocks, methanol can be produced from natural gas, coal, oil shale, or biomass. The abundant coal and oil shale reserves throughout the United States make these resources a viable option for methanol feedstock (Luce, 1974); however, the production of each has potential adverse ecological impacts from mining and processing. Environmental impacts are also associated with biomass as a feedstock. Gases released will include methane, CO, CO<sub>2</sub>, methyl sulfide, and carbonyl sulfide, many of which are RITGs. Mining and drilling operations fragment the landscape and destroy plant and wildlife habitats (Institute for Land Rehabilitation, 1978). These local land disturbances may result in regional pollution of the atmosphere and waterways through erosion and chemical emissions. Wildlife deprived of food and shelter will emigrate to more suitable habitats (Schreiber, 1985). Threatened and endangered species (plants and animals) will be particularly vulnerable to habitat modification and loss. After mining or drilling ceases, restoration of wildlife habitats, rangeland, and agricultural land may require years before a return to premining conditions is accomplished (Institute for Land Rehabilitation, 1978).

Methanol production may also be based on biomass, from either farms or forests. In addition to changes in terrestrial systems due to land use practices, extensive degradation of freshwater systems (habitat and quality) throughout the country could be expected from the intensive agricultural and silvicultural practices that might be required to meet biomass production needs, particularly on marginal lands not competing for food production. Impacts of biomass production are further considered in the discussions that follow in the section on ethanol fuels. However, research needs on this important topic are not considered further because such impacts can be assessed by relating impacts of mining, drilling, etc., to the altered volume of such effort resulting from fuel switching. Also, such impacts are largely the responsibility of other Federal agencies to assess.

### 3.2.2.2.3 *Aquatic Ecosystem Effects*

Surface freshwater systems are most likely to be adversely affected by large accidental releases of fuels (e.g., barge, storage tank, and pipeline failures and accidents), although exposure by more routine leakages and discharges should also be considered. These effects can change drastically with a switch from gasoline to methanol fuels. The acute toxicity of methanol is much lower than for most gasoline components, especially the aromatic compounds that characterize gasoline's water soluble fraction. Lethal concentrations of methanol for 50% of fish and aquatic invertebrates have been reported to be 10 to 30 g/L (Bengtsson et al., 1984; Bowman et al., 1981; Poirier et al., 1986), 2 to 4 orders of magnitude higher than for most gasoline components. Chronic toxicity values are comparably higher. Although methanol is much less toxic, exposures from methanol fuels are expected to be much higher than from conventional fuel components, and methanol will exert its toxicity much faster. For methanol blended with gasoline, toxicity is untested and potential impacts of methanol on the dispersion and availability of gasoline toxic components are unknown. Methanol may also affect the disposition and availability of other contaminants in an ecosystem (e.g., by solvation of sorbed hydrophobic toxics on suspended and bottom sediment). It could alter oxygen demand of the system due to microbial oxidation of the methanol itself, thereby reducing dissolved oxygen levels throughout. This in turn could both affect organisms directly (e.g., fish kills) and alter the toxicity of other contaminants through a combined stress mechanism. Methanol will be more easily distributed throughout the system, will accumulate to a lower degree, and will be more bioavailable. When all these factors are considered, the hazard of spills from methanol fuels relative to conventional fuels is unclear.

The effects of a methanol catastrophic release (e.g., from a supertanker) are not fully understood and must be investigated to document potential impacts on aquatic ecosystems. A chronic, low-level discharge of methanol to marine waters is likely to be associated with its transfer between tankers, barges, and land-based storage facilities. The release of ballast water and cleaning of ballast tanks is also a potential source of contamination. A considerable body of literature on the fate and effects of certain petroleum products, such as No. 2 Fuel Oil, in marine systems has been developed (Hyland and Schneider, 1976;

Whittle et al., 1982). This information on the transport, transformation, and toxicological effects of petroleum products and compounds has proven to be valuable in predicting, understanding, and dealing with the impacts of oil spills. Only limited work (Price et al., 1974) has been done on gasolines. Basic methanol toxicity studies on sentinel species and marine mesocosm experiments are needed initially to determine the biological fate and effects (including community structure) of acute and chronic doses over a wide range of concentrations and episodic events. In addition, the synergistic effects of methanol inputs on oxygen depletion and microbial enrichment need to be determined. Large amounts of methanol spilled into a marine embayment could also influence the partitioning and bioavailability of contaminants already present in the system, such as chlorinated hydrocarbons or PAHs sorbed to suspended and bottom sediments. Additional studies are needed to determine how methanol may influence the bioavailability and toxicity of various other contaminants, such as neutral organic compounds.

### 3.2.3 Global Warming

Levels of RITGs will change as a result of increased use of methanol. Carbon dioxide emissions from methanol production using coal as a feedstock could be both quite substantial and variable and warrant engineering research attention to find solutions to this potential problem. The exact nature of the change will be a complex function of feedstock and production technologies, emissions from mobile and stationary sources, and transformation products. Because this issue was discussed earlier (Section 3.1.1.1) and is also covered in the following section on risk reduction (Section 3.2.4.1), it will not be discussed further here.

### 3.2.4 Risk Prevention/Mitigation

#### 3.2.4.1 Stationary Sources

##### 3.2.4.1.1 Aboveground Sources

The primary concerns here are the sources and levels of emissions and discharges that will result from the extraction of feedstocks through refining and conversion to methanol. Control of methanol volatile emissions in both new and existing fuel storage, distribution,

1 and handling systems is an area of high uncertainty. Guidelines for control of methane leaks  
2 and other releases relative to methanol use are needed.

3 Control evaluation and demonstration are especially needed for future coal-based  
4 methanol plants because the few existing gasification plants in the United States have all  
5 experienced problems with various control systems. Control application to water discharges  
6 could be a problem and needs specific attention.

7 Another uncertain control area is the prevention of containment loss of methanol by  
8 leaks, spills, and catastrophic accidental releases and the mitigation measures to be applied  
9 after a release of methanol has occurred. Because distribution and marketing areas are  
10 normally close to population centers, a catastrophic accidental release of methanol would  
11 potentially pose a major threat to the surrounding communities and to local vegetation. The  
12 chemical industry has developed systems to identify potential release problems and  
13 prevention measures (e.g., plant design, operational procedures, and emergency procedures)  
14 to reduce the severity of the releases; however, wider storage and handling by possibly  
15 less-experienced individuals would require the development of better fail-safe systems and  
16 procedures to ensure safe handling. This problem is especially true for filling station  
17 operations, where prevention and mitigation measures have not been standard in their  
18 operation. In the marketing area, control approaches to provide reliable emission/discharge  
19 controls and containment systems that would not require the technical expertise or  
20 maintenance capabilities available to industrial facilities will be needed.

21 The accidental releases of methanol (as well as other fuels) from industrial and  
22 commercial operations are a concern, and most likely, could result in injuries and fatalities to  
23 the population near facilities handling methanol, through either direct exposure or explosion  
24 and/or fire. The SARA, Title III, caused state and local authorities to develop emergency  
25 response plans to deal with potential releases for a large number of chemicals, including  
26 methane, to eliminate or reduce the potential effects of these releases and, most importantly,  
27 to maximize the prevention of accidents.

28 The approach to prevention deals with all aspects of the location, design, construction,  
29 operation standards, upset and emergency procedures, training, maintenance, and  
30 management practices of an industrial/commercial facility. In general, the primary focus of

1 prevention is to ensure that the primary containment is not breached. Additional protective  
2 measures involve the capture or destruction (sorption, scrubbing, and incineration) of the  
3 hazardous substances if primary containment has been breached. Prevention technology is  
4 intimately interwoven with quality process design, good engineering practices, appropriate  
5 process control/monitoring technology, and safe generating practices. Mitigation measures  
6 are those applied after a release has taken place (e.g., capturing, containing, reducing  
7 evaporation rates, and increasing dispersion of the gases). The use of specific technological  
8 process controls and practices depends upon the chemical and the complexity of the process.  
9 With methanol, as with other fuels, prevention and proper response to fire are important  
10 aspects; however, the problems of low luminosity and other factors need to be addressed.

11 Existing data on stationary-source combustion of methanol are limited, but they  
12 generally indicate a positive impact on emission controls when methanol is used in large,  
13 efficient, stationary combustion sources. Thus, research efforts in the stationary utilization  
14 area should also focus on the use of methanol as a pollution prevention option when possible.

#### 16 ***3.2.4.1.2 Underground Storage Tanks***

17 The concern about loss of containment in USTs and the potential contamination of  
18 groundwaters has resulted in the issuance of EPA regulations for many of the nation's  
19 underground storage systems. These regulations require new tanks to have properly installed  
20 spill and overfill protection, corrosion protection, and leak detection devices (Federal  
21 Register, 1988; Code of Federal Regulations, 1990). The regulations theoretically include  
22 alternative fuels, even though petroleum is still the most commonly used fuel and some of  
23 the newer fuels did not exist, or were not widely used, at the time the regulations became  
24 effective. Because of the differences between motor fuels currently in use and alternative  
25 fuels under consideration, additional research is needed to determine whether the same  
26 engineering solutions are applicable to both types of fuel and whether both can comply with  
27 the same regulations. For example, external leak detectors utilize the easy mobility and  
28 detectability of the lighter petroleum fractions. Guidance documents on site investigations  
29 (where leaks are suspected) are based on an understanding of the fate and transport of  
30 gasoline in the soil/groundwater environment. Guidance documents on soil cleanup and

1 aquifer restoration are based primarily on the properties of, and experience with, gasoline.  
2 A switch to alternative fuels, with somewhat different properties, will require a reevaluation,  
3 revision, and expansion of much of the research conducted and guidance prepared. External  
4 leak detection devices effective for gasoline might not be effective with other fuels, and vice  
5 versa. Certain soil cleanup technologies that may have somewhat limited applicability to  
6 gasoline-contaminated soils may find, for example, a much greater applicability to  
7 methanol-contaminated soils.

8 The UST research program of EPA has focused on scientific and engineering solutions  
9 to a problem which, as a result of a leak from one UST, is manifested on a microscale in a  
10 relatively small and confined environment. The overall UST problem is, however, of very  
11 large proportions because of the number of tanks involved, the serious potential impacts on  
12 public water supplies, and the large cleanup costs. Accordingly, a research program that  
13 focuses on the special problems of alternative fuels and USTs is required.

14 The first step in such a program should be to assess the impacts on, and issues  
15 associated with, the introduction of alternative fuels into existing storage and handling  
16 systems. Methodologies established for the prevention, detection, and corrective action of  
17 petroleum fuel leaks would have to be modified to accommodate alternative fuels.

18 The prevention of fuel releases from USTs involves a number of structural and  
19 nonstructural design and operating considerations. The initial thrust of prevention work  
20 would be to examine the compatibility of the alternative fuels with the construction materials  
21 associated with existing fuel storage and handling systems. To the extent that changes are  
22 required, consideration would be given to preventive measures that could be undertaken to  
23 minimize system failures. Other elements of prevention work would include secondary  
24 containment features; corrosion protection systems; installation procedures; and good  
25 operating procedures, including spill prevention. For all these considerations, knowledge of  
26 the fate and transport of alternative fuels is required.

27 Although many detection techniques will be effective with alternative fuels, some of the  
28 approaches that have been developed for petroleum products may not be suitable because the  
29 physical and chemical properties of the alternative fuels are different from those of  
30 conventional fuels. An examination of the impact of alternative fuels on existing release

1 detection technology is required. Such technologies include volumetric methods for leak  
2 detection, out-of-tank liquid detection devices, out-of-tank vapor detection devices, and  
3 interstitial devices for detecting releases from double-walled tanks. The performance of  
4 many of these detector devices, especially with respect to detection interference and device  
5 installation, is dependent on groundwater hydrology/geohydrology conditions as well as on  
6 chemical characteristics of the fuel themselves. If existing release detection technology is  
7 unsuitable, alternative approaches should be considered, with particular attention paid to the  
8 cost and performance of alternative release detection schemes.

9       Corrective action encompasses the application of a variety of techniques to different  
10 phases of a release in different environmental media. This is currently an area in which a  
11 great deal of research and study is underway with current petroleum fuels and other  
12 chemicals. An immediate need is to provide site assessment/decision tools and cleanup  
13 technologies for application to leaking USTs containing alternative fuels. To accomplish  
14 this, research is required to interpret items such as the mobility of contaminants at a site, site  
15 conditions that limit in-place cleanup, site conditions that suggest the site is stable and not  
16 worsening, and data that show cleanup progress (i.e., when cleanup should stop). Achieving  
17 these goals will require in-depth studies of certain site characteristics, transport and  
18 transformation processes, and subsurface conditions, as well as of specific corrective action  
19 technologies at actual sites of leaking USTs. Cleanup technologies have been, and continue  
20 to be, developed for petroleum and hazardous chemical releases under the Resource  
21 Conservation and Recovery Act and the Comprehensive Environmental Response,  
22 Compensation, and Liability Act; however, further research may be required to adapt these  
23 technologies to the unique problems associated with USTs containing alternative fuels.

#### 24 25 **3.2.4.2 Mobile Sources**

26       Engine exhaust emissions are controlled by oxidation-reduction catalyst systems, and  
27 evaporative emissions are controlled by adsorption-desorption carbon canisters. Performance  
28 is certified against published standards for THC, CO, and NO<sub>x</sub>. Control system performance  
29 typically deteriorates with mileage accumulation or fails abruptly under certain malfunction  
30 conditions, causing emissions to rise significantly. Inspection and maintenance programs are

1 used in some urban areas (generally those with O<sub>3</sub> and/or CO noncompliance) to flag grossly  
2 failing vehicles for repair.

3        Formaldehyde emissions from methanol-fuel motor vehicles are important to urban  
4 O<sub>3</sub> impact, health risk, and ecosystem risk. These emissions can be reduced by using  
5 properly functioning catalyst control systems, but are generally higher than those from  
6 gasoline-fuel vehicles. Engine-out formaldehyde emissions are considerably greater with  
7 methanol fuels, increasing the importance of successful after-engine (tailpipe) control. Horn  
8 and Hoekman (1989) recently observed that engine-out formaldehyde emissions from  
9 flexible-fuel vehicles using gasoline were about one-third of those when using M85 fuel.  
10 Surveillance procedures suitable for monitoring in-use emission control system performance  
11 for reduction of emissions important to the environmental impact of methanol (e.g.,  
12 formaldehyde) should be defined.

13        A majority of the formaldehyde emissions occur during vehicle cold-start operation  
14 (Gabele, 1990). Optimum control is characterized by rapid catalyst "light-off" (temperature  
15 at which organic oxidation begins). Evolving rapid light-off catalyst systems should be  
16 characterized for reduction of engine-out formaldehyde and other organics, as well as for CO  
17 and NO<sub>x</sub>. System durability should be evaluated to assure adequate performance at high  
18 mileage accumulation.

### 19 20 **3.2.4.3 Fuel Transport Sources**

21        Pollutants arising from the transportation of methanol fuels have the potential to impact  
22 aquatic ecosystems due to water discharges of pollutants and accidental spills/leaks. Control  
23 and containment technology development of fuel tankers, barges, and pipelines to reduce  
24 accidental spills and leakage will help prevent the entry of methanol fuels into aquatic  
25 ecosystems. Insofar as spills pose a significant adverse risk, cleanup technologies must be  
26 improved through research and development.



### 3.3 RESEARCH NEEDS

As alternatives to petroleum-based distillates are considered for motor vehicle fuels in the United States, methanol has emerged as a leading candidate. Both economic considerations and the potential for positive environmental impact have focused attention on this transportation fuel alternative. The motor vehicle industry has developed prototype vehicle configurations compatible with M100, M85, and flexible fuels (i.e., any mixture of gasoline and methanol). Potential also exists for reduced emissions in stationary combustion applications (peaking turbines, stand-by boilers/engines, pile drivers, and possibly other construction equipment) from use of this fuel. Further, overfired or cofired methanol could be used as a possible NO<sub>x</sub> control strategy in boilers and gas turbines.

The impact of transition from petroleum-distillate fuels to methanol on risk to public health, ecosystems, and global climate requires a comprehensive understanding of the impact of this fuel on emissions, atmospheric transformation processes, target population exposure, health/ecosystem effects, and potential for emissions control/risk reduction. Although substantial information exists in several of these disciplines, additional research is indicated and is discussed below.

In this section, broad research objectives for each key element of risk assessment are described and priorities are assigned. The priorities across all fuels were considered with the understanding that future knowledge, technology changes, and market factors are likely to have some impact on them. One major difficulty in developing a prioritization scheme is accounting for scientific pacing. For example, in many cases, knowledge of dose response is a higher priority than knowledge of hazard identification, but hazard-identification research must proceed first to guide the dose-response work. Due to the extent of the uncertainties about fuels, the approach chosen for prioritization would, in this example, rank hazard-identification research higher than dose-response research. Each research objective is coded with one of the following prioritization phrases.

- Priority 1 for the next 2 to 4 years. This is the highest priority research over the near term. The research generally entails resolution of major issues of known concern, identification of new issues likely to be critical to risk assessment/risk reduction, crucial methods development that paces much other

work, and major mandates of the CAAs. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.

- Priority 2 for the next 2 to 4 years. This is medium priority research over the near term. Work in this category generally entails pursuing key issues that have importance for either the exposure or effects phase of hazard identification or for evaluating key elements of risk reduction. Gaining such information will certainly be important, but is less crucial than work under Priority 1. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.
- Priority 3 for the next 2 to 4 years. Although this research is of lower priority relative to other categories, it is still critical to development of comprehensive baseline information for all fuels. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.
- Longer term priority. This research is essential to developing comprehensive, quantitative risk assessments and/or risk reduction approaches. However, its initiation is paced by the completion of earlier research. When major elements of the earlier research are completed, it will be possible to more definitively prioritize this category of work.

### **3.3.1 Exposure Assessment**

#### **3.3.1.1 Source Characterization**

##### ***3.3.1.1.1 Stationary Source Characterization***

The primary environmental concerns for methanol are the sources and levels of emissions/discharges that will result at all stages of processing, from the extraction of feedstocks through refining, conversion to methanol, and its utilization in stationary sources. The near-term feedstock would be natural gas; coal-based processes would become more important in the future. The large increases in CO<sub>2</sub> emissions associated with coal as a feedstock now raise substantial concerns. Although extraction of natural gas and methanol synthesis are commercial processes, adequate data on the various emissions/discharges that are involved, with and without applied controls, are lacking. The potential for increased methane emissions is also a concern from a global warming standpoint. This lack of useful data is greater for emerging feedstocks, such as coal and biomass.

1 Because methanol is flammable and can burn with an invisible flame, the potential for  
2 an accidental release is of substantial concern. Distribution and marketing areas are normally  
3 close to population centers, posing a severe threat to surrounding communities should  
4 catastrophic accidental releases of methanol occur. Along with air release-related accident  
5 scenarios, assessment of large spill scenarios into water and leak/spill scenarios into  
6 groundwater require study.

7 The following important stationary-source emission points for VOCs must be included.  
8 Many of the listed sources of emissions already are regulated or have pollution control  
9 guidance in existence for conventional fuels.

10  
11 Production (extraction/conversion/refining)

- 12  
13 (1) Petroleum refineries  
14 (a) VOC equipment leaks  
15 (b) Fuel-gas combustion  
16 (c) Petroleum refinery wastewater streams  
17

18 Storage, transportation, and marketing

- 19  
20 (1) Barge, tanker, tank truck, and railcar cleaning  
21 (2) Barges, tankers, tank trucks, and railcars in transit  
22 (3) Chemical manufacturing–volatile organic liquids (VOLs) storage  
23 (4) Formulation and packing VOLs for market  
24 (5) Local storage (airports; industries that use fuels, solvents, and reactants in their  
25 operation)  
26 (6) On-shore natural gas production  
27 (7) Petroleum industry–bulk gasoline plants  
28 (8) Petroleum industry–bulk gasoline terminals  
29 (9) Petroleum industry–fixed-roof storage tanks  
30 (10) Petroleum industry–leaks from gasoline tank trucks and vapor collection equipment

- (11) Petroleum industry–petroleum fixed-roof storage tanks
- (12) Petroleum industry–service stations (Stage I)
- (13) Petroleum industry–service stations (Stage II)
- (14) Petroleum product and crude oil storage
- (15) Petroleum refineries (petroleum refinery fugitive emissions)
- (16) Petroleum refinery wastewater streams (petroleum refinery fugitives)
- (17) Storage vessels for petroleum liquids; gasoline, crude oil, and distillate storage tanks  
>40,000 gal; bulk terminals/plants
- (18) Storage vessels for VOL (including petroleum); bulk terminal/plants

#### Utilization source characterization for stationary sources

- (1) Power generation
  - (a) Utility boilers
  - (b) Gas turbines
- (2) Heat generation
- (3) Cogeneration
- (4) Stationary IC engines

#### Research Objectives:

1. Determine the overall net change in VOCs, methane, CO<sub>2</sub>, and other stationary-source multimedia emissions/discharges resulting from one or more key scenarios of methanol market penetration by (a) developing emission factors for production, distribution, and utilization for the sources listed above; and (b) determining the impact that methanol will have on existing storage, distribution, and marketing controls and how its use could affect control system effectiveness, with the potential result of increased emissions. (Priority 1 for the next 2 to 4 years.)

2. Perform a catastrophic-release hazard assessment study to identify specific areas of concern that may require prevention-oriented risk-reduction work. (Priority 1 for the next 2 to 4 years.)
3. Confirm low emission potential (reduced hydrocarbons, CO, and NO<sub>x</sub>) for neat methanol used in power generation (including utility boilers and gas turbines), heat generation sources such as industrial/commercial boilers, cogeneration units, and stationary IC engines. (Priority 2 for the next 2 to 4 years.)
4. Develop a source characterization profile for aldehyde emissions from certain sources utilizing methanol for which exposure will be important, including stationary IC engines and other nonhighway vehicles. (Priority 2 for the next 2 to 4 years.)

The emission/discharge problems addressed by this research must include continuous/routine emissions, short-term releases, and catastrophic-scale releases.

#### ***3.3.1.1.2 Mobile Source Characterization***

Assessment of the impact of alternative fuels on air quality problems such as O<sub>3</sub>, CO, NO<sub>2</sub>, particulate matter, and other toxic compounds, or on global climate change requires comprehensive examination of emissions from several vehicle categories under the widely variant operating conditions typical of motor vehicle fleets. The limited emissions speciation data available in the literature for methanol-fuel vehicles are dominated by certification driving conditions (i.e., about 70 °F [60 to 84 °F diurnal range] and 20 mph average speed). Emission rates are sensitive to variations in average speed and ambient temperature. Based on experience with conventional gasoline vehicles, hydrocarbon and CO emission rates (grams of emissions per vehicle mile traveled) typically increase as temperature is increased or decreased from 70 °F. These emission rates also increase as average speed is decreased. Oxides of nitrogen emission rates increase as temperature is decreased, and increase as speed is increased or decreased from 20 mph; however, they are generally less sensitive to

operating variables than hydrocarbon and CO emissions. Carbon monoxide air-quality violations often occur at temperatures well below 70 °F, and O<sub>3</sub> air-quality violations occur at temperatures well above 70 °F. The emission rates and composition are also very sensitive to fuel characteristics such as volatility and composition.

American motorists often drive their automobiles for many years, with a significant contribution to fleet VMT from vehicles as old as 20 years. Emissions control systems deteriorate over that period, and emission rates increase. Most urban areas with excessive O<sub>3</sub> and/or CO pollution problems administer Inspection and Maintenance programs to identify inoperative control systems requiring repair.

The relative importance of the various categories of motor vehicles depends upon the target air quality problem. The mobile source emissions model, MOBILE 4, can be used to examine the sensitivity of emissions to ambient temperatures. At 100 °F, light-duty gasoline vehicles were responsible for about 90% of O<sub>3</sub>-precursor hydrocarbons from vehicles, and at 25 °F they were responsible for about 85% of CO in 1990. Motor vehicle NO<sub>x</sub> and particulate emissions were distributed about 2/3 and 1/3 between light-duty cars/trucks and heavy-duty trucks/buses, respectively, in 1990. Thus, study of the air-quality impact of alternative transportation fuels should be directed to the category of vehicles most responsible for the air-quality problem being addressed (i.e., light-duty passenger cars and trucks for O<sub>3</sub> and CO air quality and all categories for NO<sub>2</sub> and particulate air quality).

To assess the impact of emissions from vehicles using methanol fuels on risk to public health and welfare, three general categories of variables will require study.

1. Vehicle-fuel technology: (1) flexible-fuel light-duty cars and trucks using fuels from 100% gasoline to 100% methanol (M100) and intermediate blends, (2) dedicated M85 and M100 light-duty passenger cars and trucks, and (3) heavy-duty methanol-fuel trucks and buses (using varied formulations such as M100, M85, or M95 with ignition improvers). These are developing technologies, and studies will be required until vehicle designs and fuels stabilize. Observed emissions characteristics and estimated health and welfare effects will influence the development of both vehicles and fuels.

2. Operating conditions: (1) varied average vehicle speed and engine load, (2) varied ambient temperature, (3) varied age (control system deterioration), and (4) varied altitude.

3. Emission sources: (1) tailpipe emissions, (2) evaporative emissions (e.g., diurnal, hot soak, and running-loss), and (3) refueling.

Assessment of the potential impact of these fuels on O<sub>3</sub> levels and air quality will require determination of organic emission rates and detailed species composition (hydrocarbons, aldehydes, organic acids, etc.), as well as of CO and NO<sub>x</sub> emission rates. Detailed organic compound compositions will also be necessary to assess the impact of these fuels on air concentrations of and exposure to toxics such as benzene, formaldehyde, and 1,3-butadiene. Operating conditions should be varied to provide data representative of the motor vehicle microenvironments dominating human exposure to the primary emissions (e.g., parking garages, congested freeways, and urban street canyons). Data representative of overall urban use are needed to estimate impact on O<sub>3</sub>, CO, NO<sub>2</sub>, and particulate air quality and to assess exposure to atmospheric transformation products of the emissions. The emission rates of compounds important to climate change, such as CO<sub>2</sub>, methane, N<sub>2</sub>O, and other radiatively significant species, will also be examined. Contrasts with classical gasoline and diesel fuels will be required for all scenarios identified. When data permitting this contrast do not exist in the literature, they will be developed.

A number of public and private sector organizations will be undertaking similar emissions characterization efforts. For example, the Air Pollution Research Advisory Committee of the Coordinating Research Council (CRC) sponsored a workshop (held in April 1988) to discuss technical issues related to widespread use of methanol as an alternative fuel. The workshop provided a statement of current knowledge, critical issues, and future research needs. Many of the issues and needs were similar to those identified in this Research Strategy. The CRC will be sponsoring research on alternative fuel issues in its extramural contractual program, and its membership (i.e., the petroleum industry and engine manufacturers) will be conducting related in-house research. To ensure that the program

1 results are complementary, efforts to coordinate these and other related programs will be  
2 undertaken.

3  
4 Research Objective:

- 5  
6 1. Characterize emissions from motor vehicles designed for methanol fuels as a  
7 function of speed, ambient temperature, and mileage accumulation. Emission  
8 levels and speciations suitable for estimating impacts on O<sub>3</sub>, NO<sub>2</sub>, CO, and  
9 particulate air quality, as well as on other factors such as global climate change  
10 and toxic compound exposure, will be provided. (Priority 1 for the next  
11 2 to 4 years.)  
12  
13

14 **3.3.1.2 Environmental Fate**

15 **3.3.1.2.1 Air Fate**

16 The chemistry of methanol is fairly well understood; however, the chemistry of  
17 gasoline emissions is not well understood. As stated earlier, formaldehyde is the principal  
18 product of photooxidation. In the presence of NO<sub>x</sub>, some methyl nitrite can be produced.  
19 Methanol, when present in the atmosphere, is expected to be scavenged by aqueous aerosols;  
20 if sulfuric acid is present in the aerosols, MMS and DMS may be produced. Formic acid  
21 emissions may also be associated with use of methanol fuel.

22 To assess the impact of the use of methanol fuels on air quality, basic mechanistic,  
23 modeling, and smog-chamber studies on the auto exhaust gases must be conducted. Nitrogen  
24 oxides might be expected to increase 4 to 8% with oxygen blends as a fuel. This increase in  
25 NO<sub>x</sub> can be expected to decrease photooxidation the first day, but second-day photochemistry  
26 may increase. Also, if NO<sub>x</sub> increases, more nitrates can be expected. Formaldehyde  
27 emissions can be expected to increase, at least during cold-start operation. Formaldehyde  
28 from secondary atmospheric processes may decrease with methanol fuels relative to gasoline  
29 fuels, depending upon precursor concentrations and reaction rates. Monitoring of all major  
30 reactants and products in the photooxidation of methanol-gasoline blends is proposed.



Multiple-day smog-chamber studies are needed. Biotesting of both reactant and product mixtures using the Ames testing procedure (*Salmonella typhimurium*) should be undertaken. Both the Empirical Kinetic Modeling Approach and airshed-type models will be used to determine the benefits derived from the use of oxygenated fuels and blends.

#### Research Objectives:

1. Develop a mechanism with demonstrated performance for predicting O<sub>3</sub>, NO<sub>x</sub>, formaldehyde, acetaldehyde, and PAN levels in several smog chambers of different characteristics. (Priority 1 for the next 2 to 4 years.)
2. Report on the transport and fate of the emission products and transformation products in the atmosphere. (Priority 1 for the next 2 to 4 years.)
3. Report on air quality predicted by airshed models with the use of methanol. (Priority 1 for the next 2 to 4 years.)
4. Determine DMS formation from the reaction of methanol exhaust with SO<sub>2</sub> on aerosols. (Priority 1 for the next 2 to 4 years.)

#### **3.3.1.2.2 Soil and Groundwater Fate**

The potential for subsurface and groundwater contamination from the use of methanol as an alternative fuel will depend upon the probability that methanol will get into the subsurface, the rate at which it will move toward groundwater once it is introduced into the subsurface, and the rate at which it is attenuated by chemical and biological processes. Although each of these factors has been studied to some extent, the studies for the most part have not been oriented towards the use of methanol as an alternative fuel. The information has been published in diverse reports and journals and is not available in a form that would make it readily accessible to decision makers. A state-of-the-science paper summarizing available information on corrosive effects of methanol on USTs; methanol leak detection

1 technology; and processes controlling the mixing, dissolution, fate, and transport of methanol  
2 in the subsurface is needed.

3 If pure methanol were released into the subsurface, its movement would be controlled  
4 by advective transport downward toward groundwater and by volatilization, which would  
5 tend to move it upward towards the atmosphere. The ability to predict this behavior is  
6 currently very poor. Research related to the movement of methanol in the unsaturated zone  
7 is needed in at least two areas: (1) determining the effect of methanol and methanol-water  
8 mixtures on the hydraulic properties of different types of soils under a variety of conditions;  
9 and (2) assessing the importance of factors such as moisture content and temperature on the  
10 rate of methanol vapor transport, as well as the effect of the gaseous phase on chemical and  
11 biological processes. This information should then be incorporated into predictive transport  
12 models for threat analyses.

13 In addition to advective transport and volatilization, the fate of methanol will depend  
14 upon chemical and biological transformation processes. Substantial research information  
15 concerning the microbial transformation of methanol at low concentrations is available;  
16 however, this information must be interfaced with the dynamics of methanol transport and  
17 extended to very high concentrations to be environmentally applicable. A dynamic,  
18 functional relationship between the microbial transformation of methanol and its spatial and  
19 temporal distribution in soil or groundwater is anticipated. Research to incorporate this  
20 relationship into an environmentally realistic model is needed. Ongoing research conducted  
21 by ORD's Environmental Research Laboratory (in Ada, OK) in the Ground Water Model  
22 Validation Project (NAPL fate and transport) and in the Biosystems Project (in situ  
23 bioremediation of aquifers) being conducted at EPA's R. S. Kerr Environmental Research  
24 Laboratory will contribute significantly to the development of theory and assessment  
25 methodologies. Actual field/laboratory data and an implementation focused on methanol-  
26 based scenarios are needed for this project.

1 Research Objective:

- 2
- 3 1. Assess the potential for groundwater contamination resulting from the use of
- 4 methanol as a replacement fuel. (Priority 2 for the next 2 to 4 years.)
- 5

6 **3.3.1.2.3 Surface Water Fate**

7 For both fresh and marine surface water systems, mixing-dissolution, volatilization,

8 dispersion, biological oxidation kinetics (algorithms and rate constants), and photolysis

9 reactions are the key fate, transport, and pathway processes requiring quantification and

10 research. One main factor, throughout, is the requirement to handle a very wide range of

11 concentrations that vary rapidly in time and space (i.e., pulse loads). Biological inhibition,

12 oxygen depletion (biological oxygen demand [BOD] effect), and possible solvating or

13 extraction effects of methanol or high-concentration methanol-water mixtures on releasing

14 accumulated benthic sediment-related organic pollutants (e.g., PAHs and organochlorines) to

15 the water column must also be accounted for quantitatively. This research, incorporated into

16 a suitable transport/exposure framework, then provides a defensible foundation for the

17 needed risk and policy assessment applications. To this end, ongoing exposure and decision

18 support systems methodology development components of EPA's Ecological Risk Assessment

19 Program (managed at the Athens Environmental Research Laboratory) will augment and

20 support the Alternative Fuels Program needs. Another possible effect is the influence of

21 methanol on the behavior and toxicity of other contaminants present in marine systems (e.g.,

22 gasoline-blend components and sorbed hydrophobic toxicants). The suspended particulate

23 material and sediments of many near-shore locations contain high concentrations of

24 anthropogenically produced or mobilized contaminants. A massive spill of methanol in a

25 shallow area could extract or release compounds from contaminated sediments to the water

26 column or alter the partitioning of compounds between dissolved and particulate phases.

27 This could influence the bioavailability of these other contaminants. Studies to determine the

28 extent to which methanol can change the bioavailability of other classes of compounds such

29 as chlorinated hydrocarbons and PAHs should be undertaken.

30

## Research Objectives:

1. Develop a state-of-the-science surface (marine and fresh) water transport and fate methodology for use in comparative exposure assessment analyses of catastrophic methanol (and gasoline) spills. (Priority 1 for the next 2 to 4 years.)
2. Determine the influence of methanol on the bioavailability of neutral organic compounds in the marine environment. (Priority 2 for the next 2 to 4 years.)

### **3.3.1.3 Exposures**

#### ***3.3.1.3.1 Human Exposures***

Human exposure assessment research will focus on inhalation exposures related to air quality. Accidental oral exposure can be assessed with existing data (see Chapter 7, Scientific Assessment), rather than immediately researched. Research on soil/groundwater fate will provide much of the information needed to forecast human exposure via drinking water, which must await development of this information.

The transition of transportation fuels from gasoline to alternative fuels such as methanol will significantly change the characteristics of motor vehicle emissions, which, in turn, significantly changes human exposures to both regulated and unregulated toxic pollutants. In addition, changes in emissions will likely change transformation by-products, which also could result in increased or decreased exposures to pollutants such as formaldehyde, O<sub>3</sub>, and benzene. To measure, interpret, and characterize human exposures accurately, consideration must be given to addressing the general issues regarding other sources and pathways that contribute to total human exposure and to relating the exposure to that which might be expected for gasoline. This suggests that some baseline measurements of exposure that result from gasoline emissions are a first requirement.

As a result of studies conducted by the Office of Mobile Sources, methanol concentration levels have been estimated for various vehicle and traffic conditions in order to predict concentrations that may occur under both typical and severe conditions. Drawing upon earlier work for CO, locations of maximum concentrations were selected for modeling.

1 These included street canyons, roadway tunnels, and expressways, as well as personal and  
2 public parking garages. Model predictions indicate that maximum exposures are expected in  
3 personal garages, with some estimates of short-term peak exposures ranging as high as  
4  $650 \text{ mg/m}^3$  (500 ppm) methanol. In contrast, maximum in-traffic predicted concentrations  
5 are expected to be considerably lower (approximately 5 to 6  $\text{mg/m}^3$ , 4 to 5 ppm), which  
6 would occur while traveling through a roadway tunnel. These results highlight the  
7 importance of the personal garage as the microenvironment that is likely to be of greatest  
8 concern for methanol and for other fuel substitutes as well. Note that the personal garage  
9 estimate is based on a single vehicle, not on a fleet of vehicles with similar emissions  
10 characteristics. Furthermore, personal garage emissions may contribute to indoor air-quality  
11 problems via door openings or air-exchange systems.

12 The most important uncertainties to be resolved prior to developing a comparative risk  
13 assessment for alternative versus conventional fuels would be addressed by:

- 14
- 15 (1) Measuring the contribution of emissions from alternative-fuel vehicles in various  
16 exposure scenarios, at both sea-level and high-elevation locations, including  
17 in-transit exposures, exposures during service-station refueling and in repair  
18 facilities, and other appropriate exposure situations. This will involve the  
19 development of selective, accurate, and precise procedures for measuring a  
20 variety of compounds and atmospheric transformation products for ambient,  
21 microenvironment, and personal measurements. Studies will address the impact  
22 on air quality for both regulated and unregulated pollutants, the impact on  
23 transformation by-products, and the impact on exposure in microenvironments of  
24 greatest exposure potential (e.g., personal and public garages and indoor rooms  
25 adjacent to garages or affected through direct input from air-handling systems).  
26 Later studies, if deemed necessary, would measure total human exposure through  
27 monitoring each of the routes of exposure and validating the total exposure with  
28 applicable biomarkers of exposure. The resulting exposure distributions should  
29 be contrasted with those obtained from studies of gasoline-fuel vehicles.  
30

- (2) Obtaining accurate, representative activity pattern data related to automotive-generated exposures (e.g., time spent in personal garages and time spent in rooms adjacent to parking garages).
- (3) Validating the modified NAAQS Exposure Model (NEM) to the extent possible through appropriate measurements. New models will be developed that incorporate emissions data, microenvironmental data, and specific time spent in significant microenvironments.
- (4) Obtaining better measurements of exposures through other pathways (e.g., accidental swallowing, food/beverage, and dermal).

To quantify human health risks resulting from exposures to evaporative and combustion emissions and the transformation products from use of alternative fuels, sensitive compound-specific procedures for collecting and analyzing samples need to be required. Monitoring techniques to collect exposure information need to be developed and implemented, following results of emissions studies. These studies will help identify likely compounds of interest and situations that could lead to high exposures.

Assessment of the potential impact of these fuels on regulated pollutants (e.g., O<sub>3</sub>, CO, and NO<sub>2</sub>) can, hopefully, be accomplished through existing models, with changes in emission rates, transformation rates, and transformation by-products serving as input to the modeled estimates. Model validation by actual measurements may be required to test the efficacy of the approach.

A basic input to the models used for *estimating* exposures from mobile source emissions, independent of fuel used, is the time-activity pattern in locations apt to be significantly impacted by the resulting emissions. Through the Research to Improve Health Risk Assessments (RIHRA) program (Sexton and Reiter, 1989), a major effort to acquire a national time-activity pattern data base was initiated in FY89. This effort will be patterned after the study conducted by the California Air Resources Board (CARB) in 1987 to 1988 (Robinson et al., 1989). Results from this study will provide (1) accurate information on the

percentage of the population that engages in a particular activity (e.g., commuting) or that frequents a selected microenvironment (e.g., parking garages), and (2) input to mathematical models used to calculate exposure profiles.

Research Objectives:

1. Exposure assessment of the identified pollutants that are primarily, if not specifically, related to use of methanol, including methanol and formaldehyde. (Priority 1 for the next 2 to 4 years.)
2. Development and application of validated human exposure models to predict changes in exposure resulting from methanol fuels. (Priority 1 for the next 2 to 4 years.)

**3.3.1.3.2 Biota Exposures**

**Terrestrial Exposures.** Research should initially be targeted within the South Coast Air Basin, CA, and compared with the potential exposure of conventional-fuel pollutants. Environmental exposure models such as those developed as part of NAPAP and the SMCM should be used to evaluate pollutant exposure to urban, agricultural, and natural ecosystems within the South Coast Air Basin. A wind-rose model should be used to model the transport of the pollutants into the surrounding areas within a GIS framework to estimate urban, agricultural, forest, and chaparral land area exposed to various pollutant concentrations.

Research Objective:

1. Exposure assessment of methanol-fuel pollutants (e.g., formaldehyde and methanol) to terrestrial ecosystems within the South Coast Air Basin, CA. (Priority 1 for the next 2 to 4 years.)

1        ***Aquatic Exposures.*** Characterization of exposure from methanol fuel spills and  
2 discharges will parallel conventional fuels studies. Test cases and generic scenarios will be  
3 identical with respect to system characterization and the magnitude of fuel inputs, with  
4 differences arising from applying fate assessments appropriate for methanol fuels.

5  
6        Research Objective:

- 7  
8            1.    Develop example cases for methanol fuel spills and leakages to freshwater and  
9                estuarine ecosystems that include characterizations of system morphometry,  
10                organism types and locations, and physical/chemical properties that regulate fate  
11                and effects. Apply source scenarios and fate/transport models to these test cases to  
12                develop exposure-time series for target organisms. (Priority 1 for the next  
13                2 to 4 years.)

14  
15  
16        **3.3.1.4 Analytical Methodology**

17        Analytical methods will be developed, upgraded, and/or evaluated for measurement of  
18 source emissions, atmospheric transport and transformation of the emissions, and population  
19 (human and ecosystem) exposure to the emissions and transformation products as necessary  
20 to support assessments of the impact of varied fuel formulations on risk to public health and  
21 welfare.

22        Procedures suitable for certification of regulated source emissions (THC, NMHC, CO,  
23 NO<sub>x</sub>, and particles) at levels mandated by the CAAAs and procedures for the detailed  
24 speciation necessary to support estimation of the impact on O<sub>3</sub> and toxics air quality will be  
25 required. The procedures must permit accurate and precise determination of large numbers  
26 of compounds in very complex mixtures.

27        Ambient-air monitoring techniques for emissions and atmospheric transformation  
28 products of methanol-powered vehicles are not significantly different from those used to  
29 measure direct emissions. Again, as with conventional gasoline, the samples need to be  
30 concentrated with the use of cryogenic traps employing either liquid argon or oxygen.



Compounds to be analyzed are unburned methanol, some VOCs that result from cracking, formic acid, formaldehyde, and possibly methyl nitrite and DMS. Methyl nitrite has been observed by some investigators, but its formation could be a result of wall reactions on the collection vessel. Dimethyl sulfate may be produced by the heterogeneous reaction of methanol with SO<sub>2</sub> on aerosols. Methodologies are needed to measure low levels of DMS, methanol, and formic acid. In addition, personal monitors for the key pollutants (e.g., methanol and formaldehyde) will be required if population exposure studies are undertaken in later years.

#### Research Objectives:

1. Develop/upgrade/evaluate analytical procedures for measurement of source emissions potentially associated with methanol fuels (e.g., methanol, formaldehyde, methyl nitrite, and formic acid). (Priority 1 for the next 2 to 4 years.)
2. Validate classical procedures for certification of organic carbon, CO, NO<sub>x</sub>, PM, and CO<sub>2</sub> emissions from methanol-fuel vehicles; identify problems, provide corrective actions, and/or develop new, more simplistic, lower cost acceptable procedures. (Priority 1 for the next 2 to 4 years.)
3. Develop/upgrade/evaluate analytical procedures for measurement of ambient air concentrations of compounds potentially associated with methanol fuels (e.g., methanol, formaldehyde, methyl nitrite, formic acid, and DMS). (Priority 2 for the next 2 to 4 years.)
4. Develop/upgrade/evaluate analytical procedures for measurement of exposure to compounds potentially associated with methanol fuels (e.g., O<sub>3</sub>, methanol, formaldehyde, methyl nitrite, formic acid, and DMS), including passive personal and microenvironment monitors). (Priority 2 for the next 2 to 4 years.)

## 3.3.2 Effects Assessment

### 3.3.2.1 Human Health Effects

#### 3.3.2.1.1 Overview

The goal of the alternative fuels health research is to provide the necessary information for a comprehensive, quantitative assessment of human health risks resulting from exposures to alternative fuels relative to conventional fuels. To set the methanol research priorities, the criteria articulated in the Introduction (Section 1.4.2.1) were utilized. To briefly summarize, these criteria emphasize: (1) chemicals specifically identified in the CAAA, (2) agents/mixtures with greatest exposure potential, (3) relevance to the real world, and (4) efficiency. When the above criteria are applied to the existing data base, research priorities emerge. The highest research priorities for methanol are: (1) development of pharmacokinetic models, (2) dose-response assessment of methanol for selected endpoints (e.g., developmental effects, nervous system effects) via inhalation exposure, (3) evaluation of the carcinogenic potential of the combustion and transformation products, and (4) evaluation of the respiratory toxicity of formaldehyde. Concerns about formaldehyde- and DMS-induced cancer are also noted, although research on these topics is not proposed. Results from proposed research will be used in conjunction with exposure data to develop a risk characterization of methanol and its combustion and transformation products for comparison to other alternative fuels and conventional fuels.

#### 3.3.2.1.2 Primary Fuel–Methanol

Several health effects associated with methanol have been identified and require further evaluation. Currently, the toxicologic endpoints of greatest concern for methanol exposures are as follows: developmental effects, changes in hormone levels and the potential impacts on reproduction, impacts on the visual system, neurobehavioral alterations, and potentiation of chemically-induced liver toxicity. Each of these endpoints will be discussed briefly below. Also, it is important to consider that M85 is likely to be more commonly used than M100. As a consequence, the effects of the more complex mixture (M85) also must be evaluated. Study of such a mixture obviously presents its own set of experimental difficulties.

1        Pharmacokinetic studies of M100 and M85 constitute the highest priority research area.  
2        Studies should focus on evaluation of important metabolic pathways, development of  
3        metabolic constants, and estimation of dose to target tissue(s). Currently, dose to the fetus  
4        and interspecies comparisons of metabolism are of particular interest for M100. Because of  
5        the technical problems inherent in assessing the metabolism of complex mixtures, M85  
6        research would likely focus on evaluating alterations in the metabolism of methanol induced  
7        by coexposure to the gasoline. Pharmacokinetic research and model development should be  
8        coupled to health effects research and dose-response model development.

9        The evaluation of the developmental toxicity of methanol is also of high priority in this  
10       Strategy for the following reasons: (1) developmental effects have been reported in two  
11       species of rodents, (2) in mice, the more sensitive species, the observed effects (exencephaly  
12       and cleft palate) are of a serious nature, and (3) some of the predicted microenvironmental  
13       exposures (e.g., garages) have been within an order of magnitude of the LOAEL for  
14       developmental effects in mice exposed by inhalation. Further research on the developmental  
15       effects of methanol have already begun at EPA and elsewhere, with attention being given to  
16       dose-response characteristics, critical exposure timing and duration, and the relevance of  
17       these observations to humans. Development of a biologically-based dose-response model,  
18       which will include low-dose extrapolation, has been initiated. The study of other species  
19       (especially nonhuman primates) may be necessary, depending upon the pharmacokinetic  
20       evaluation of the optimal animal models for methanol. Because gasoline has also been  
21       suggested as a developmental hazard, and co-exposure to methanol and gasoline may alter  
22       metabolism in some manner critical to development, both M100 and M85, as well as  
23       gasoline itself, will need to be evaluated for developmental risks.

24       Investigation of other potential reproductive effects (e.g., altered sex hormone levels,  
25       severe testicular toxicity at high concentration) is important but of somewhat lower priority.  
26       Recent work suggests that male hormone levels do not appear to be adversely altered by  
27       methanol at environmental concentrations and that testicular toxicity appears to occur only  
28       with very high, accident-type exposure levels. Evaluation of the potential for testicular  
29       toxicity at low-level chronic exposures, the mechanism of high-exposure testicular toxicity,  
30       and the relevance of observed effects to humans is needed. Preliminary work suggests that

1 female reproductive cycles in rats may be disrupted by methanol exposure; evaluation of the  
2 developmental impact of delayed ovulation caused by altered hormone levels in female rats is  
3 currently underway. In the longer-term, comparison of methanol-related reproductive and  
4 developmental effects with other fuel-related hazards (e.g., 1,3-butadiene-induce testicular  
5 atrophy) will be necessary.

6       Neurotoxic effects, including effects on the visual system and behavioral effects, must  
7 be investigated. Existing data indicate that high doses of ingested methanol affect the  
8 nervous system, especially vision, producing blindness in primates due to an accumulation of  
9 formate in the blood. Evidence for direct effects of methanol or its metabolites at low levels  
10 of exposure on visual function is lacking. The dose-response relationships and mechanism of  
11 action of formate in producing visual system damage are, however, poorly understood.  
12 A careful analysis of methanol metabolism and the visual system would be prudent,  
13 particularly as related to chronic, low-level exposures. Also, astrocytosis, in repeatedly  
14 exposed monkeys, and neurobehavioral effects, in prenatally exposed rodents, have been  
15 reported and could be further explored using sensitive biochemical markers of cell injury, in  
16 addition to other techniques. Again, the question of the appropriate animal model must be  
17 considered, given differences between rodents and primates in metabolism of methanol.  
18 If rodents are inappropriate models, then experimental work must be carried out with  
19 nonhuman primates.

20       In addition to the direct effects of fuel and fuel-related mixtures, the potentiation of  
21 toxicity must also be considered. Data in the literature and research ongoing at EPA  
22 demonstrate that significantly increased liver toxicity, induced by carbon tetrachloride, occurs  
23 with co-exposure to methanol or ethanol. Additional research should be conducted, with an  
24 emphasis on understanding mechanisms of action underlying potentiation and relevance to  
25 environmental exposures. Research should include consideration of other possible  
26 interactions with fuel-related compounds, including combustion and transformation products.

27       Results obtained by Cook et al. (1991) suggest the need to conduct further work on the  
28 neurobehavioral effects of methanol vapor at concentrations and durations likely to be  
29 experienced in human populations. Among the factors to be considered in the design of such  
30 work are increased sample size (to afford adequate statistical power), use of subjects from

1 potentially susceptible populations (e.g., elderly, visually impaired), varied concentrations  
2 and durations of methanol vapor exposure (to elucidate the dose-response and  
3  $C \times T$  relationships), and other considerations as noted in the report and commentary of  
4 Cook et al. (1991).

5 Based on evaluations of existing data, only limited evaluation of genotoxicity appears  
6 warranted for neat methanol. Some evaluation of the co-carcinogenic activity of M100 and  
7 M85 should be planned, particularly in conjunction with likely mutagenic  
8 combustion/transformation products.

### 9 10 ***3.3.2.1.3 Combustion and Atmospheric Transformation Products***

11 Alternative fuels may provide substantial reductions in the health effects associated with  
12 conventional fuels by reducing ozone and the carcinogenic products of incomplete  
13 combustion. There is, however, insufficient information to evaluate adequately the health  
14 effects of methanol combustion and atmospheric transformation products. The health  
15 research proposed here is a high priority, because of the substantial anticipated exposure to  
16 methanol combustion and transformation products, and the carcinogenic nature of many of  
17 the combustion and transformation products. Because of the complexity of this research,  
18 initial health research should focus on evaluating the potential carcinogenic and respiratory  
19 toxicity of the whole complex combustion and transformations mixtures and previously  
20 identified components of concern (e.g., formaldehyde). Although no research is proposed at  
21 this time, pending an improved exposure evaluation, potential research needs for DMS also  
22 are noted.

23 Exposure assessment to assess potential changes in known key components (e.g.,  
24  $O_3$ ,  $NO_2$ , CO, PM, PAN, and formaldehyde), as well as the formation of new or less well  
25 studied compounds (e.g., DMS) are proposed in this Strategy (see Section 3.3.1.3.1). The  
26 emissions and exposure assessments must be coordinated with health research, and in many  
27 cases will be the determinants for the initiation of health research.

28 Proposed research on the complex mixtures is focused on determining the relative  
29 potency of the combustion and transformation products of all fuels under consideration,  
30 including methanol. Chronic bioassays for all fuel-related mixtures generated by various

1 vehicles and operating conditions is, however, prohibitively expensive and not necessary.  
2 As an alternative to conducting time-consuming and costly chronic bioassays, the Strategy  
3 proposes that shorter duration studies be conducted initially on the relative mutagenicity and  
4 respiratory toxicity of the mixtures of concern. This assessment should start with an  
5 extensive screening effort, using in vitro and/or short-term in vivo techniques, to determine  
6 and compare the relative potency of the various mixtures of concern. For cancer, various  
7 standard mutagenicity bioassays and, if appropriate, the mouse skin painting bioassay should  
8 be used. Evaluation of less well understood models, such as the lung implantation model and  
9 the transgenic mouse model, also could be included. For respiratory system effects,  
10 screening should begin with in vitro bioassays (using both animal and human cells) and short-  
11 term in vivo bioassays of animals (using inhalation exposures) to assess functional,  
12 biochemical, and histopathological indicators of effects. Specialized studies, such as on host  
13 resistance to infectious and neoplastic disease, also should be included. If effects and  
14 potencies are noteworthy in the screening studies, relative to conventional and/or other  
15 alternative fuel combustion and transformation products, then chronic animal bioassays would  
16 be conducted. If chronic bioassays of methanol combustion and transformation products  
17 appeared warranted, then both cancer and noncancer endpoints should be evaluated.  
18 Additionally, bioassay-directed fractionation should be used to identify those classes of  
19 compounds within a mixture that are associated with mutagenicity and/or toxicity.

20 This comparative potency/bioassay directed fractionation approach has proved to be  
21 extremely useful in previous EPA efforts to evaluate relative risks from other combustion  
22 sources. In addition, the screening approach described above can be used to assist control  
23 technology development efforts. These short-term bioassays can be used to compare and  
24 contrast the mutagenicity and toxicity of emissions under various control conditions in order  
25 to target certain components for emissions reduction and to provide an additional measure of  
26 control effectiveness.

27 Field studies (using the Integrated Air Cancer Project model) should also be planned,  
28 possibly in conjunction with epidemiologic studies (considering both cancer and noncancer  
29 effects). Possible targets of interest would be a city before and after fuel switching, or  
30 cohorts with personal garage exposures to high levels of conventional or alternative fuels.

1 A careful evaluation of the design and power of any epidemiologic study would be necessary  
2 before a decision can be made about feasibility. Results of studies of this nature will not be  
3 available for near-term risk assessments and decision-making.

4 Formaldehyde is a component of methanol combustion and transformation mixtures that  
5 is of particular interest, primarily because it is currently predicted to increase in  
6 microenvironments (e.g., garages) to levels that may be associated with respiratory system  
7 effects. Specifically, respiratory tract inflammation, alteration in pulmonary immune  
8 function, increased susceptibility to infectious diseases and allergic disease, and potential  
9 long-term respiratory impairment should be investigated. Assessment of respiratory effects  
10 also is desirable for other aldehydes, such as acrolein, associated with gasoline and methanol-  
11 fuel vehicles. At this time, additional health research is not proposed for evaluation of the  
12 potential cancer risks posed by formaldehyde and other aldehydes. This is because the  
13 chronic aldehyde exposure levels resulting from alcohol fuel use are not yet clear, and  
14 considerable work is already ongoing at the Chemical Industry Institute of Toxicology and  
15 elsewhere to address key health issues pertaining to the carcinogenicity of formaldehyde.

16 Dimethyl sulfate is another chemical for which environmental levels may increase with  
17 use of methanol or MTBE. Several animal studies have indicated that DMS is a carcinogen;  
18 however, these studies are inadequate as a basis for developing cancer potency estimates.  
19 If currently ongoing emissions and exposure evaluations predict that environmental levels of  
20 DMS will significantly increase with methanol and MTBE fuel use, then a high priority will  
21 be placed on chronic inhalation bioassays of DMS needed to support a quantitative dose-  
22 response assessment for cancer.

#### 23 24 **3.3.2.1.4 Research Objectives**

- 25 1. For methanol (M100): (1) evaluate important metabolic pathways, develop in vivo  
26 and in vitro metabolic constants for humans and laboratory animals and estimate  
27 dose to target tissue(s), (2) develop physiologically-based pharmacokinetic models  
28 for the experimental species relevant to humans (and potentially relevant to human  
29 subpopulations), and (3) validate these models with experimental data. This effort  
30 is key to facilitating extrapolation (species-to-species, route-to-route, etc.) and

1 estimating dose to target tissue, including dose to the fetus. Subsequently, explore  
2 the impact of co-exposure to gasoline (M85) on the metabolism of methanol.  
3 (Priority 1 for the next 2 to 4 years.)  
4

- 5 2. Evaluate the potency of M100 and M85 for developmental effects, with an  
6 emphasis on (1) determination of the appropriate animal model, including cross-  
7 species comparisons of metabolism, critical exposure timing and duration, and low-  
8 dose response estimation, (2) determine the mechanism of action and develop  
9 biologically based dose-response models for the experimental species relevant to  
10 humans (and potentially relevant to human subpopulations), and (3) couple this  
11 model with the pharmacokinetic model noted in Objective 1 and validate with  
12 experimental data. (Priority 1 for the next 2 to 4 years.)  
13

- 14 3. Further explore the potential human health hazards associated with exposure to  
15 methanol. Include neurotoxicity (especially for neurobehavioral effects and visual  
16 system toxicity), testicular toxicity, hormonal alterations, and exacerbation of  
17 chemically induced hepatotoxicity by co-exposure to methanol and other liver  
18 toxicants. Emphasize understanding dose-response relationships, mechanisms of  
19 action, and relevance to environmental exposures. (Priority 1 for the next  
20 2 to 4 years.)  
21

- 22 4. Evaluate the potential ability of methanol combustion and transformation products  
23 to induce cancer or respiratory toxicity, relative to conventional fuel combustion  
24 and transformation products. Initially use in vitro and short-term in vivo assays to  
25 target vehicle types and operating conditions of concern, then compare estimates of  
26 potency for methanol products to similar estimates of potency conventional fuels  
27 and other alternative fuels. These comparative potency estimates (in conjunction  
28 with improved estimates for emissions, exposure and market penetration) will  
29 determine the need for chronic bioassays for methanol combustion and  
30 transformation products. If needed, use bioassay-directed fractionation to identify



particularly potent components of these mixtures. (Priority 1 for the next 2 to 4 years.)

5. Investigate potential formaldehyde-induced respiratory system effects: pulmonary inflammation, increased susceptibility to infectious and allergic diseases, and the potential for long-term respiratory impairment with recurrent acute exposures. (Priority 1 for the next 2 to 4 years.)
6. Conduct chronic inhalation bioassays of methanol fuel (M85 and/or M100), assessing both cancer and noncancer endpoints, if warranted. Chronic bioassays should await the outcome of research described in Objectives 1 and 5, and improved estimates for emissions, exposure, and market penetration. (Priority 2 for the next 2 to 4 years.)

### 3.3.2.2 Ecosystem Effects

The main goal of the methanol-fuel ecosystem research is to provide data to complete ecological risk assessments that can be compared to gasoline assessments. This section briefly describes the terrestrial and aquatic (freshwater and marine) research needed to complete the assessments. The research needs are progressive in nature, with the first research project providing information for subsequent ones. Preliminary assessments will identify methanol-fuel pollutants of concern and biota and ecosystem components that are at risk. If information in the literature is weak, research projects are proposed to strengthen the data base. Proposed research projects will be ranked according to scientific prioritization and pacing issues. For example, exposure-response studies of a single species must be carried out before proceeding to complex mesocosm studies of simulated ecosystems. Finally, research should focus on concentrations and exposure durations that are environmentally realistic. The exposure assessment research described earlier is critical to provide guidance to studies of terrestrial and aquatic ecosystem effects.

### 3.3.2.2.1 *Terrestrial Ecosystem Effects*

Methanol-fuel pollutants (e.g., methanol and formaldehyde) produced from evaporative emissions and fuel combustion have the potential to impact terrestrial ecosystems through atmospheric gaseous and wet/fog exposures. To assess the hazards posed to terrestrial ecosystems, several research projects are necessary. Each project builds upon information gained from the previous project, proceeding from laboratory/greenhouse experiments to field research. Appropriate literature will provide guidance to the research.

Exposure-response experiments should expose plants to methanol, formaldehyde, and, perhaps, formic acid, individually and in combination with O<sub>3</sub>. During the growing season, a minimum of two trees and two crops should be treated with various exposure regimens in plant chambers to develop exposure-response relationships for plant process functions such as photosynthesis. Experimental designs should include both contaminated fog and gaseous exposure scenarios.

Research should then progress to sophisticated mesocosm studies. First, experiments should evaluate methanol-fuel pollutant environmental partitioning within the soil-plant-air continuum. To evaluate the interactions of possible global climate change and pollutant effects, pollutant environmental partitioning and plant effects need to be studied in response to altering temperature and water stress. Lastly, plants should be exposed to the complete combustion products of methanol fuel after irradiation. This would allow an evaluation of the effects of the complete array of pollutant/transformation products on plant growth and development.

Finally, in a proposed field study, biomarkers (e.g., abnormal enzyme activity) and other ecological endpoints should be used to monitor the effects of pollutants on vegetation within urban, agricultural, and natural ecosystems as methanol fuel gains prominence within the Los Angeles Basin. Research results could be used to establish biomonitoring sites throughout the country to evaluate forest and crop responses as fuel switching occurs.

## Research Objectives:

1. Evaluate the responses of plants to formaldehyde and methanol exposures (dry and wet/fog), individually and combined with O<sub>3</sub> at various concentrations, to assess the sensitivity of plant process functions. (Priority 1 for the next 2 to 4 years.)
2. Evaluate the effects of formaldehyde and methanol binary exposures (dry and wet/fog) on plants to assess the sensitivity of plant process functions. (Priority 1 for the next 2 to 4 years.)
3. Evaluate the effects of formaldehyde and methanol within plant mesocosms with altered temperature and water stress variations. (Priority 2 for the next 2 to 4 years.)
4. Evaluate the effects of methanol-fuel tailpipe emissions/transformation products on plant growth and development, using various exposure scenarios. (Longer term priority.)
5. Evaluate the use of biomarkers for monitoring the effects of methanol-fuel pollutants on vegetation as the fuel gains prominence in the South Coast Air Basin, CA. (Longer term priority.)

**3.3.2.2 Freshwater Effects**

Toxicity tests need to be conducted on various freshwater organisms using both pure methanol and methanol-gasoline blends. The effects of methanol on the bioavailability of gasoline components and their joint toxicity should be investigated. The kinetics of toxicity need to be studied to predict responses to transient exposure. Consideration should be given to toxicity tests with sediment-dwelling organisms, laboratory microcosms, and experimental ecosystems. As justified by preliminary exposure assessments and hazard identification, additional effects data might be needed to evaluate the impacts of methanol-induced oxygen

demand/depletion, the effects of other contaminants that are made bioavailable by methanol in aquatic systems, and expected changes in general contamination of urban waters by fuels and fuel transformation products via multiple pathways.

#### Research Objectives:

1. Evaluate the toxic effects of methanol and its joint toxicity with soluble conventional fuel components, selected other hydrophobic contaminants, and reduced dissolved oxygen levels on various freshwater aquatic organisms; develop dose-response models suitable for application to various exposure situations. (Priority 1 for the next 2 to 4 years.)
2. Test the effects of a simulated methanol spill on an experimental freshwater aquatic ecosystem to evaluate assessment techniques and to empirically determine system level effects. (Priority 2 for the next 2 to 4 years.)

#### ***3.3.2.2.3 Marine Effects***

To develop a better understanding of methanol and gasoline effects on marine systems, several types of studies should be conducted. Biodegradation studies are needed to predict the extent and duration of exposures. Because methanol may be rapidly degraded or diluted, direct exposure should decrease quickly. A large spill into a relatively enclosed body of water, however, could produce a massive BOD that may deplete oxygen levels and, thereby, cause mortality. Methanol chronic release at a docking facility could also produce microbial and algal enrichment that may negatively impact the environment. Information on the biodegradation rate over a wide range of concentrations is critical for predicting direct exposure and effects associated with the release of methanol. Some of this information is presently available for gasoline, but more research is needed to ensure that the data sets needed for comparative exposure and effects assessment are complete.

Information on the toxicity of methanol to marine biota is very limited. Toxicity testing with various species will be needed for ecological risk assessments associated with the

potential release of this compound. Unlike petroleum hydrocarbons, methanol is highly water soluble and will readily mix into the water column. Because of its solubility, a methanol spill could impact the entire water column, but remain at toxic concentrations for only a short period of time. Toxicity testing should be conducted on sensitive species from all zones of the water column and for different durations of exposure.

#### Research Objectives:

1. Assess the effects of methanol when added to marine mesocosms under conditions of acute (spill) and chronic exposure. (Priority 1 for the next 2 to 4 years.)
2. Determine the influence of methanol on the joint toxicity with selected neutral organic compounds in the marine environment. (Priority 1 for the next 2 to 4 years.)
3. Develop saltwater quality criteria for methanol. (Priority 2 for the next 2 to 4 years.)

### **3.3.3 Global Warming**

The research described on source characterization, environmental fate in ambient air, and risk reduction/control technology will result in identification of changes in RITGs due to the manufacture and combustion of various alternative fuels and will not be repeated here. The primary focus relative to global warming will be the potential for increased methane emissions from existing sources of natural gas and CO<sub>2</sub> emissions from the longer range coal feedstock option.

1 Research Objective:

- 2
- 3 1. Identify and characterize RITGs affected by methanol fuel production and use as
- 4 part of source characterization research (Section 3.3.1.1). This information will be
- 5 used as an input to global climate models being developed and applied under the
- 6 global climate research program. (Priority 2 for the next 2 to 4 years.)
- 7

8 **3.3.4 Risk Prevention/Mitigation**

9 **3.3.4.1 Stationary Sources**

10 Risk reduction research must focus on (1) those areas that are already current problems

11 for conventional fuels, (2) new areas of uncertainty brought about by methanol fuels, and

12 (3) areas likely to be aggravated by use of methanol.

13 Substantial effort must be made to ensure that the existing O<sub>3</sub>-nonattainment problem is

14 not further aggravated, which means that the adequacy and impacts of alternative fuels on

15 existing controls must be examined. Existing combinations of emission sources and typically

16 applied controls must be evaluated to determine applicability and effectiveness of add-on

17 control technology. Opportunities for applying prevention technologies and strategies must

18 be identified. Existing information on VOC-rule effectiveness seems to indicate poor

19 performance of controls in areas such as gasoline distribution. Emissions of the greenhouse

20 gas CO<sub>2</sub> are a major concern with respect to global climate change. Uncertainties relative to

21 the greenhouse effect for methanol depend up on the particular feedstock option. For

22 example, the use of coal as a future feedstock for methanol warrants research efforts that

23 focus on improved emission, effluent, and discharge controls and on technology for CO<sub>2</sub>

24 utilization.

25 Risk reduction research is needed on emissions of methane resulting from its increased

26 use as a feedstock for methanol. Compared to CO<sub>2</sub>, methane is a potent greenhouse gas.

27 Research should address the formulation of strategies that could minimize its release on a

28 global basis.

1        Several accidental release hazards can be identified with the production, distribution,  
2 and use of methanol. Safe-handling guidelines and procedures must be developed and  
3 disseminated.

4        For USTs, significant data gaps related to leak detection, leak prevention, and  
5 corrective action exist. Regarding detection, for example, the lower volatility of methanol  
6 will reduce the utility of external leak detectors developed for gasoline, but research might  
7 show that modified vapor detectors would still be useful. Some changes may be required for  
8 in-tank volumetric leak detectors. In the area of prevention, different types of corrosion  
9 protection (e.g., interior linings and impressed current/cathodic protection) are likely to be  
10 required; factors here include materials compatibility and phase separation behavior. Unlike  
11 a gasoline UST, no separate water layer would be expected in a methanol UST because of  
12 the miscibility of methanol with water. The lack of a separate water phase could  
13 significantly reduce internal tank corrosion. On the other hand, methanol is more corrosive  
14 than gasoline. Several physicochemical properties of methanol (especially as they differ from  
15 gasoline) would require reevaluation and/or new research in the area of corrective action.  
16 The lower volatility and higher water solubility, for example, could drastically reduce the  
17 utility of vacuum extraction in the unsaturated zone and of any attempt to recover product  
18 from the top of the groundwater table. On the positive side, no hydrocarbon residue would  
19 be left on the soils (after a few flushes of infiltrating water), and extraction of contaminated  
20 groundwater could be achieved more quickly for methanol than for gasoline. A series of  
21 pilot- and full-scale research studies would be needed to evaluate the actual effectiveness of  
22 these corrective actions.

23  
24        Research Objectives:

- 25  
26        1.    Assess the impact of methanol on existing stationary source control technology  
27            (e.g., carbon absorbers used in controlling evaporative emissions from  
28            distribution/marketing). The impact of methanol on control system performance  
29            will be quantified. The potential for aldehydes from catalytic and direct flame  
30            oxidizers will be determined via testing. Guidance on new or improved control

1 systems, design methods, and operating procedures will be developed to minimize  
2 emissions/discharges. (Priority 1 for the next 2 to 4 years.)

- 3
- 4 2. Develop user-oriented accidental release reference manuals/guidelines for  
5 prevention of accidental releases of methanol from storage, transportation, and  
6 marketing. (Priority 1 for the next 2 to 4 years.)
- 7
- 8 3. Analyze the overall global hydrocarbon system relative to production of methanol  
9 from natural gas. The best strategies for minimizing methane efficiency losses and  
10 leaks will be identified. For example, should methane be converted to methanol  
11 outside of the United States and then be shipped to the United States, or,  
12 alternatively, should methane be shipped to the United States and converted in  
13 U.S. refineries? (Priority 1 for the next 2 to 4 years.)
- 14
- 15 4. Perform an environmental engineering evaluation of means for reducing the  
16 potential problems associated with the longer range coal-based options. This  
17 would include determining the feasibility of producing methanol from CO<sub>2</sub> and  
18 reviewing the Tennessee Eastman and Electrical Power Research Institute  
19 processes (for methanol production from coal) for potential improvements in CO<sub>2</sub>-  
20 efficiency. Other prevention/mitigation opportunities beyond CO<sub>2</sub> would be  
21 identified for the Tennessee Eastman process in the review. (Priority 3 for the  
22 next 2 to 4 years.)
- 23
- 24 5. Confirm low emission potential (reduced hydrocarbons, CO, and NO<sub>x</sub>) for neat  
25 methanol used in power generation (including utility boilers and gas turbines), heat  
26 generation sources such as industrial/commercial boilers, cogeneration units, and  
27 stationary IC engines. Also, evaluate the barriers for extending the use of  
28 methanol to stationary combustion sources and develop control options for  
29 aldehydes from certain sources utilizing methanol where exposure may be  
30 important. (Priority 3 for the next 2 to 4 years.)



6. Study the areas of leak detection, leak prevention, and corrective action related to USTs. For leak detection, the focus is primarily on external detectors, although some in-tank investigations may be required. For prevention, the focus is on materials compatibility (e.g., methanol with tank seals and liners) and corrosion protection. For corrective action, the focus is primarily on evaluations of the effectiveness of existing technologies used for gasoline releases. (Priority 1 for the next 2 to 4 years.)

#### **3.3.4.2 Mobile Sources**

The performance of motor vehicle emissions control systems will be monitored as a function of consumer mileage accumulation. With methanol fuels, special emphasis will be given to formaldehyde. Engine-out emissions of this compound are projected to increase significantly with methanol fuel (flexible-fuel vehicles, M85, and/or M100). The impact of this technology on urban O<sub>3</sub> will weigh heavily on the effectiveness of control systems for reduction of these and other photochemically reactive emissions. In the near term, vehicles from federal, state, and local government fleets will be evaluated; and in the future, vehicles owned and operated by private citizens will provide an additional source for study.

#### **Research Objective:**

1. Assess the effectiveness of motor vehicle emissions control systems for reduction of formaldehyde as a function of consumer mileage accumulation. (Priority 1 for the next 2 to 4 years.)

#### **3.3.4.3 Fuel Transport Sources**

Although major attempts are made to reduce major spills of fuels, accidents and problems do occur with shipping and other forms of transporting fuels. Thus, important issues are whether current containment systems are adequate for methanol and, if not, the best options for clean-up.

Research Objectives:

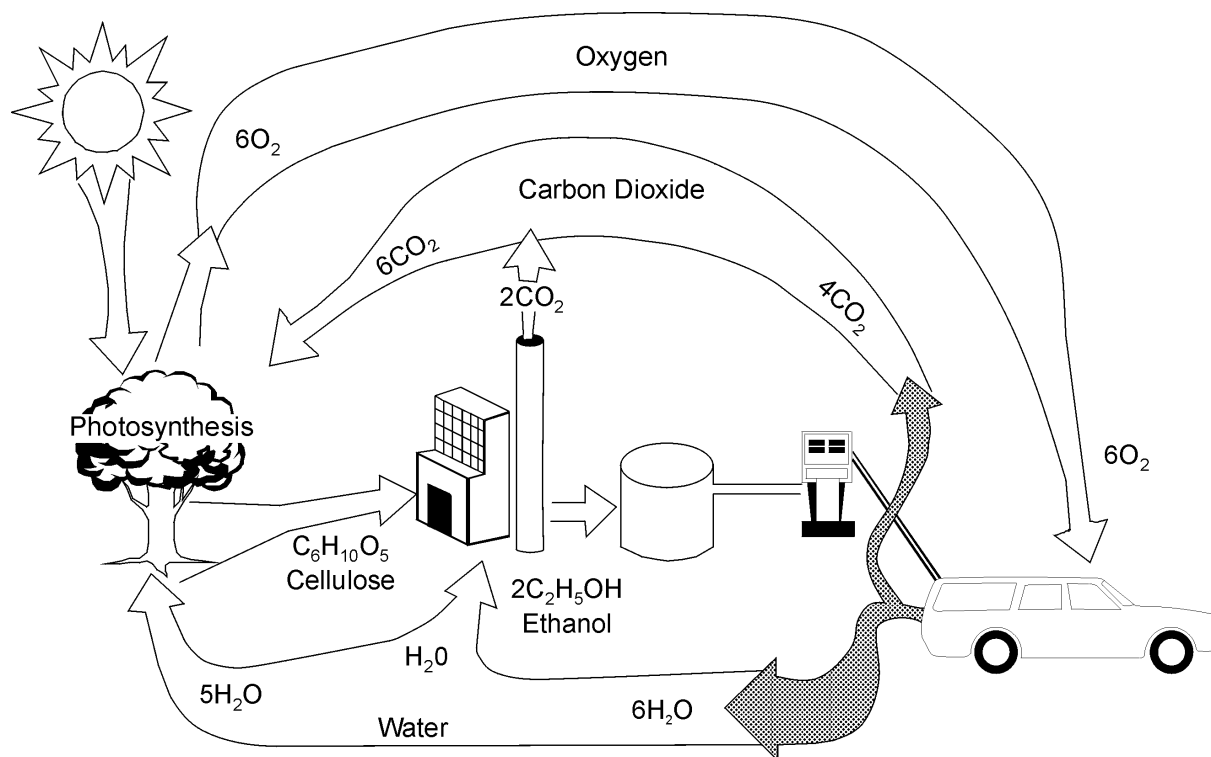
1. Evaluate adequacy of transport system containment of methanol fuels for preventing major spills and leaks. (Priority 2 for the next 2 to 4 years.)
2. Assess clean-up options to reduce the impact of a methanol fuel spill on sensitive biota and ecosystems. (Longer term priority.)

## 4.0 ETHANOL

### 4.1 RISK ASSESSMENT RESEARCH FRAMEWORK

Ethanol is not yet receiving the same attention as methanol as a replacement for petroleum-distillate fuels in the United States, but it does pose many interesting possibilities that merit examination (Alternate Fuels Committee of the Engine Manufacturers Association, 1982). It is attractive for preventing future global climate change, especially if the technology for its production can be enhanced (Segal, 1989). Ethanol can be produced from renewable biomass resources and offers most of the environmental benefits of methanol as an alternative fuel (Sperling, 1988). The use of renewable biomass resources (e.g., agricultural grain crops) has the advantage of cycling significant amounts of carbon dioxide (CO<sub>2</sub>), which are emitted from ethanol production and from vehicles, back into the growing of more biomass feedstock (see Figure 4-1). Current production economics have limited consideration of ethanol to date; however, if future developments alter the economic factor, this fuel could develop as a viable alternative to classical petroleum fuels. The Solar Energy Research Institute predicts that ethanol will be cost competitive in the future. Expanded understanding of associated emissions, atmospheric chemistry, target population exposures, health/ecosystem effects, and possibilities for risk reduction/control will be necessary to assess potential impacts on public health and the environment.

Advancements in electronic fuel sensing and control suggests the possibility of multialcohol-compatible vehicles (U.S. Environmental Protection Agency, 1990b). These vehicles could use either methanol or ethanol fuels, with appropriate adjustment of fuel injection and cold-start drivability enhancement. Methanol and ethanol share many characteristics that make them potentially attractive alternatives to gasoline and diesel fuels. Moreover, like methanol, ethanol is a familiar chemical; indeed, it is widely ingested as a beverage. However, the use of ethanol as a fuel raises many questions that cannot be fully answered at present.



**Figure 4-1. Carbon dioxide recycling with ethanol fuel.**

1           This chapter first highlights some key points of information and issues about ethanol  
 2 fuels in a risk assessment research format. The risk assessment research section uses  
 3 Section 1.4, Introduction to Risk Assessment Framework for Fuels, as its point of departure,  
 4 but it focuses only on those facets of the generic framework that are specific to ethanol fuels.  
 5 The next section (Section 4.2) is intended to provide a background and rationale for the  
 6 research. It is not intended to be a complete review of the literature. The last section  
 7 (Section 4.3) describes research needed to provide the foundation for a quantitative risk  
 8 assessment and risk mitigation of these fuels.

## 4.1.1 Exposure Assessment

### 4.1.1.1 Source Characterization

#### 4.1.1.1.1 Emissions from Feedstocks and Fuel Production, Storage, and Distribution

**Feedstocks.** Corn is the feedstock currently used to produce fuel grade ethanol in the United States; however, other biomass-related feedstocks, different petroleum fractions, coal, oil shale, and natural gas could potentially be used. Other biomass processing, such as cellulosic or hemicellulosic fermentation, is under steady development, using wood or refuse as the feedstock. The Department of Energy, through its national laboratories, has focused research on the development of techniques to biochemically convert cellulosic feedstock to ethanol. In the last decade, this research has reduced the cost of wood-derived ethanol to \$1.35/gal. Current research plans estimate that a \$0.60/gal cost could be obtained (Goodman and Wyman, 1990). Ethanol is also used to produce ethyl-tertiary-butyl ether (ETBE). The radiatively important trace gases (RITGs) and volatile organic compounds (VOCs) emitted from energy required to plant, grow, harvest the corn, and distill the fermented mash are major concerns. Evaluation of the overall net change in RITGs, VOCs, and other stationary source multimedia emissions/discharges resulting from one or more key scenarios of ethanol market penetration is needed.

Biomass production will also alter land-use patterns and practices and the use of agricultural pesticides, fertilizers, and herbicides, creating potential impacts on human health and ecosystems. Soil erosion and pesticide and fertilizer runoff may increase, contaminating both surface and groundwater resources as marginal agricultural lands are put into biomass production. However, these topics are subject to assessments rather than research within this Strategy.

**Production.** Production of ethanol from fermentation of corn and other biomass sources would involve emission of RITGs, VOCs, microbes, enzymes, and ethanol. Emission of RITGs would be the primary concern. Because RITG (especially carbon dioxide [CO<sub>2</sub>]) and VOC emissions impact global climate change and ozone (O<sub>3</sub>) nonattainment, respectively, a quantitative understanding of the contribution of biomass feedstock processes to levels of these gases is important. Development of an accurate CO<sub>2</sub> balance for the

1 production of ethanol from biomass would be critical in the evaluation and should include  
2 projections for new biomass conversion systems (wood and refuse). Potential water  
3 discharges would include ethanol, microorganisms, biocides, microbes, trace metals,  
4 enzymes, and mash solid waste. Information on the specific types or quantities of  
5 compounds that would be emitted or discharged is not available, thereby necessitating  
6 screening-level studies to determine the need for a fuller scale characterization.  
7 An accidental-release hazard-assessment study is needed to identify specific areas of concern  
8 that may need prevention-oriented risk-reduction work.  
9

10 ***Storage and Distribution.*** The potential problems would primarily be related to  
11 conventional, transient, or accidental releases of ethanol. Engineering emission estimates of  
12 ethanol from new and modified stationary sources are of great concern, because increases in  
13 VOC emissions from such sources could offset gains from ethanol use in fuels. The impact  
14 of ethanol on existing storage, distribution, and marketing controls, where its use could affect  
15 control system effectiveness and result in increased emissions, must be determined. Large  
16 accidental releases of ethanol are also of concern. Potential releases may occur in the  
17 distribution and handling facilities where industrial prevention/control approaches are not  
18 widely practiced and expertise is the weakest. In storage vessel head spaces, ethanol  
19 equilibrium concentration is within its flammability limits; if ignited, it could rupture the  
20 vessel and result in major releases and fires.

21 Leakage and spills, especially large accidental releases, of ethanol fuels from  
22 distribution and storage systems to ecosystems could pose a significant hazard to freshwater,  
23 marine, groundwater, and soil systems. The probability and extent of such releases from  
24 pipelines, tankers, storage tanks, and other systems could probably be estimated from  
25 experience with conventional fuels. Because ethanol fuels may be more corrosive than  
26 conventional fuels, the compatibility of fabrication materials and the internal corrosion and  
27 reactive potential with ethanol must be compared to the data available on conventional fuels  
28 and be examined vis-à-vis both current and future designs of underground storage tank (UST)  
29 systems (tanks and piping). Research to identify the hazard that fuel leaks and spills pose to

1 terrestrial and aquatic ecosystems and approaches for mitigating their occurrences is also  
2 needed.

#### 4 ***4.1.1.1.2 Emissions Related to Fuel Use***

5 ***Stationary Source Emissions.*** Emissions of RITGs (primarily CO<sub>2</sub>) from the  
6 combustion of ethanol are the dominant concern. Confirmation of the estimated low  
7 emissions potential (reduced hydrocarbons, carbon monoxide [CO], and nitrogen oxides  
8 [NO<sub>x</sub>]) for ethanol in power utility boilers, turbines, cogeneration units, and stationary  
9 internal combustion (IC) engines is needed. Emissions of aldehydes from IC engines need to  
10 be better quantified. Potential releases of ethanol from storage and handling at the user  
11 facilities, where release prevention/control approaches are not practiced, would be of  
12 concern.

13  
14 ***Mobile Source Emissions.*** The largest demonstration of ethanol as a motor vehicle fuel  
15 has been in Brazil; in 1989 about 40% of this nation's 14 million vehicles were operated on  
16 neat ethanol (95% ethanol, 5% water) and 60% on a blend of 78% gasoline, 22% ethanol.  
17 The Brazilian motor vehicle technology is unlike that used in the United States (i.e.,  
18 carburetors and no catalysts versus electronic fuel injection and closed-loop three-way  
19 catalysts), so extrapolation from their emissions experience to that possible in the United  
20 States is very difficult. In the United States, substantial amounts of ethanol are marketed in  
21 10% blends with gasoline for motor vehicle fuel (about 840 million gallons in 1988), but  
22 little has been done to develop advanced technology vehicles for neat or near-neat ethanol  
23 fuel. The State of California has identified E95 (95% ethanol, 5% unleaded gasoline) and  
24 E85 as potential "clean-fuel" alternatives, but has been unable to report emissions data for  
25 vehicles optimized for these fuels. Available data are generally associated with ethanol use  
26 in flexible-fuel vehicles optimized for methanol fuels. Engineering judgment suggests that  
27 the impact of ethanol fuels on motor vehicle emissions, relative to conventional gasolines and  
28 diesel fuels, would be similar in many regards to that of methanol fuels.

29 The vapor pressure of ethanol is less than methanol (2.5 psi vs. 4.6 psi at 100 °F),  
30 suggesting the possibility for reduced evaporative emission rates (both parking and

running-losses). The organic emissions composition should be dominated by ethanol and include significant amounts of acetaldehyde and nonmethane hydrocarbons (NMHCs), depending upon the amount and composition of gasoline blended with the ethanol. Ethanol, like methanol, generally has lower O<sub>3</sub> photochemical reactivity than most gasoline hydrocarbons (especially at a low local VOC/NO<sub>x</sub> ratio). The potential O<sub>3</sub> benefit depends on many factors, including mixture reactivity and absolute emission rates. Ethanol, like methanol, offers potential for both reduced motor vehicle organic emission rates and reduced photochemical reactivity relative to conventional gasolines. The emission rates of toxics associated with gasoline combustion, such as benzene and 1,3-butadiene, will also likely be reduced; acetaldehyde emissions will be increased.

Like methanol, the impact of ethanol fuel on CO and NO<sub>x</sub> emissions will depend on engine and emissions-control design. Engines designed for stoichiometric combustion will likely have reduced NO<sub>x</sub>, but no significant change in CO emissions (assuming cold-start drivability problems are successfully eliminated); and engines designed for fuel-lean combustion will have reduced CO emissions, but little impact on NO<sub>x</sub> relative to three-way catalyst gasoline vehicles (lean combustion prevents the use of three-way catalysts).

Motor vehicle CO<sub>2</sub>-emission rates may be somewhat less with ethanol than with gasoline, if potential efficiency improvements (estimated 15 to 30%) are realized. Global climate impact analyses must also consider the CO<sub>2</sub> emissions associated with fuel production and distribution as well as other RITG emissions of importance (e.g., methane and N<sub>2</sub>O).

As with methanol, potential exists for development of heavy-duty engines using ethanol fuel. Reduced particulate and NO<sub>x</sub> emissions would be projected relative to petroleum distillate diesel engines.

A comprehensive understanding of the potential impact of ethanol on risk to public health and ecosystems will require research on the characteristics of emissions under varied driving conditions (e.g., ambient temperature, average speed, altitude, and malfunction operation) typical of U.S. motor vehicle fleets. Very little information on advanced technology vehicles designed for ethanol fuel is available, so future research must consider such vehicles.



#### 4.1.1.2 Environmental Fate

##### 4.1.1.2.1 Air Fate

As with methanol, the most important consideration with the use of ethanol as a motor fuel is its role in the production of O<sub>3</sub> in the troposphere. Again, like methanol, the amount of O<sub>3</sub> produced by an organic compound is dependent upon several factors, including solar intensity, boundary conditions, wind velocity, concentration of VOCs, VOC/NO<sub>x</sub> ratio, and VOC reactivity. The reactivity of ethanol is less than most VOCs in conventional gasolines; thus, on a per equivalent carbon of emissions, the use of ethanol as a fuel should reduce photochemical O<sub>3</sub> production. Again, as with methanol, the VOC/NO<sub>x</sub> ratio is very important. At high ratios, differences in VOC reactivities have little effect on O<sub>3</sub> formation.

Ethanol is removed from the atmosphere by reaction with hydroxyl (OH) radicals and by wet deposition. Its tropospheric lifetime through the homogeneous OH radical reaction is approximately 6 days. When both gas-phase and heterogeneous wet removal processes are considered, the lifetime should be closer to 3 to 5 days. Acetaldehyde is the principal product from both the combustion of ethanol and OH radical attack. Because of the use of ethanol as a motor fuel, significant ambient levels of acetaldehyde have been observed in several urban centers in Brazil. These high levels are primarily a result of direct emissions from tailpipes. Because the vehicles in Brazil have no catalytic converters, the tailpipe emissions are expected to be high. Ethyl nitrite may also be a possible exhaust product. Further, the reaction of OH radicals with ethanol could produce some hydroxyacetaldehyde, and in the liquid phase, acetic acid could be produced.

Acetaldehyde, when photooxidized in the presence of NO<sub>x</sub>, can produce peroxyacetylnitrate (PAN). This compound is weakly mutagenic, a phytotoxicant, and an eye irritant. Peroxyacetylnitrate can also store NO<sub>2</sub> temporarily. This is important for second day effects when PAN is transported downwind, decomposes to give off NO<sub>2</sub>, and produces more O<sub>3</sub> in the presence of transported VOCs and natural hydrocarbons (e.g., isoprene and the terpenes). Ethyl nitrite, if an exhaust product, will photodissociate to produce free radicals (HO<sub>2</sub> and OH), which will contribute to photochemical smog production.

1 Like methanol, monitoring of all possible reactants and products in the photooxidation  
2 of exhaust from ethanol-fueled and ethanol-gasoline-fueled vehicles is needed to assess the  
3 impact of ethanol substitution on air quality and risk associated with the substitution. The  
4 chemistry and mutagenic activity of transformation products, such as PAN and  
5 hydroxyperoxyacetyl nitrate (hydroxyPAN), and the properties of other possible products  
6 must be defined.

#### 8 ***4.1.1.2.2 Soil and Groundwater Fate***

9 To determine whether ethanol-contaminated groundwater presents a potentially  
10 significant source of human exposure, the transport and fate of ethanol in soil and  
11 groundwater need to be understood. Previous discussions of methanol (Chapter 3) are  
12 directly applicable. Because little or no interaction between ethanol and the soil matrix is  
13 expected, the rate of transport will depend upon the relative amounts of ethanol and transport  
14 water, the hydraulic properties of the soil, and changes in these properties resulting from the  
15 introduction of ethanol or ethanol-water solutions. These changes are expected to be  
16 relatively small in most soils and aquifers, but they may be significant in soils containing  
17 substantial quantities of smectite minerals.

18 The extent to which groundwater quality may be impacted by ethanol is strongly  
19 dependent upon the rate at which it is attenuated by microbial degradation. At relatively low  
20 concentrations, ethanol is known to readily biodegrade in soils; however, at high  
21 concentrations, it is toxic to microbial populations. Therefore, the dynamics of ethanol  
22 mixing and dissolution in water within soils, single- and two-phase transport, the relationship  
23 between ethanol concentration and biodegradation, and the effect of ethanol on the microbial  
24 ecology of the subsurface are important to understand. Each of these requires additional  
25 research to assess the impact of ethanol fuels on groundwater quality.

26 In environments where the soil/groundwater matrix already contains other organic  
27 contaminants, high concentrations of ethanol could mobilize these compounds and result in  
28 increased potential for human or ecological exposure. For nonpolar (hydrophobic)  
29 chemicals, this solubilization or mobilization could be quantified under equilibrium  
30 conditions; however, the dynamics or kinetics of this process are dependent upon

characteristics of the medium and are less well understood. Similar considerations apply to surface freshwater and marine aqueous systems.

#### ***4.1.1.2.3 Surface Water Fate***

Ethanol spills in freshwater and near-coastal estuaries are likely to present significant hazards to aquatic life forms in both direct and indirect ways. Again, the discussions of methanol (Chapter 3) are directly applicable. Direct toxicity to exposed populations will be important if exposure levels to ethanol are sufficiently high. Accordingly, the most important fate processes regarding direct toxicity are those that determine near-field concentration gradients. Because of ethanol's properties, spills should readily mix with water and dissolve quickly; volatilization will be important, especially in the immediate area. These processes must be quantified for exposure assessment.

Another major impact of spills is the indirect effect of oxygen depletion that results from biodegradation of the ethanol. In brief, ethanol will degrade rapidly (unless microbial toxicity occurs) and possibly deplete dissolved oxygen to levels where organisms (e.g., fish) are asphyxiated. Simultaneously, reaeration will proceed to replenish the dissolved oxygen. The spatial extent and the duration of the dissolved oxygen depletion zone will depend upon the reaeration rate, the microbial degradation rate, and the rate of ethanol removal by volatilization. The concentration of ethanol as influenced by mixing and advective transport will also be important. Again, these processes must be quantified and integrated into an exposure assessment.

Priority research for the fate of ethanol in fresh water and estuaries needs to include an investigation of the rate of biological degradation; toxic thresholds for such degradation; reaeration rates within spill areas; and the mixing, advection, and volatilization of the spilled compound. Transformation products also need to be identified and their fates need to be investigated for potential additional effects.

### 4.1.1.3 Exposures

#### 4.1.1.3.1 *Human Exposure Assessment*

Unlike methanol, modeled estimates of ethanol concentrations for various vehicle and traffic scenarios under typical and severe operating conditions do not exist. The same locations of increased concentrations would be likely, however, and include street canyons, roadway tunnels, expressways, personal and public parking garages, and in-transit exposures. In the case of ethanol as a fuel, the primary route of acute human exposure is not expected to be through ingestion, but rather through inhalation. These exposures can be verified through analysis of information obtained from Brazil, where ethanol-fueled cars were introduced in 1975. Even though the cars in Brazil are not controlled, upper limits to exposure estimates as well as emission ratios (controlled vs. uncontrolled cars) by which to scale down modeled estimates can be obtained. If emissions from ethanol-fuel motor vehicles are similar to those from methanol-fuel vehicles, except that acetaldehyde replaces formaldehyde as the primary aldehyde and that ethanol replaces methanol emissions, then maximum peak exposure concentrations could be comparable to those of methanol.

Total exposure assessment becomes a very significant issue for ethanol, because voluntary oral intake is relatively widespread. This suggests that total human exposure must account for ethanol exposure resulting from oral ingestion of alcoholic beverages and that the incremental amounts that will likely result from the other pathways must be determined. Other exposure issues concern potential exposures within vehicles during normal operation and exposures during refueling and in service-station repair facilities.

#### 4.1.1.3.2 *Biota Exposure Assessment*

The biota of terrestrial and aquatic ecosystems will potentially be exposed to pollutants related to ethanol fuel (e.g., ethanol, acetaldehyde, PAN, O<sub>3</sub>) derived from fugitive emissions during ethanol-fuel manufacture, transportation, storage, and fuel combustion and subsequent atmospheric transformations. Terrestrial and aquatic ecosystems will be exposed to the pollutants through airborne deposition and accidental spills/leakage from barges, ships, and storage tanks. Airborne pollutant deposition represents the greatest threat to terrestrial ecosystems, whereas accidental spills/leakage will have the greatest impact on aquatic

1 ecosystems. Such exposures could be acute or chronic, frequent or infrequent, high level or  
2 low level, and local or regional. Scenario-driven modeling efforts (e.g., using National Acid  
3 Precipitation Assessment Program [NAPAP], User's Network for Applied Modeling of Air  
4 Pollution [UNAMAP], National Center for Intermedia Transport Research [NCITR], or other  
5 ORD multimedia models) will be needed to determine whether significant exposures are  
6 likely to occur and pose a threat to terrestrial and/or aquatic biota. For example, NCITR's  
7 Spatial Multimedia Compartmental Model (SMCM) could be used to predict pollutant  
8 concentrations and mass fraction in air, soil, water, and sediment through time.  
9 A geographic information system (GIS) framework could be used in conjunction with  
10 modeling results to provide pollutant exposures to various terrestrial ecosystems. These  
11 exposure data will then provide guidance to develop exposure-response studies for hazard  
12 identification (fuels, combustion products, transformation products, additives) of the  
13 pollutants at realistic ambient concentrations.

14 As explained in the generic fuel risk assessment (Section 1.3) in the introductory  
15 chapter, exposure assessments for aquatic ecosystems involve integration of efforts on source  
16 characterization and environmental fate with information on the populations of organisms at  
17 risk. The resulting exposure information will be used in effects assessments, as discussed  
18 below. For acute exposures from ethanol-fuel spills, this must involve (1) identifying  
19 example ecosystems at risk, (2) computing an exposure time series appropriate to the habitat  
20 and behavior of the various organisms, and (3) obtaining other exposure/environmental  
21 information needed for kinetic-based effects models. For chronic exposures from more  
22 continuous releases and from atmospheric deposition (for which more rudimentary risk  
23 assessments initially will be done), ecosystems at risk will still need to be identified, but only  
24 average, general exposures will be needed to compare with effects concentrations from  
25 chronic toxicity assessments.

#### 26 27 **4.1.1.4 Analytical Methodology**

28 Analytical methodologies for measuring source emissions, for monitoring the ambient  
29 air transport and transformation of these emissions, and for monitoring the exposure of target

1 populations (human and ecosystem) to the pollutants of interest are prerequisites for  
2 determining the relative impacts of varied motor fuels on risk to public health and welfare.

3 Source emissions characterization requires accurate, precise analytical procedures for  
4 certification of regulated emissions (total hydrocarbons [THC], CO, NO<sub>x</sub>, CO<sub>2</sub>, and  
5 particles) and comprehensive speciation of unregulated emissions. Ethanol and methanol  
6 have many similarities as motor fuels and in requirements for analytical methodology.  
7 Although regulations have not yet been promulgated for certification of emissions from  
8 ethanol-fueled vehicles, they will likely be similar to requirements for methanol fuels. With  
9 ethanol fuels, certification of organic emissions will be more complex than simple  
10 determination of THC as with conventional fuels. Measurements of ethanol and  
11 acetaldehyde, in addition to THC, will be required. Organic certification will be based on  
12 the emission rate of total organic carbon (sum of hydrocarbon, ethanol, and acetaldehyde).  
13 The recommended practice will require chromatographic measurement of ethanol and  
14 acetaldehyde, along with classical THC flame-ionization-detection (FID). The FID  
15 measurement will require correction for response to ethanol and acetaldehyde (aldehydes of  
16 two carbons and more produce FID response) to obtain THC concentrations. Improved, less  
17 costly, more simplistic procedures will be needed for emissions certification. Compounds of  
18 interest with ethanol fuels in addition to those currently regulated include acetic acid and  
19 ethyl nitrite, along with compounds emitted from conventional fuels (e.g., N<sub>2</sub>O, benzene,  
20 and 1,3-butadiene). Detailed emissions speciation is necessary for comparing the O<sub>3</sub> and  
21 toxics air-quality impact of ethanol fuels with that of conventional fuels.

22 Ambient air monitoring needs are similar to those for emissions characterization.  
23 Methodology is needed for acetic acid, ethyl nitrite, PAN, and hydroxyPAN. Ambient air  
24 monitoring and microenvironmental monitoring will require methods development for the  
25 measurement of ethanol and acetaldehyde. In addition, development of personal monitors  
26 will also be required for population characterization studies, if undertaken in later years.

## 4.1.2 Effects Assessment

### 4.1.2.1 Human Health Effects

As with methanol, ethanol-gasoline mixtures (e.g., E85) are more likely to be used than E100. This complicates predicting the effects of the actual in-use fuel, because it will be some combination of gasoline and ethanol. This argues for understanding the effects of gasoline and ethanol, predicting effects of gasoline-ethanol mixtures, and then testing the validity of the assumptions with research on the mixture. Such an approach would advance predicting the health hazards of the variety of mixtures possible.

Human data are sufficient for identifying the types of hazards that could be associated with ethanol exposure. Most of the information on the health effects of ethanol is derived from humans via oral exposure, although some inhalation data are available. Health effects associated with sufficient oral doses of ethanol include cirrhosis of the liver; cancer; developmental effects; and diseases affecting the gastrointestinal, respiratory, nervous, and reproductive systems; as well as adverse outcomes resulting from neurobehavioral alterations (e.g., accidents). Based on current crude exposure projections, the likelihood of intoxication from acute environmental inhalation exposure in adults appears to be very low; however, concern exists about potential developmental effects. The ability of high ethanol exposures (both oral and inhaled) to induce a variety of adverse developmental effects in a number of species is well established. Moderate ethanol consumption is reported to cause low birth weights, neurobehavioral effects, and learning and memory deficits. Recent interest in ethanol health effects is focused on the outcome of epidemiologic studies, which indicate that low-level oral ethanol exposures may result in learning disabilities in prenatally exposed children.

Given the numerous oral exposure health studies, the initial need would be to develop a preliminary risk estimate for inhalation exposures based on an oral-to-inhalation extrapolation. This would entail a detailed evaluation of the literature on physiologically-based pharmacokinetics for both routes of exposure, and if it were inadequate for dosimetric extrapolation purposes, additional pharmacokinetics research would be indicated. If such an extrapolation presents a rationale for a health concern, then inhalation dose-response studies would be needed, especially for developmental and neurotoxicological endpoints. As noted

1 in the discussion of methanol research, the development of methodologies to estimate  
2 developmental risks at low exposures is clearly needed. Effects have been shown to be  
3 associated with ethanol exposure. As data have developed, lower levels of exposure have  
4 been shown to be of concern.

5       Additionally, the potential role of acetaldehyde for developmental effects should be  
6 considered. Evidence of reproductive and developmental effects associated with acetaldehyde  
7 is sufficient to warrant such consideration, although most of the studies using acetaldehyde  
8 have involved nonparenteral routes of administration. Some short-term animal inhalation  
9 exposures may be necessary to adequately evaluate the potential of human exposure  
10 conditions to affect developmental processes and to support the pharmacokinetic evaluation.  
11 Subsequently, if existing data are inadequate, further human and animal inhalation data  
12 should be collected to complete the evaluation. Based on currently available data, chronic  
13 inhalation studies do not appear to be necessary; however, a reevaluation is warranted as  
14 additional exposure data become available.

15       The potential role of low-level ethanol exposures in carcinogenicity will be difficult to  
16 resolve. The International Agency for Research on Cancer (IARC) (1988) has indicated that  
17 alcoholic beverages containing ethanol are carcinogenic to humans. Although EPA assumes,  
18 in lieu of adequate evidence to the contrary, that substances found to be carcinogenic by one  
19 route may be carcinogenic by all routes, the potency by different routes may vary greatly.  
20 Much remains to be determined about the dose-response characteristics and mechanisms of  
21 ethanol carcinogenicity, especially as they relate to different routes of exposure, in assessing  
22 the potential cancer risks associated with ethanol as a fuel.

23       Information on the health effects of the complex mixtures resulting from ethanol  
24 combustion and its atmospheric transformation is not available; hence, these mixtures should  
25 be further evaluated. This is high priority research, as described in the generic overview,  
26 and includes the following primary endpoints of concern: cancer, respiratory effects, and  
27 immunotoxicity. Collection of these data would provide the basis for an adequate  
28 comparative assessment of ethanol fuel use relative to other fuels. Such research is paced,  
29 however, by progress in exposure assessment research.



#### 4.1.2.2 Ecosystem Effects

##### 4.1.2.2.1 Terrestrial Ecosystem Effects

The biological and ecological effects of ethanol-fuel pollutants (e.g., ethanol and acetaldehyde) have not been extensively studied, particularly in relation to likely ambient exposure levels or in binary combination with other pollutants such as O<sub>3</sub>. Laboratory investigations of a few plant species show that ethanol, acetaldehyde, and other air toxics (e.g., acetic acid) associated with ethanol fuels may inhibit root and leaf growth, seedling development, and/or seed germination. The effects of these chemicals on wildlife may vary from irritation of the eyes, mucous membranes, and the respiratory tract to possible changes in behavioral patterns, depending upon concentration and exposure durations. Chronic, sublethal exposures that will probably occur to vegetation may decrease plant productivity, reduce reproduction potential, and alter species competitive advantage within the plant community.

Given the lack of information on vegetal effects of ethanol pollutants, hazard identification research on plants is needed for assessment purposes. The need for wildlife research will be based upon the results of the animal research described previously. Exposure-deposition studies are required to document pollutant exposure patterns to plants. Exposure-response research is needed to identify the sensitivities of plant species to acetaldehyde and ethanol, individually and in combination with O<sub>3</sub>. Microcosm/mesocosm studies will be beneficial in identifying the environmental fate of ethanol-fuel pollutants and their potential ecological effects. Finally, as ethanol fuels gain prominence in certain urban areas, biomonitoring is necessary to evaluate ecosystem responses under natural conditions.

##### 4.1.2.2.2 Aquatic Ecosystem Effects

If ethanol is placed into large scale use as a fuel, it will be released to aquatic systems in several ways during its production, transport, storage, and use. These releases will occur as large-volume accidental spills and as chronic discharges. As for methanol, the miscibility of ethanol with water will make its dispersion within aquatic systems much faster than conventional fuels. The combination of greatly different exposures and toxicities makes the risk of this chemical relative to conventional fuels uncertain.

1       The effects of ethanol on aquatic systems will depend upon the amount released, the  
2 release rate, and its persistence. The speed with which ethanol is biodegraded in the  
3 environment is important to know, so the extent and duration of exposures can be predicted.  
4 Because ethanol may be rapidly degraded in aquatic systems, a direct release to a relatively  
5 enclosed body of water could produce a massive biological oxygen demand (BOD) that may  
6 deplete oxygen levels and cause massive mortality to organisms. The chronic release of this  
7 compound at a site could also produce microbial and algal enrichment that may negatively  
8 impact the ecosystem.

9       Information on the toxicity of ethanol to aquatic organisms is deficient. More data are  
10 needed to assess ecological risk associated with the potential release of this compound.  
11 Because of the widely different aquatic release scenarios, information on acute and chronic  
12 effects will be required. Unlike most petroleum compounds, ethanol is highly water soluble  
13 and will readily mix into the water column. Because an ethanol spill could impact the entire  
14 water column, toxicity testing should be conducted on sensitive species from all zones. Also,  
15 because of the likely transient nature of the exposures, kinetic-based toxicity models need to  
16 be developed and applied.

17       Mesocosm experiments should be conducted to determine potential community-level  
18 effects of this compound. They should include the testing of a variety of aquatic community  
19 types, because they may vary greatly in their responses and sensitivities. Integrative  
20 measurements, such as oxygen consumption and nutrient fluxes, should be included to assess  
21 changes in the state and health of these systems.

22       The potential for ethanol to influence the behavior of other contaminants present in  
23 aquatic systems also needs to be investigated. Suspended particulate material and bottom  
24 sediments found in many nearshore locations contain high concentrations of anthropogenically  
25 produced or mobilized contaminants. A massive spill of ethanol in a shallow area could  
26 extract or release compounds from contaminated sediments to the water column or alter the  
27 partitioning of compounds between dissolved and particulate phases. This could influence  
28 the bioavailability and toxicity of these other contaminants. Studies should, therefore, be  
29 undertaken to determine the extent to which ethanol can change the partitioning of other

1 classes of pollutants. Finally, joint toxicity of the ethanol-released toxicants and suppressed  
2 dissolved-oxygen levels to aquatic biota must be evaluated.

### 4 **4.1.3 Risk Prevention/Mitigation**

#### 5 **4.1.3.1 Stationary Sources**

6 Prevention/control technology assessment will need to ensure that introduction of  
7 ethanol will not further aggravate the existing global climate and O<sub>3</sub>-nonattainment problem.  
8 After assessing the adequacy of existing prevention and control technologies and practices for  
9 stationary sources, the following specific information/data deficiencies need to be addressed.

10 Of all the alternative fuels, ethanol from biomass may have the best chance of  
11 approaching a natural carbon cycle with sustainable resources from wood, other crop  
12 materials, or refuse. Because of the importance of this aspect from a global climate  
13 standpoint, overall assessment and development of the opportunities to increase effectiveness  
14 of the biomass to ethanol conversion process are needed. Two specific areas are known to  
15 be important: (1) higher yields and more effective conversion of the corn, and (2) more  
16 energy efficient concentration of the ethanol to fuel grade ethanol.

17 Guidance is needed to develop new or improved control systems, design methods, and  
18 operating procedures that would minimize emissions/discharges from the recovery of  
19 feedstocks, production, transportation, distribution, and use of ethanol.

20 User-oriented accidental release reference manuals/guidelines for prevention and  
21 mitigation of accidental releases of ethanol from storage, production, transportation, and  
22 marketing need to be developed.

23 Control options for aldehydes from specific sources utilizing ethanol where exposure  
24 may be important need to be developed. These sources include small engines, turbines,  
25 combustors, and stationary IC engines.

26 Because ethanol fuels may be more corrosive than gasoline and diesel fuels, the  
27 increased potential for leaks from USTs must be considered. Given the physical and  
28 chemical differences between these fuels, existing technologies for detecting leaks from USTs  
29 must be assessed to determine if modifications are required for application to ethanol fuels.  
30 Guidance documents on site investigations (where leaks are suspected) are based on our

understanding of the fate and transport of gasoline in the soil/groundwater environment. Guidance documents on soil cleanup and aquifer restoration are based primarily on the properties of, and experience with, gasoline. A switch to ethanol, with somewhat different properties, will require expanding upon this work. Certain soil cleanup technologies that may have somewhat limited applicability to gasoline-contaminated soils may find, for example, a much greater applicability to ethanol-contaminated soils. Leak prevention standards and protocols that may be suitable for gasoline and fuel oil may be quite unsuitable for ethanol.

#### **4.1.3.2 Mobile Sources**

As with methanol, activities should focus on assuring the durability of emissions control technology to limit emissions of environmentally damaging substances.

#### **4.1.3.3 Fuel Transport Sources**

As with other fuels, major accidental leaks from supertankers, barges, pipelines, etc., are possible. The key issues are to: (1) determine whether additional prevention measures are needed with ethanol and (2) identify optimal clean-up technologies if accidents occur.

## **4.2 BACKGROUND AND RATIONALE**

### **4.2.1 Exposure Assessment**

#### **4.2.1.1 Source Characterization**

##### ***4.2.1.1.1 Stationary Source Characterization***

***Production.*** Commercial ethanol for nonbeverage use is produced from ethylene synthesis and biomass fermentation and is primarily used as a chemical intermediate. In 1986, 257,000 tons were synthesized from petroleum feedstocks. Due to the present use in gasoline, fermentation production is significant. Although large quantities of ethanol are made by fermentation, the availability of currently needed biomass feedstocks are limited by the available cultivable land. The Solar Energy Research Institute has stated, however, that about 5 billion gallons per year could be made from surplus corn. The United States has

1 about 300,000 square miles of land under cultivation, and because the greater part of the  
2 tillable acreage is used for food crops, only a limited amount would be available for fuel  
3 preparation. A similar-sized acreage might be available in the United States for raising trees  
4 to provide wood as an ethanol feedstock. Municipal waste paper (cellulose) could also be a  
5 future feedstock (Cheremisinoff, 1979).

6 Significant amounts of commercial-grade ethanol are imported. The Caribbean Basin  
7 Initiative countries have been a large source of ethanol derived primarily from fermentation.  
8 Imported ethanol also includes wine alcohol from the European countries (Alcohol Week,  
9 June 26, 1989).

10  
11 **Feedstocks.** Ethanol is primarily produced from fermented molasses and grain cereals.  
12 Only abundant crops, such as corn and potatoes, are commonly used to any extent to produce  
13 ethanol (Faith et al., 1965). Cellulose in municipal solid waste and woody crops could  
14 provide a future feedstock. Synthesized ethanol is produced from ethylene, which is  
15 presently produced from various petroleum feedstocks. Today's technology would allow any  
16 petroleum materials to be used (Faith et al., 1965). Although synthesis of ethanol from coal  
17 has not been practiced, coal certainly is a potential source. The reactions would most likely  
18 be the synthesis of ethylene and conversion of ethylene to ethanol.

19  
20 **Processes.** Ethanol has been produced by fermentation from sugar-containing material  
21 (sugar cane molasses) and starchy materials such as grains (corn, oats, grain sorghum, rye,  
22 rice, barley, wheat), potatoes, sweet potatoes, and Jerusalem artichokes; however, only the  
23 most abundant grains (e.g., corn) are used for production of industrial alcohol (Faith et al.,  
24 1965). Research to produce ethanol from cellulose and hemicellulose materials such as trees,  
25 wood grasses, and herbaceous crops (e.g., grasses and legumes) is being conducted. Other  
26 materials such as algae and biomass wastes are also being investigated as possible sources  
27 (Klass, 1989).

28 Ethanol is produced from petroleum ethylene by absorption of ethylene in sulfuric  
29 acid-making ethyl sulfates, which are hydrolyzed to crude ethanol. The crude ethanol is  
30 purified by distillation; the sulfuric acid is concentrated and reused.

1 Coal, natural gas, and oil shale could be used as feedstocks; however, the production of  
2 ethanol would be somewhat more complicated than the production of methanol. Instead of  
3 direct conversion of the synthesis gas (CO and hydrogen) to ethanol, a conversion to longer-  
4 chain hydrocarbons using a catalyst such as Fischer-Tropsch might be necessary.  
5 Subsequently, ethylene could be made by standard refinery-type processing.

6  
7 ***Cost of Production.*** Costs for methanol production were discussed previously  
8 (Section 3.2.1.1.1). Ethanol production would appear to be even more expensive (using  
9 different feedstocks, with the exception of ethanol from wood), unless a catalyst for direct  
10 conversion of synthesis gas into ethanol could be developed.

11 Types of emissions and current treatment/control methods for fermentation processes  
12 are shown in Table 4-1 (U.S. Environmental Protection Agency, 1984). The major air  
13 contaminants are CO<sub>2</sub>, methane, aerosols, volatilized products, microbes/enzymes, and  
14 odiferous compounds.

15 The emissions of organics, other than alcohols, from methane synthesis of ethanol  
16 would be exceptionally low. The major concern would be the release of ethanol, including  
17 higher alcohols, and methane from vents and fugitive emissions. Emissions from petroleum  
18 processing would be similar to those from existing petroleum operations. Organic emissions  
19 from coal-based synthesis would be similar to ethanol production and would depend upon the  
20 type of coal conversion system utilized. Air toxics would follow the trend of organics.  
21 Ethanol would be the primary emissions concern for feedstocks, with the exceptions of coal  
22 and petroleum.

23 Carbon monoxide emissions would be primarily from the combustion of fuel for power  
24 and steam and from the production of the synthesis gas and ethanol. Because CO is a  
25 primary reactant, high efficiencies of operation would result in very low emissions. Carbon  
26 dioxide emissions from fermentation are large and equal the molecular quantity of ethanol  
27 produced, or 0.96 lb of CO<sub>2</sub> for every pound of ethanol. Additional CO<sub>2</sub> would come from  
28 the generation of steam and energy. Nitrogen oxides are related to combustion activities,  
29 boilers/heaters, and incinerators. These NO<sub>x</sub> sources have been fairly well documented.

**TABLE 4-1. WASTE STREAMS FROM FERMENTATION PROCESSES**

| Fermentation Process     | Waste Streams                | Potential Contaminants   | Current Treatment  |
|--------------------------|------------------------------|--|--|
| Air/Oxygen sterilization | Spent filter                 | <ul style="list-style-type: none"> <li>• Particles and microbes found in ambient air</li> </ul>  | <ul style="list-style-type: none"> <li>• No data</li> </ul>  |
| Fermentation             | Off gases                    | <ul style="list-style-type: none"> <li>• Carbon dioxide</li> <li>• Aerosols</li> <li>• Volatilized product</li> <li>• Microbe/enzymes</li> <li>• Odiferous compounds</li> </ul>  | <ul style="list-style-type: none"> <li>• Vented to atmosphere</li> <li>• Scrubbers</li> <li>• CO<sub>2</sub> recovery</li> <li>• Methane recovery</li> <li>• Incineration</li> </ul> |
|                          | Off gas filtration           | <ul style="list-style-type: none"> <li>• Spent filters</li> <li>• Viable microorganisms</li> </ul>   | <ul style="list-style-type: none"> <li>• No data</li> </ul>  |
|                          | Scrubber blowdown            | <ul style="list-style-type: none"> <li>• Absorption chemicals</li> <li>• Light soluble organics</li> <li>• Organic oils and waxes</li> </ul>   | <ul style="list-style-type: none"> <li>• Conventional biological wastewater treatment</li> </ul>   |
|                          | Vessel cleaning wastes       | <ul style="list-style-type: none"> <li>• Detergents</li> <li>• Biocides</li> <li>• Viable microbes/enzymes</li> <li>• Feedstock residue</li> <li>• Product residue</li> <li>• Intermediate product residue</li> <li>• Nutrients</li> </ul> | <ul style="list-style-type: none"> <li>• Conventional biological wastewater treatment</li> </ul>   |
|                          | Contaminated batches         | <ul style="list-style-type: none"> <li>• High BOD, COD, TSS</li> <li>• Viable microbes/enzymes</li> <li>• Virus</li> <li>• Feedstock</li> <li>• Product</li> <li>• Intermediate products</li> <li>• Nutrients</li> </ul>                   | <ul style="list-style-type: none"> <li>• Conventional biological wastewater treatment</li> </ul>   |
| Immobilization processes |                              |  |  |
| Adsorption               | Solution wash                | <ul style="list-style-type: none"> <li>• No data (enzymes)</li> </ul>  | <ul style="list-style-type: none"> <li>• No data</li> </ul>  |
| Covalent bonding         |                              |  |  |
| Cross-linking            |                              |  |  |
| Entrapment               | Spent microbe/support matrix | <ul style="list-style-type: none"> <li>• Microbes/enzymes</li> <li>• Polymers</li> <li>• Gels</li> <li>• Other supports</li> </ul>   | <ul style="list-style-type: none"> <li>• No data</li> </ul>  |
| Encapsulation            |                              |  |  |

CO<sub>2</sub> = Carbon dioxide.

BOD = Biological oxygen demand.

COD = Chemical oxygen demand.

TSS = Total suspended solids.

Source: U.S. Environmental Protection Agency (1984).

1 Extraction of natural gas (methane) worldwide results in substantial release (waste  
2 gases, leaks, etc.). Methane is a key global climate gas. The extraction of coal is also a  
3 source of methane release. Because methane is a key global climate gas, these methane  
4 releases must be quantified.

5  
6 **Discharges.** Types of discharges to water and current treatment/control methods for  
7 fermentation processes are shown in Table 4-1 (U.S. Environmental Protection Agency,  
8 1984). The major concern about discharges to water would be related to high biological  
9 oxygen demand (BOD), chemical oxygen demand, total suspended solids, viable microbes,  
10 enzymes, and nutrients. Due to the increased diversity of organic and inorganic pollutants  
11 from coal-based systems, thorough evaluations of these discharges are needed.

12 Discharges from coal or petroleum-based processes would be similar to those from coal  
13 conversion or petroleum refining. From fermentation processes, solid waste discharges  
14 would be similar to those that appear in the air and water discharges.

15  
16 **Accidental Releases.** Like all fuels, any accidental release of ethanol is a concern  
17 because of its flammability. Due to its low volatility, however, ethanol is of less concern  
18 than gasoline. Large releases of ethanol could have significant ecological effects, because of  
19 its solubility in water. Assessment of large releases to water and air, including prevention  
20 and mitigation procedures, is needed. In the hundred largest property losses worldwide,  
21 petroleum refining represented 38% of the accidents (Marsh and McLennan, 1985).

22  
23 **Primary Issues and Unsolved Problems.** Primary concerns include (1) the current high  
24 cost of ethanol because ethanol provides a potential global climate mitigation alternative if  
25 made from biomass and (2) the sources and levels of emissions and discharges that will result  
26 at all stages of processing, from the extraction of feedstocks through the refining and  
27 conversion to ethanol. Emissions from stationary sources for storage, distribution, and  
28 handling of ethanol require the most attention because little, if any, information exists in this  
29 area. The potential release of RITGs has not been fully evaluated. Initial research,  
30 therefore, would focus on the fermentation and petroleum-based feedstock system, whereas



longer range research would address the problems and releases of other feedstocks, such as coal and natural gas.

#### **4.2.1.1.2 Mobile Source Characterization**

In 1975, Brazil launched a program to provide ethanol-fueled cars to reduce the country's dependence on imported oil and to utilize the country's great capacity for growth of agricultural crops suitable for fermentation production of ethanol (Sperling, 1988). Although the motor vehicle technology is not like that projected for U.S. ethanol fleets (e.g., Brazilian passenger cars do not utilize catalysts for emissions reduction), insight into possible worst-case scenarios and general emissions composition can be extracted from the Brazilian example. Their experience with ethanol can also provide insight to potential air chemistry concerns (e.g., increased acetaldehyde emissions resulting in increased atmospheric PAN and possible associated health and/or ecological concerns [Tanner et al., 1988]). The economic situation in recent years (i.e., the relative costs of gasoline and fermentation ethanol) has slowed transportation use of ethanol in Brazil.

Essentially no information on emissions from ethanol cars designed to comply with current U.S. emission standards or from advanced-technology ethanol vehicles is available. In its efforts to characterize emissions from motor vehicles using alternative fuels, however, the State of California Air Resources Board operated a methanol-gasoline flexible-fuel automobile on E95 and E85 using EPA emissions certification driving simulations (California Air Resources Board, 1989). The results are presented in Table 4-2. Although this vehicle was not optimized for ethanol, the data provide an idea of what can be expected.

Emissions from ethanol-fuel motor vehicles are expected to be very similar to those from methanol-fuel vehicles, except that acetaldehyde will be the prevalent aldehyde (rather than formaldehyde) and the organic emissions will be dominated by ethanol (rather than methanol). Because of the reduced volatility of the fuel (ethanol RVP is 2.5 psi), substantially reduced evaporative emissions are expected.

Like methanol, the impact of ethanol fuel on CO and NO<sub>x</sub> emissions will depend upon engine and emission control design. Engines designed for stoichiometric combustion will likely have reduced NO<sub>x</sub>, but no significant impact on CO (assuming cold-start drivability

**TABLE 4-2. EMISSIONS FROM A MOTOR VEHICLE USING  
ETHANOL-GASOLINE BLENDED E95 AND E85 FUELS**

| Fuel | Federal Test Procedure Emissions, g/mile |                     |                       |               |                  | Total |
|------|--|---------------------|-----------------------|---------------|------------------|-------|
|      | Tailpipe<br>NMHC                         | Tailpipe<br>Alcohol | Tailpipe<br>Aldehydes | Evap.<br>NMHC | Evap.<br>Alcohol |       |
| E95  | 0.12                                     | 0.74                | 0.075                 | 0.01          | 0.02             | 0.97  |
| E85  | 0.17                                     | 0.78                | 0.065                 | 0.01          | 0.04             | 1.07  |

| E85 Organic Composition, wt% of Total (1.07 g/mile) |          |       |  |
|---|----------|-------|--|
|   | Tailpipe | Evap. |  |
| Total   | 95.0     | 5.0   |  |
| Ethanol   | 73.1     | 3.7   |  |
| Acetaldehyde  | 4.9      | --    |  |
| Ethane  | 1.0      | --    |  |
| Ethylene  | 3.3      | --    |  |
| Ethyne  | 1.6      | 0.01  |  |
| Butane  | 0.5      | 0.1   |  |
| Isopentane  | 1.1      | 0.1   |  |
| Pentane   | 0.5      | 0.1   |  |
| 2,2,4-Trimethyl pentane                             | 1.3      | 0.07  |  |
| Toluene   | 1.5      | 0.2   |  |
| Others  | 6.2      | 0.7   |  |

Source: California Air Resources Board (1989).

problems are successfully eliminated); and engines designed for fuel-lean combustion will have reduced CO emissions, but little impact on NO<sub>x</sub> relative to three-way catalyst gasoline vehicles (lean combustion prevents the use of three-way catalysts).

Motor vehicle CO<sub>2</sub>-emission rates with ethanol may be somewhat less than with gasoline if potential efficiency improvements (estimated 15 to 30%) are realized. Global

1 climate impact must also consider the CO<sub>2</sub> emissions associated with fuel production and  
2 distribution and with other emissions of importance, such as methane and N<sub>2</sub>O.

3 As with methanol, potential exists for development of heavy-duty engines using ethanol  
4 fuel. Reduced particulate and NO<sub>x</sub> emissions would be projected relative to petroleum  
5 distillate diesel engines.

6 Data on unregulated emissions from catalyst-equipped, ethanol-fuel motor vehicles (i.e.,  
7 compounds other than THC, CO, and NO<sub>x</sub>, and under nonfederal test procedure [non-FTP]  
8 driving conditions [varied speeds, temperatures, etc.]) are limited; however, available data  
9 suggest that benzene, 1,3-butadiene, and gasoline vapor emissions will decrease and that  
10 ethanol and acetaldehyde emissions as well as atmospheric PAN will increase. Substantially  
11 expanded research with advanced vehicle technologies is necessary.

#### 13 **4.2.1.2 Environmental Fate**

##### 14 ***4.2.1.2.1 Air Fate***

15 The photochemical reactivity of ethanol is greater than that of methanol, but like  
16 methanol, ethanol is much less reactive than most VOCs in gasoline. A recent modeling  
17 study has shown that ethanol may have an equal or even lower O<sub>3</sub>-forming potential because  
18 its primary photooxidation product, acetaldehyde, is less reactive than formaldehyde, the  
19 primary oxidation product of methanol (Whitten, 1989). Ethanol is also removed from the  
20 atmosphere through its reaction with OH radicals, having a tropospheric lifetime of  
21 approximately 6 days. The principal product from its homogeneous gas-phase oxidation  
22 process is acetaldehyde, with some hydroxyacetaldehyde. Peroxyacetyl nitrate, a  
23 phytotoxicant and mutagen, can be produced when NO<sub>x</sub> is present with acetaldehyde  
24 (Jacobson and Hill, 1970; Kleindienst et al., 1985). This product, PAN, also temporarily  
25 stores NO<sub>x</sub> and consumes free radicals, which in some cases add to lowering the reactivity of  
26 ethanol (Whitten, 1992). However, because PAN only temporarily stores NO<sub>x</sub>, second- and  
27 third-day effects can become important. As with methanol, the benefits in O<sub>3</sub> reduction may  
28 not be significant on second- and third-day irradiations. Like methanol, ethanol is highly  
29 soluble in water and can be removed by wet deposition. Fog may concentrate ethanol and its

1 combustion products, creating the potential for effects on the biota. Ethanol may also  
2 oxidize in liquid droplets to acetaldehyde and possibly an organic acid (acetic).

#### 4 **4.2.1.2.2 Soil and Groundwater Fate**

5 The environmental behavior of ethanol will be controlled by the same processes that  
6 determine the fate of methanol in soil and water; however, the magnitude of the relevant  
7 transport and fate parameters may differ. Given the probable release scenarios, these  
8 parameters must be compared and contrasted over the wide range of concentrations expected.  
9 Basically the same fate, transport, and transformation processes data and assessment needs  
10 outlined for methanol are also appropriate for ethanol.

#### 12 **4.2.1.3 Exposures**

##### 13 **4.2.1.3.1 Human Exposures**

14 Ethanol and its combustion by-products could cause human health effects, depending  
15 upon the exposure level, duration, and frequency. As with methanol, exposures are  
16 dependent upon numerous factors that may increase either exposure levels or the number of  
17 people exposed, which, in turn, would increase the risks. In the case of ethanol, the primary  
18 route of acute human exposure is likely to be through ingestion, which has been studied  
19 rather extensively. Potential inhalation exposure, however, would be a likely impact of  
20 increased use of alternative fuels. As with methanol, microenvironments (e.g., personal and  
21 public garages) and activities (e.g., commuting and refueling) that typically result in higher  
22 exposure levels could markedly increase risk to some individuals.

23 Total human exposure studies of the impact of changing from gasoline to ethanol are  
24 important to provide an understanding of the resulting risks to health. These studies will  
25 necessitate identification of the microenvironments in which high concentrations are likely to  
26 be found, the activities and time durations associated with high exposures, and the numbers  
27 of people likely to be exposed. Without these data, our ability to predict the level of human  
28 exposure that will result from the use of ethanol as an alternative fuel is very limited, and the  
29 exposure estimates are probably no better than plus-or-minus several orders of magnitude for

1 the maximum predicted exposures. Indoor concentrations will also be affected because of the  
2 changes resulting from outside ambient air and from possible intrusions into the home from  
3 personal garages. Also, alcoholic beverages will contribute substantially to exposure for  
4 numerous people. Conversely, ethanol exposure from vehicles could be incrementally  
5 insignificant for those people. Total exposure, the microenvironment, activities, and people  
6 affected are clearly not known, and our ability to predict the health risks associated with  
7 ethanol as an alternative fuel is limited. Total human exposure studies for gasoline-fueled  
8 vehicles must also be undertaken to provide a relative exposure comparison.

9 Although widespread use of ethanol fuels is likely to create an interest in diversion for  
10 oral beverage use, it is assumed that regulatory and education actions will discourage this  
11 through addition of a nontoxic denaturant. Therefore, purposeful oral exposures will not  
12 be considered further. Accidental ingestion will be considered for assessments, prior to  
13 initiating any research.

#### 15 ***4.2.1.3.2 Biota Exposures***

16 Exposure issues for ethanol are very similar to those for methanol (see  
17 Section 3.2.1.3.2). However, ethanol-fuel combustion products may result in increased  
18 atmospheric PAN, a highly phytotoxic pollutant. Monitoring/modeling is needed to evaluate  
19 the characteristics of PAN exposure to vegetation.

#### 21 **4.2.1.4 Analytical Methodology**

22 A wide range of analytical procedures are required to facilitate examination of the  
23 impact of changes in motor fuels on risk to health and welfare. The procedures can  
24 generally be categorized according to procedures for characterizing source emissions,  
25 procedures for monitoring the transport and transformation of the emissions in ambient air,  
26 and procedures for monitoring human and ecosystem exposure.

27 Procedures both for certification of regulated emissions (THC, CO, CO<sub>2</sub>, NO<sub>x</sub>, and  
28 particles) and for comprehensive characterization of unregulated emissions are required for  
29 sources. Nondispersive infrared analyzers are commonly used to determine CO and CO<sub>2</sub>;

1 chemiluminescence is used to determine NO<sub>x</sub>; and THC FID is used to determine total  
2 organic carbon. Care must be taken to assure that emissions associated with ethanol fuels  
3 can be accurately determined with these classical procedures at concentrations dictated by the  
4 CAAAs. Chromatography, infrared spectroscopy, and mass spectroscopy are often used for  
5 detailed characterization of unregulated emissions.

6 With ethanol fuels, certification of total organic emissions will be complicated by the  
7 presence of significant levels of ethanol and acetaldehyde, in addition to the routinely  
8 measured THC. Procedures similar to those for methanol and formaldehyde can be  
9 recommended for measurement of ethanol and acetaldehyde and for compensation of the  
10 THC-FID system response to ethanol and acetaldehyde, thereby permitting determination of  
11 THC (U.S. Environmental Protection Agency, 1983h; Tejada, 1986; Federal Register,  
12 1989a). Oxides of nitrogen chemiluminescence procedures should be examined for problems  
13 similar to those noted with methanol fuels (see Section 3.2.1.4) (Gabele, 1988). The  
14 development of more simple, less costly procedures than chromatography for determining  
15 ethanol and acetaldehyde and for permitting continuous "real-time" measurement of ethanol  
16 and acetaldehyde will be of interest (Butler et al., 1985; Staab et al., 1985). Measurement of  
17 acetic acid and ethyl nitrite emissions from vehicles using ethanol fuels will also likely be of  
18 interest. Assessment of the impact of ethanol fuel on O<sub>3</sub> and toxics air quality will require  
19 analytical procedures for determining the detailed composition of associated source organic  
20 emissions. With all measurements in source emissions, care must be taken to assure that  
21 artifactual chemistry during sampling and analysis does not bias observations.

22 Ambient air monitoring needs are similar to those for emissions characterization.  
23 Methodology is needed for acetic acid, ethyl nitrite, PAN, and hydroxyPAN. Ambient air  
24 monitoring and microenvironmental monitoring will require methods development for the  
25 measurement of ethanol and acetaldehyde. In addition, development of personal monitors  
26 ill be required for population characterization studies, if undertaken in later years.

## 4.2.2 Effects Assessment

### 4.2.2.1 Human Health Effects

Many of the general health effects issues discussed in Section 3.2.2.1 under methanol fuels apply here as well. The individual chemicals of most interest are ethanol itself and specific combustion products (e.g., acetaldehyde). The health effects of complex mixtures of combustion emissions of ethanol and their transformation products have not been studied, but have similar issues to those described under conventional and methanol fuels (see Sections 2.2.2.1 and 3.2.2.1). As with methanol, vehicular technology development and marketing decisions will have a major impact on air quality. There is a higher probability that ethanol-gasoline mixtures (e.g., E85) will be used, rather than E100. In such an event, the need to understand the effects of the mixture gains prominence.

#### 4.2.2.1.1 Ethanol

Although a great deal of information on the toxicological and health effects of ingested ethanol (primarily as a beverage) is available, relatively little is known about this alcohol's effects by exposure routes that are relevant to its use as a fuel. Although several inhalation exposure animal bioassays have been performed, methods and data for dosimetric and toxicologic extrapolation from animals to humans are limited. Even in the case of epidemiological studies of the effects of ingested ethanol, data on the amounts consumed are generally only rough estimates of exposure. The appropriateness of extrapolating across routes of exposure or from high to low dose for assessing the potential health effects of ethanol fuels is not clear; indeed, these issues are among several matters that must be addressed through further research. For current analyses, however, the types of potential hazards posed by ethanol may be identified qualitatively on the basis of existing data obtained primarily from oral exposures.

Humans can be exposed to ethanol via inhalation, oral ingestion, or dermal contact. About 60% of inhaled ethanol is retained by the body; the gastrointestinal (GI) tract completely absorbs ethanol in 2 to 6 h; dermal absorption is insignificant (Pohorecky and Brick, 1988; Ritchie, 1980). From the portal(s) of entry, ethanol distributes fairly uniformly throughout all tissues and organs, including the cerebrospinal fluid; brain; and, in the

1 pregnant human and laboratory animal, placenta and fetal tissues (Pohorecky and Brick,  
2 1988; Ritchie, 1980). The distribution depends on many factors including route of entry,  
3 sex, animal species, specific metabolism and excretion rates, partition coefficients, blood  
4 flow rates, and other physiological factors.

5 Ethanol is cleared from the body by four routes: renal excretion, direct pulmonary  
6 excretion, sweat, and metabolism. Total body clearance rates and relative route clearances  
7 rates depend on ethanol blood levels. Below blood levels corresponding to effects of  
8 incoordination, slowed reaction time, and blurred vision (0.5 g/L), metabolism accounts for  
9 98 to 99% of ethanol elimination. At the level of 15 g/L, the renal, pulmonary, and dermal  
10 routes were estimated to account for 7.5, 20, and 2.5%, respectively, of the total body  
11 clearance rate (Holford, 1987).

12 Traditionally, ethanol metabolism has been assumed to occur mainly in the liver;  
13 however, recent work suggests that, in humans, significant metabolism may occur in the GI  
14 tract (Frezza et al., 1990). In humans and laboratory animals, ethanol is metabolized by  
15 two, and possibly three, pathways. At blood levels due to typical oral doses, the alcohol  
16 dehydrogenase pathway accounts for most of the metabolism, and a microsomal ethanol  
17 oxidizing system accounts for the remainder. In humans, the latter contributes to an  
18 increased rate of elimination at high ethanol blood levels. Both pathways are influenced by  
19 diet, endocrine factors, and smoking. Also, humans inherit different types of alcohol  
20 dehydrogenase isoenzymes that have different kinetic properties. A third pathway, possibly  
21 first-order, appears to be manifested at very high blood levels. At the high concentrations,  
22 this pathway is 10 times faster than would be predicted by the first two pathways and would  
23 contribute about 30% to elimination at typical dose levels. Ethanol is metabolized to  
24 acetaldehyde, which is then metabolized to CO<sub>2</sub> and water. Values of the parameters that  
25 characterize the net metabolic rate of ethanol in humans, V<sub>max</sub> and the Michaelis constant,  
26 have been reported (Holford, 1987).

27 In general, aliphatic alcohols are weak sensory (i.e., eye, nose, throat) and respiratory  
28 tract irritants. The concentration necessary to decrease respiratory rate by 50% (RD<sub>50</sub>) is  
29 approximately 42,000 ppm for methanol and 27,000 ppm for ethanol, and tends to decrease  
30 with increased chain length (Alarie and Luo, 1986). Nevertheless, the increasing use of



1 various inhalation regimens as a means of establishing ethanol dependency in animal  
2 bioassays necessitates further investigation into the impact of long-term exposure to ethanol  
3 vapors on lung structure.

4 The neurotoxicity of aliphatic alcohols has also been shown to increase with chain  
5 length (up to six or eight carbons), ethanol being more inebriating than methanol at low  
6 concentrations (Shoemaker, 1981). Both Nelson et al. (1988) and Shoemaker (1981) discuss  
7 the acute and chronic toxicity of alcohols, including ethanol, and note that inhalation  
8 exposure to alcohols produces effects (both neurotoxic and developmental) similar to those  
9 induced by oral exposure. Transient neuroleptic effects (e.g., euphoria) and subtle cognitive  
10 and psychomotor impairments may occur at quite low acute levels of exposure (well below  
11 the usual legal definition of impairment, 0.10% blood ethanol level), although thresholds for  
12 such subtle neurotoxic effects have not been clearly established (U.S. Department of Health  
13 and Human Services, 1987). The lowest observed adverse effect levels (LOAELs) must be  
14 determined for neurobehavioral effects in individuals who may be at greater risk for such  
15 impairments, particularly in children and young adults or other individuals who for various  
16 reasons (including genetic differences in enzymes) may not be able to metabolize ethanol as  
17 readily as the average person.

18 Reproductive function is also known to be affected by ethanol. As noted with regard to  
19 methanol, however, establishing the LOAEL and dose-response relationship for these effects  
20 is difficult because of the feedback response of the hypothalamic-pituitary-gonadal axis  
21 (Phipps et al., 1987; Van Thiel et al., 1974). Six hours of exposure to ethanol vapors at  
22 1,000 ppm (the ACGIH TLV) may significantly reduce circulating testosterone levels in male  
23 rats; however, recovery before the second day and compensation by the end of the first week  
24 of exposure also appear to occur (Cameron et al., 1985). Other changes, functional or  
25 structural, may accompany these seemingly transient effects of "acceptable" ethanol exposure  
26 on testosterone levels, but this has not yet been determined.

27 The effects of exposure to ethanol during gestation have been well documented as the  
28 Fetal Alcohol Syndrome in offspring of mothers who ingested above-average amounts of  
29 ethanol during pregnancy (U.S. Department of Health and Human Services, 1987). Even at  
30 somewhat lower levels of ingestion, several more subtle Fetal Alcohol Effects have been

1 identified. Experimental studies using volunteer pregnant women (McLeod et al., 1983) and  
2 sheep (Urfer et al., 1984) have shown rather immediate effects on fetal breathing movements  
3 or electrocardiograms at blood alcohol concentrations below the legal limit of 0.10%.  
4 Recent work (Chandler et al., 1989, 1991) indicates that sheep metabolize ethanol at a slower  
5 rate than human infants, whereas piglets metabolize ethanol at a rate similar to infants.  
6 Thus, pigs may be a more appropriate animal model for future evaluation of developmental  
7 effects from maternal ethanol exposure.

8       The scope and significance of these subtle acute effects must be examined in greater  
9 detail and extended to other routes of exposure. Inhalation studies in rats revealed no  
10 morphologic or behavioral developmental effects from maternal and paternal exposure to up  
11 to 20,000 ppm ethanol for 7 h/day on Days 1 to 19 of gestation, despite blood levels of up to  
12 180 mg/dL (0.18%) (Nelson et al., 1985a,b). However, maternal or paternal exposure to  
13 10,000 ppm for 7 h/day throughout gestation can cause neurochemical changes in offspring  
14 (Nelson et al., 1988), as has been reported after other routes of exposure (Boggan, 1982).  
15 An evaluation to determine if other effects may be mediated through paternal exposure to  
16 ethanol, as suggested by a growing body of experimental animal work (e.g., Nelson et al.,  
17 1988; Abel and Tan, 1988), is also important.

18       A variety of other health effects have been associated with ethanol. Alterations in the  
19 immune and hematopoietic systems have been observed. Oral (Mufti et al., 1988; Gluckman  
20 et al., 1977) and inhalation (Marietta et al., 1988) experimental studies have established that  
21 both cellular and humoral aspects of immunity are compromised by ethanol. Marietta et al.  
22 (1988) did not observe effects on the RBC count, white blood cell count, or hemoglobin  
23 concentration but did observe significant decreases in number of cells in the spleen, thymus,  
24 and bone marrow; a decrease in number of lymphocytes in the peripheral blood; and  
25 suppression of erythroid progenitor cells following inhalation exposure of rats to 25 mg  
26 ethanol/L ( $\approx$  13,300 ppm) for 14 days to produce a mean blood ethanol level (over the  
27 14 days) of 169 mg/dL (0.17%). Similar results have been obtained from in vitro laboratory  
28 studies (Meagher et al., 1982). This loss of the ability of bone marrow to produce  
29 erythrocytes may contribute to reported increased incidence of anemia in alcoholics (Eichner  
30 and Hillman, 1971). However, very little dose-response information exists for these

1 endpoints. Some evidence indicates that cardiovascular function shows a U-shaped dose-  
2 response relationship to ethanol exposure, perhaps because ethanol, despite its basically  
3 depressant effect on the heart, also decreases resistance to blood flow throughout the body  
4 and can, thereby, reduce blood pressure in normal, healthy subjects (U.S. Department of  
5 Health and Human Services, 1987). Any protective effect of "moderate" ethanol ingestion  
6 on cardiovascular function, however, remains controversial. The liver is well known to be  
7 affected by chronic ethanol consumption. In one study, even moderate intake of ethanol was  
8 associated with increased risk for developing cirrhosis (Pequignot and Tuyns, 1980); less  
9 severe effects on the liver would be expected at lower exposure levels. Also, ethanol  
10 potentiates the effects of other hepatotoxicants and drugs (Traiger and Plaa, 1971; Cornish  
11 and Adefuin, 1967; Shibayama, 1988; Nakajima et al., 1988; Strubelt, 1982), a concern  
12 from the standpoint of general population exposure. Some concerns exist about acetaldehyde  
13 because it has been suggested to be the active metabolite in ethanol-induced developmental  
14 effects. (See the following section, Section 4.2.2.1.2, for discussion of acetaldehyde.)

15 The IARC has concluded that alcoholic beverages containing ethanol are carcinogenic to  
16 humans (International Agency for Research on Cancer, 1988). Although IARC judged the  
17 evidence of ethanol carcinogenicity from experimental animals to be inadequate, it concluded  
18 that the occurrence of malignant tumors of the oral cavity, pharynx, larynx, esophagus, and  
19 liver in humans was causally related to the consumption of alcoholic beverages containing  
20 ethanol and constituted sufficient evidence of carcinogenicity in humans. Thus, IARC  
21 designated alcoholic beverages a Group 1 carcinogen (i.e., carcinogenic to humans).  
22 No position was taken by IARC with respect to other routes of exposure. Although evidence  
23 of the carcinogenicity of ethanol via inhalation is inadequate, it has been the position of the  
24 EPA that a substance found to be carcinogenic by one route may be carcinogenic by all  
25 routes. However, the potency by different routes may vary greatly. Research is needed on  
26 the mechanisms of ethanol carcinogenicity at low levels of exposure and through different  
27 routes of exposure.

28 Better data on the pharmacokinetics of ethanol by different routes of exposure and in  
29 various species would help to determine the appropriateness of using existing oral human and  
30 animal inhalation data to predict ethanol inhalation effects in humans. Even if extrapolation

1 across exposure routes and species is acceptable, extrapolations from high- to low-dose levels  
2 may be problematic.

#### 4 **4.2.2.1.2 Acetaldehyde**

5 Acetaldehyde is a saturated aliphatic aldehyde that is highly reactive and readily  
6 oxidized in air. Acetaldehyde, like formaldehyde, owes its reactivity to the electrophilic  
7 nature of its carbonyl moiety and has been shown to nonenzymatically bind covalently with  
8 biologically important molecules, such as proteins and nucleic acids. Acetaldehyde is the  
9 immediate metabolite of ethanol oxidation and is produced endogenously in an ethanol dose-  
10 related manner primarily by the liver. Whether from exogenous sources or generated from  
11 ethanol metabolism, acetaldehyde undergoes rapid metabolic oxidation to acetate, primarily  
12 by aldehyde dehydrogenase in mammalian systems. Acetate enters the metabolic pool of  
13 intermediary metabolism and is used in cellular energy production to be eventually released  
14 as CO<sub>2</sub> and water, or is used in synthesis of cell constituents.

15 There are few studies of the kinetics of acetaldehyde of exogenous origin. The uptake  
16 of acetaldehyde into the body from either dermal or inhalation exposure has not been  
17 systematically studied. Retention of acetaldehyde in humans under "physiologic conditions"  
18 of breathing rate and tidal volume has been shown to be approximately 60% at exposure  
19 concentrations between 100 and 200 mg/m<sup>3</sup> for a few minutes (Egle, 1970). Breathing rate  
20 and volume and concentration were shown to influence the retention. Systemic uptake in rats  
21 has been demonstrated at high concentrations (9,000 to 10,000 ppm) for 1 h (Watanabe  
22 et al., 1986). Binding and metabolism in both blood and nasal mucosa of rats has been  
23 demonstrated (Hagihara et al., 1981; Casanova-Schmitz et al., 1984). Casanova-Schmitz  
24 et al. (1984) observed that rats exposed to 700 ppm for 2 h demonstrated only 0.7 mM in  
25 circulating blood 5 min after exposure termination, suggesting that binding in the respiratory  
26 tract and rapid metabolism significantly reduces systemic circulation at steady state.

27 The kinetics of portal-of-entry binding and distribution to tissues remote to the  
28 respiratory tract are important data gaps for this chemical, particularly because no  
29 developmental or reproductive studies have been conducted by either oral or inhalation  
30 routes. Cardiotoxicity (Egle et al., 1973; Mohan et al., 1981; Condouris and Havelin, 1987)

1 in various species and effects on erythrocytes and leukocytes (Kukielka, 1987) are other  
2 systemic toxicities of acetaldehyde that have been reported after intraperitoneal (ip) or  
3 intravenous (iv) administrations. Zorzano and Herrera (1989) studied the pattern of  
4 acetaldehyde appearance in maternal and fetal blood, maternal and fetal liver, and placenta  
5 after oral ethanol administration or iv acetaldehyde administration (10 mg/kg body weight  
6 [BW]) to pregnant Wistar rats. The study demonstrated that acetaldehyde was able to cross  
7 the placental barrier at high concentrations (fetal blood concentrations were only detectable  
8 when maternal blood concentrations were greater than 80  $\mu$ M). The fetal oxidation capacity  
9 in liver and placenta was shown to be lower than that of the maternal liver. A threshold  
10 above which the removal capacity of acetaldehyde metabolism by the fetoplacental unit would  
11 be surpassed was estimated to be 80  $\mu$ M (maternal blood concentration) in the 21-day  
12 pregnant rat and plausibly lower at early pregnancy when aldehyde dehydrogenase is absent  
13 from fetal liver. Acetaldehyde was also shown to be present in fetal mouse tissue after  
14 ip administration of ethanol at 7 g/kg.

15 The primary acute effect elicited by acetaldehyde via inhalation, as with formaldehyde,  
16 is irritation of the eyes and upper respiratory tract. Humans exposed in a chamber to  
17 acetaldehyde vapor at 135 ppm for 30 min reported mild irritation to the upper respiratory  
18 tract (Sim and Pattle, 1957). Acetaldehyde vapor is also irritating to the skin (Babiuk et al.,  
19 1985). Clinical effects of exposure to acetaldehyde vapors also include erythema, coughing,  
20 pulmonary edema, and narcosis at higher (100 to 200 ppm) concentrations (Dreisbach, 1980).

21 Again in similar fashion to formaldehyde, inhalation exposures to acetaldehyde have  
22 been shown to produce compound-related histophysiological changes such as degeneration,  
23 hyperplasia, and metaplasia of the epithelium in the respiratory tract (olfactory and  
24 respiratory nasal epithelium, laryngeal epithelium, tracheal epithelium) after both short-term  
25 and chronic exposure in rats and Syrian golden hamsters (Appelman et al., 1982, 1986;  
26 Woutersen and Appelman, 1984; Woutersen et al., 1985, 1986; Woutersen and Feron, 1987;  
27 Kruijsse et al., 1975; Feron, 1979; Feron et al., 1982). Effects on the number and  
28 phagocytosing ability of cells harvested in lavage fluid from exposed rats were also  
29 demonstrated in one short-term study of these endpoints (Appelman et al., 1986).

1       Short-term (4-week) studies in Wistar rats established a concentration-response  
2 relationship for lesions of the respiratory tract. Appelman et al. (1986) exposed male Wistar  
3 rats to 0, 150, or 500 ppm acetaldehyde for 6 h/day, 5 days/week. The exposure regimen  
4 also included some groups exposed to interrupted and superimposed peaks at sixfold the  
5 baseline concentration for 3 h per exposure period. No compound-related effects were seen  
6 in rats exposed to 150 ppm interruptedly or with peak exposures. At 500 ppm, degeneration  
7 of the olfactory epithelium was observed. No changes were noted in the larynx or trachea.  
8 Appelman et al. (1982) conducted another 4-week intermittent exposure at concentrations of  
9 0, 400, 1,000, 2,200, or 5,000 ppm. Respiratory distress, growth retardation, and some  
10 mortality occurred at the highest concentration. Compound-related histopathological changes  
11 were observed only in the respiratory epithelium. The nasal cavity was the most severely  
12 affected, and exhibited a concentration-response relationship. At the 400-ppm level,  
13 compound-related changes included slight to severe degeneration of the nasal olfactory  
14 epithelium, without hyperplasia and metaplasia, and disarrangement of epithelial cells.  
15 At the 1,000- and 2,200-ppm levels, more severe degenerative changes occurred, with  
16 hyperplastic and metaplastic changes in both the olfactory and respiratory epithelium of the  
17 nasal cavity. Degeneration with hyperplasia/metaplasia also occurred in the laryngeal and  
18 tracheal epithelium. At the highest concentration, changes included severe degenerative  
19 hyperplastic and metaplastic changes of the nasal, laryngeal and tracheal epithelia.

20       Kruysse et al. (1975) conducted a 90-day inhalation study in hamsters exposed to  
21 0, 390, 1,340, or 4,560 ppm for 6 h/day, 5 days/week. Histopathological changes that could  
22 be attributed to exposure were observed only in the respiratory tract. At the highest  
23 concentration, body weights and relative weights of heart, kidney, brain, testicle, and lungs  
24 were significantly increased. Histopathological changes of the nasal cavity, larynx, trachea  
25 and bronchi included necrosis, inflammatory changes, and hyperplasia and metaplasia of the  
26 epithelium. No effects were observed at 390 ppm, with the exception of a tiny focus of  
27 metaplastic epithelium in 1 trachea out of 20 examined. Due to differences in concentrations  
28 at which similar effects are manifest, differences in dosimetry between species are thus  
29 suggested. Feron (1979) exposed male Syrian golden hamsters by inhalation to 1,500 ppm,  
30 7 h/day, 5 days/week for 52 weeks. No evidence of carcinogenicity was observed, but

1 epithelial hyperplasia and metaplasia, accompanied by inflammation in the nasal cavity and  
2 trachea, were observed. A subsequent study by these same researchers (Feron et al., 1982)  
3 using higher concentrations (2,500 ppm for 9 weeks; 2,250 ppm for Weeks 10 to 20;  
4 1,800 ppm for Weeks 30 to 44 and 1,650 ppm for Weeks 42 to 52) showed rhinitis;  
5 hyperplasia and metaplasia of the nasal, laryngeal, and tracheal epithelia; and nasal and  
6 laryngeal carcinomas. Differences between effects in hamsters and rats may also be due to  
7 different pharmacokinetics and/or sensitivities.

8 Characterization of dosimetry or the relationship between the degenerative and  
9 hyperplastic changes to the neoplastic changes has not been done in any species, with the  
10 exception of Woutersen et al. (1985) and Woutersen and Feron (1987). No mechanistic  
11 studies, as have been described for formaldehyde, have been reported. Woutersen et al.  
12 (1985) exposed Wistar rats to 0, 750, 1,500, and 3,000/1,000 ppm for 6 h/day, 5 days/week  
13 for up to 28 mo. The highest concentration was gradually decreased due to severe growth  
14 retardation and early mortality in this group. Rats in the high-exposure concentration showed  
15 excessive salivation, labored respiration, and mouth breathing that was still observed after the  
16 reduction in concentration took place. The cause of early death or moribund condition was  
17 nearly always partial or complete occlusion of the nose by excessive amounts of keratin and  
18 inflammatory exudate. The most severe abnormalities were again seen in the nasal cavity.  
19 Basal cell hyperplasia of the olfactory epithelium was seen in the low- and mid-concentration  
20 groups. The decrease in these changes in the olfactory epithelium was attributed to the  
21 incidence of adenocarcinomas at the higher concentrations. The respiratory epithelium of the  
22 nasal cavity was involved (hyperplasia and squamous metaplasia with keratinization) at the  
23 mid and high concentrations. Hyperplasia and squamous metaplasia occasionally  
24 accompanied by keratinization occurred in the larynx of rats exposed at the mid and high  
25 concentrations. The tracheal epithelium was not visibly affected at any exposure level.  
26 Adenocarcinomas occurred at all exposure concentrations and squamous cell carcinoma at the  
27 mid and high concentrations only. It thus appeared that the nasal tumors induced could be  
28 distinguished into two major types: adenocarcinomas from olfactory epithelium and  
29 squamous-cell carcinoma from the respiratory epithelium.

1       Woutersen and Feron (1987) conducted another inhalation study in Wistar rats exposed  
2 to the same regimen as just described for 52 weeks with recovery periods of either 26 or  
3 52 weeks. After 52 weeks of recovery, the degeneration of the olfactory epithelium was still  
4 visible to a slight degree in animals from all exposure groups. Animals of the high-  
5 concentration group did not show restoration of the olfactory epithelium. At the low  
6 concentration, normal olfactory epithelium was present in some animals. Replacement of  
7 olfactory epithelium by respiratory epithelium was frequently seen. These data suggest that  
8 there is incomplete recovery of olfactory and respiratory epithelium at all exposure  
9 concentrations for periods as long as 52-weeks postexposure.

10       An inhalation reference concentration (RfC) for acetaldehyde has been derived using  
11 data from Appleman et al. (1982, 1986) showing a concentration-response relationship for  
12 olfactory epithelial degeneration (IRIS, 1991). Adjustments for the intermittent experimental  
13 exposure regimen and for interspecies dosimetry were applied to calculate a human  
14 equivalent concentration (HEC). This HEC served as the operational basis for estimating an  
15 RfC of  $0.009 \mu\text{g}/\text{m}^3$  after applying uncertainty factors to account for sensitive human  
16 populations, for subchronic to chronic extrapolation, and for interspecies extrapolation and  
17 data base comprehensiveness. Confidence in the RfC is low because comprehensive chronic  
18 data were lacking, only a LOAEL was identified, and only a small number of subjects of one  
19 species were tested at short durations.

20       The current EPA carcinogenicity assessment for lifetime exposure classifies  
21 acetaldehyde as B2, a probable human carcinogen, based on sufficient animal data (IRIS,  
22 1988b). The data used for the weight-of-the-evidence classification of "sufficient" animal  
23 evidence of carcinogenicity and for the quantitative assessment are that of Woutersen and  
24 Appelman (1984) and Woutersen et al. (1985) described above. An inhalation cancer unit  
25 risk of  $2.2 \times 10^{-6}$  per  $\mu\text{g}/\text{m}^3$  was derived. It is considered to be a weak carcinogen, ranking  
26 57 out of 58 chemicals assessed for carcinogenicity. Human evidence for the carcinogenicity  
27 of acetaldehyde is inadequate. Only one epidemiological study involving acetaldehyde  
28 exposure exists (Bittersohl, 1974). An increased crude incidence rate of total cancer in  
29 acetaldehyde production workers as compared with the general population was shown, but  
30 because the rate was not age adjusted, concurrent exposures (chemicals and cigarettes) were



not accounted for, a small number of subjects were studied, and details were lacking on subject selection and demographics, it was considered inadequate for quantitative evaluation (U.S. Environmental Protection Agency, 1989b).

The similarities of acetaldehyde-induced noncancer and cancer effects to those of formaldehyde are striking. Hyperplasia observed in the laboratory animal studies is indicative of an effect on cell proliferation, and Lam et al. (1986) have provided evidence indicating a likelihood of cross-linking by acetaldehyde. Studies to elucidate mechanisms of preneoplastic changes, dosimetry and species sensitivity, and integration into a biologically based model appear warranted.

#### ***4.2.2.1.3 Peroxyacetyl Nitrate***

Information on the health effects of PAN shows that high concentrations produce a variety of effects in experimental animals. These effects were all seen at concentrations that are orders of magnitude higher than the maximally reported ambient air concentrations (U.S. Environmental Protection Agency, 1986a). Data on the effects of PAN in humans are limited mainly to results of controlled studies of pulmonary function in young and middle-aged males (3.5-h exposures to 0.24 ppm with intermittent treadmill exercise) (Raven et al., 1974a,b). In these studies, small, but significant, effects on forced vital capacity were observed. Because O<sub>3</sub> and PAN occur together in high-oxidant pollution, studies of their combined effects (0.45 ppm O<sub>3</sub> plus 0.30 ppm PAN) were undertaken. These studies were suggestive of effects; however, they were not conclusive (Drechsler-Parks et al., 1984). Eye irritation in humans is a documented effect, but concentration thresholds vary among individuals (U.S. Environmental Protection Agency, 1986a).

#### ***4.2.2.2 Ecosystem Effects***

##### ***4.2.2.2.1 Terrestrial Ecosystem Effects—Atmospheric Exposures***

Releases of ethanol and its combustion products into the atmosphere from production, storage, transportation, and vehicle exhaust could pose a threat to terrestrial and aquatic ecosystems (Weinstein and Birk, 1989). The use of ethanol as a replacement fuel within the alternative fuels program may result in increased atmospheric loads of this alcohol in addition

1 to other toxic chemicals (e.g., acetaldehyde, acetic acid) that are produced as exhaust  
2 products from its combustion. In addition, O<sub>3</sub>, PAN, acetaldehyde, and perhaps acetic acid  
3 are expected transformation products as a result of atmospheric photochemical reactions.  
4 Both O<sub>3</sub> and PAN are strong phytotoxicants and can reduce crop yields and forest-tree  
5 growth. Effects with conventional gasoline and diesel-fuel combustion products (e.g., CO,  
6 CO<sub>2</sub>, NO<sub>x</sub>, VOCs, and PM) and transformation products (e.g., O<sub>3</sub> and PAN) need to be  
7 compared to ethanol ecosystem effects to evaluate which fuel may pose the greatest hazard to  
8 terrestrial ecosystems.

9 The effects of CO, CO<sub>2</sub>, NO<sub>x</sub>, and O<sub>3</sub> on plants and animals (including wildlife) are  
10 well documented (e.g., Smith, 1990; Newman and Schreiber, 1988); however, the biological  
11 and ecological effects of ethanol, acetaldehyde, and acetic acid may inhibit root and leaf  
12 growth, seedling development, and/or seed germination (Table 4-3). The effects of these  
13 chemicals on animals is described in the Health Effects Section. Ecological perturbations  
14 resulting from ethanol, acetaldehyde, and acetic acid deposition and exposure may have  
15 ramifications through all levels of biological organization (Moriarty, 1978; Treshow, 1978)  
16 (Figure 2-9). A complete analysis of the effects of these chemicals on plants and animals  
17 cannot be ascertained from the literature because of limited references, unreliable data, and  
18 insufficient concentration/exposure scenarios; therefore, research must be conducted to fill  
19 these information gaps. The discussion on anticipated ecological effects of methanol  
20 (Section 3.2.2.2.1) is also applicable and appropriate for ethanol.

#### 22 ***4.2.2.2.2 Landscape and Watershed Alterations from Ethanol Production***

23 In addition to the ecological issues for using ethanol as an alternative fuel that were  
24 discussed earlier, the conversion of nonagricultural land or diversion of cropland to biomass  
25 fermentation feedstock production is a concern (D'Souza et al., 1989). Habitat simplification  
26 and fragmentation will be the prime cause of lowered biodiversity in agroecosystems.  
27 Impacts will be not only on species richness and abundance, but also on trophic and habitat  
28 diversity for both terrestrial ecosystems and aquatic drainage networks. Wildlife populations  
29 currently associated with agroecosystems represent the integration of those species that are

**TABLE 4-3. SUMMARY OF ETHANOL, ACETALDEHYDE, AND ACETIC ACID  
POTENTIAL EFFECTS ON PLANTS<sup>a</sup> AND FISH<sup>b,c</sup>**

| Species                    | Exposure                       | Effect                                    |
|----------------------------|--------------------------------|---|
| <b><u>Ethanol</u></b>      |                                |   |
| Red fir tree               | 1,000,000 ppm, liquid, 10 days | Seed germination decrease                 |
| Pea                        | 1,000,000 ppm, liquid          | Seed germination no effect                |
| Soybean                    | 276 ppm, liquid, 4 days        | Seedling root size decrease               |
| Sugarcane                  | 100,000 ppm, liquid            | Mature plant root number increase         |
| Sugarcane                  | 4,000 ppm, liquid, 4 weeks     | Mature plant root number increase         |
| Lupine                     | 100 ppm, liquid, 24 h          | Seedling root size decrease               |
| Lettuce                    | Stock solution, liquid, 24 h   | Seed germination decrease                 |
| Pea                        | Stock solution, liquid, 24 h   | Seed germination increase                 |
| Oat                        | 3,000 ppm, liquid, 7 days      | Seedling coleoptile size decrease         |
| Impatiens                  | 1,000,000 ppm, liquid, 24 h    | Male gametophyte growth decrease          |
| Potato                     | 5,000 ppm, gas, 24 h           | Tuber respiration increase                |
| Potato                     | 5,000 ppm, gas, 12 h           | Tuber respiration increase                |
| Lupine                     | 100 ppm, gas, 24 h             | Seedling injury no effect                 |
| Pea                        | 100 ppm, gas, 24 h             | Seedling root size decrease               |
| Potato                     | 40,000 ppm, liquid, 5 days     | Tuber enzymatic rate increase             |
| Pea                        | 276,000 ppm, liquid, 51 h      | Mature leaf cell membrane damage          |
| Pea                        | 46,000 ppm, liquid, 30 h       | Seedling root cell membrane damage        |
| Pea                        | 69,000 ppm, liquid, 25 h       | Seed cell membrane damage                 |
| Rainbow trout              | 11,200 ppm, liquid, 24 h       | LC <sub>50</sub>                          |
| Creek chub                 | 7,000 ppm, liquid, 24 h        | LC <sub>0</sub>                           |
| Creek chub                 | 9,000 ppm, liquid, 24 h        | LD <sub>100</sub>                         |
| <b><u>Acetaldehyde</u></b> |                                |   |
| Wheat                      | 13.2 ppm, liquid, 7 days       | Seedling root no effect                   |
| Wheat                      | 44 ppm, liquid, 7 days         | Seedling root size and cell size increase |
| Potato                     | 400 ppm, gas, 24 days          | Tuber enzymatic activity increase         |
| Potato                     | 200 ppm, gas, 24 days          | Mature plant shoot dry mass increase      |
| Pinperch                   | 70 ppm, liquid, 24 h           | TLm                                       |

**TABLE 4-3 (cont'd). SUMMARY OF ETHANOL, ACETALDEHYDE, AND ACETIC ACID POTENTIAL EFFECTS ON PLANTS<sup>a</sup> AND FISH<sup>b,c</sup>**

| Species                   | Exposure                  | Effect                                      |
|---------------------------|---------------------------|---|
| Sunfish                   | 53 ppm, liquid, 96 h      | TLm   |
| <b><u>Acetic acid</u></b> |                           |   |
| Rice                      | 60 ppm, liquid, 7 h       | Seedling root and shoot dry mass decrease   |
| Rice                      | 300 ppm, liquid, 7 h      | Seedling root and shoot dry mass decrease   |
| Lupine                    | 605 ppm, liquid, 20 h     | Seedling root dry mass decrease             |
| Lupine                    | 19 ppm, liquid, 20 h      | Seedling root dry mass decrease             |
| Lupine                    | 3,024 ppm, liquid, 20 h   | Seedling root cell size and number decrease |
| Wheat                     | 120 ppm, liquid, 7 days   | Seedling root cell size and number decrease |
| Wheat                     | 4,800 ppm, liquid, 7 days | Seedling root cell size and number decrease |
| Creek chub                | 200 ppm, liquid, 24 h     | LD <sub>100</sub>                           |

<sup>a</sup>Source: PHYTOTOX (Royce et al., 1984).

<sup>b</sup>Source: Verschueren (1983).

<sup>c</sup>See Health Effects section for effects on other animals.

Key: LC<sub>50</sub> = lethal concentration for 50% of the subjects, LD<sub>100</sub> = lethal dose.

TLm = median threshold limit.

1 adapted to anthropogenic vegetal and landscape alterations. Changes in agroecosystems  
2 structures with increased pesticides and fertilizers would affect wildlife habitat quality.

3 Although extensive precautionary narrative could be written about the effects of  
4 increasing U.S. acreage under cultivation and about increasing the amounts of agricultural  
5 chemicals applied to current and future crop/biomass acreage, the primary anticipated  
6 impacts are:

- 7 1. fragmentation of natural vegetation and wildlife habitats as new lands are brought into  
8 cultivation;

2. decreased vegetal cover serving as CO<sub>2</sub> sinks; however, this should be offset through the production of the biomass crop (increased fertilization may also influence global warming through increased utilization of NO<sub>x</sub> and increased methane emissions, both of which gases are also RITGs);
3. increased contamination of surface waters, groundwaters, soils, and forage by increased loads of agricultural chemicals (e.g., pesticides, nitrates, and phosphorus);
4. movement (via surface waters, atmospheric drift, reentrainment of dust, or volatilization) of agricultural chemicals to nontarget species resulting in accelerated eutrophication, acute/chronic toxic impact, or pathogenic/viral contamination;
5. increased displacement of topsoil through erosion; and
6. loss of marginal agricultural lands used for livestock production to crop (biomass) production.

This list of the realistic potential effects from the production and use of biomass as feedstock for ethanol is extensive, but not comprehensive. It indicates, however, that a thorough study of the environmental impacts of using biomass for large-scale ethanol production in the United States is needed.

#### ***4.2.2.2.3 Aquatic Effects***

Effects of ethanol on aquatic ecosystems are expected to be similar to those for methanol (see Section 3.2.2.2.3). Ethanol and methanol have similar physical-chemical properties and should exhibit similar exposure and toxicological behavior. Ethanol is expected to be somewhat more toxic, with LC50s reported to be approximately twofold

lower for ethanol than for methanol (Mattson et al., 1976; Majewski et al., 1978; Bengtsson et al., 1984; Bowman et al., 1981).

### 4.2.3 Global Warming

As with methanol, the feedstock used to produce ethanol will influence the emissions of RITGs. For example, production from plants may reduce CO<sub>2</sub>, whereas production from coal may increase CO<sub>2</sub>. The net CO<sub>2</sub> balance with respect to feedstocks, however, is far more complex, depending upon the biomass used, the replacement method, and the specific coal- or petroleum-extraction process. Ethanol from biomass appears to have impressive potential as a mitigation option for global climate warming, particularly if non-energy intensive technologies to concentrate the ethanol in fermentation mash are developed. In light of this, substantial exploration to find and evaluate means for removing obstacles to economic production of ethanol is needed. (The discussion on ethanol feedstocks, source characterization, and environmental fate provides more details.)

### 4.2.4 Risk Prevention/Mitigation Technologies

#### 4.2.4.1 Stationary Sources

Ethanol from biomass has potential for mitigating global warming; therefore, the means for producing it at competitive costs are extremely important. Use of the cellulose in municipal waste as part of a recycling program could conceivably have multiple benefits, if feasible.

Although extraction of feedstock materials and ethanol fermentation/synthesis are commercial systems, data on the various emissions/discharges, with and without applied controls, are still lacking. Evaluation of the applicability of existing VOC emission controls for new and existing fuel storage, distribution, and handling systems is needed.

As production of ethanol increases and process configuration changes, evaluation of control needs and availability must be determined. This need is especially true for coal-based ethanol plants. The present gasification plants have all experienced problems with various control systems. Control applications to water discharges could be a problem requiring specific attention.

1 Another major gap in information is the availability and applicability of prevention and  
2 mitigation measures for large spills of ethanol-based fuels.

3 As with other fuels, the concerns about loss of containment of ethanol in USTs apply.  
4 Leak prevention, leak detection, and cleanup technologies would require evaluation based on  
5 the physicochemical properties specific to ethanol.  
6

#### 7 **4.2.4.2 Mobile Sources**

8 As discussed with methanol fuels, motor vehicle emissions are controlled using catalysts  
9 for tailpipe emissions and regenerative carbon canisters for evaporative emissions. Engine-  
10 out acetaldehyde is substantially elevated with ethanol fuel compared to gasoline fuel.  
11 Control system deterioration must be monitored as mileage accumulates to ensure acceptable  
12 levels of emissions reduction.  
13

#### 14 **4.2.4.3 Fuel Transport Sources**

15 The discussion in the methanol chapter (Section 3.2.4.3) is also appropriate for ethanol  
16 fuels.  
17  
18

### 19 **4.3 RESEARCH NEEDS**

20 Ethanol has not received as much attention in the United States as methanol for  
21 replacement of petroleum-based fuels, due primarily to current production economics. This  
22 organic chemical has many attractive fuel characteristics, however, including production  
23 from renewable biomass resources. Should production economics change, this alternative  
24 would receive more attention. Most of the motor vehicle technologies being advanced for  
25 methanol could easily be compatible with ethanol. Ethanol could also provide emission  
26 benefits with stationary combustors. As with methanol, expanded understanding of  
27 emissions, environmental fate, exposure, health/ecosystem effects, and risk reduction/control  
28 is required.

29 In this section, broad research objectives for each key element of risk assessment are  
30 described and priorities are assigned. The priorities across all fuels were considered with the

1 understanding that future knowledge, technology changes, and market factors are likely to  
2 have some impact on them. One major difficulty in developing a prioritization scheme is  
3 accounting for scientific pacing. For example, in many cases, dose-response information is  
4 a higher priority than hazard identification per se, but hazard-identification research must  
5 proceed first to guide the dose-response work. Due to the extent of the uncertainties about  
6 fuels, the approach chosen for prioritization would, in this example, rank hazard-  
7 identification research higher than dose-response research. Each research objective is coded  
8 with one of the following prioritization phrases.

- 10 • Priority 1 for the next 2 to 4 years. This is the highest priority research  
11 over the near term. The research generally entails resolution of major  
12 issues of known concern, identification of new issues likely to be critical to  
13 risk assessment/risk reduction, crucial methods development that paces  
14 much other work, and major mandates of the CAAAs. Characterizing this  
15 work as over the next "2 to 4 years" does not necessarily denote that it can  
16 be accomplished within that time frame.
- 18 • Priority 2 for the next 2 to 4 years. This is medium priority research over  
19 the near term. Work in this category generally entails pursuing key issues  
20 that have importance for either the exposure or effects phase of hazard  
21 identification or for evaluating key elements of risk reduction. Gaining  
22 such information will certainly be important, but is less crucial than work  
23 under Priority 1. Characterizing this work as over the next "2 to 4 years"  
24 does not necessarily denote that it can be accomplished within that time  
25 frame.
- 27 • Priority 3 for the next 2 to 4 years. Although this research is of lower  
28 priority relative to other categories, it is still critical to development of  
29 comprehensive baseline information for all fuels. Characterizing this work  
30 as over the next "2 to 4 years" does not necessarily denote that it can be  
31 accomplished within that time frame.
- 33 • Longer term priority. This research is essential to developing  
34 comprehensive, quantitative risk assessments and/or risk reduction  
35 approaches. However, its initiation is paced by the completion of earlier  
36 research. When major elements of the earlier research are completed, it  
37 will be possible to more definitively prioritize this category of work.



## 4.3.1 Exposure Assessment

### 4.3.1.1 Source Characterization

#### 4.3.1.1.1 Stationary Characterization

Although extraction of feedstock materials and ethanol fermentation/synthesis are commercial systems, adequate data on the various emissions/discharges that are involved, with and without applied controls, are lacking. The primary concerns are the sources and levels of emissions and discharges that will result from the extraction of feedstocks (e.g., crop management); from the refining and conversion to ethanol (e.g., fermentation); and from storage, transportation, and marketing. Although many of these discharges have been quantified and/or qualitatively described to various degrees, data that would be needed to develop viable risk, health, or potential ecological impact assessments are not now available. Initial research will focus on the biomass and petroleum-based feedstocks. Longer range research will address the problem of releases from other feedstocks, such as coal. Assessment of accidental releases is needed to define potential release scenarios and provide a basis for defining emergency procedures.

Key factors to be investigated in the source characterization are emission factors, impacts on existing control technology affecting emissions, and characterization of the integrated CO<sub>2</sub> emissions from the entire production-distribution process (i.e., from crop production through product utilization).

The sources to be evaluated include those listed for methanol plus additional ones in the production and refining area, namely biomass (crop) production, fermentation, and product refining (distillation and other separation technologies to increase ethanol concentration).

#### Research Objectives:

1. Determine the overall net change in CO<sub>2</sub>, VOCs, and other multimedia emissions/discharges resulting from one or more key scenarios of ethanol market penetration by (1) developing emission factors for production, distribution, and utilization for the sources defined above; and (2) determining the impact of ethanol on existing controls, especially those in which the potential exists for reduced

performance that results in increased emissions. (Priority 2 for the next 2 to 4 years.)

2. Develop an accurate CO<sub>2</sub> budget for ethanol from biomass, including the impacts of crop used, land productivity, types and quantity of fertilizer used, energy for production and harvesting of the feedstock, processes (and efficiency) for ethanol production, type of fuel used for plant energy, and by-product usage. (Priority 2 for the next 2 to 4 years.)
3. Perform a catastrophic-release hazard assessment to identify specific areas of concern that may need prevention-oriented risk-reduction work. (Priority 2 for the next 2 to 4 years.)
4. Confirm low emission potential (reduced hydrocarbons, CO, and NO<sub>x</sub>) for: neat ethanol used in power generation, including utility boilers and gas turbines; heat generation sources, such as industrial/commercial boilers; cogeneration units; stationary IC engines; and small engines. Develop a source characterization profile for aldehyde emissions for certain sources utilizing ethanol in which exposure will be important, including stationary IC engines and other nonhighway vehicles. (Priority 2 for the next 2 to 4 years.)
5. Assess energy efficiency changes for the above stationary source applications. (Longer term priority.)

The emissions/discharges problem addressed by the research must include continuous/routine emissions, short-term releases, and catastrophic-scale releases.

#### **4.3.1.1.2 Mobile Source Characterization**

Characterization of emissions from motor vehicles fueled with ethanol should be structured similarly to that discussed for methanol. The emission rates of regulated (total

organic, CO, NO<sub>x</sub>, and particles) and unregulated (aldehydes, organic acids, benzene, 1,3-butadiene, CO<sub>2</sub>, N<sub>2</sub>O, and others) compounds must be determined as a function of vehicle-fuel technology, varied operating conditions (speed, ambient temperature, and age) and emissions source (tailpipe, evaporation, and refueling).

Emissions data that are useful for assessing the impact of ethanol-fueled motor vehicle emissions on air quality problems such as O<sub>3</sub>, CO, particles, and global climate change, as well as for estimating changes in exposure to toxics such as benzene, formaldehyde, acetaldehyde, and 1,3-butadiene, are needed. As with methanol fuels, the characteristics of emissions from vehicles using ethanol fuels will be contrasted with those of emissions from vehicles using conventional gasoline and diesel fuels.

#### Research Objective:

1. Characterize emissions from motor vehicles designed for ethanol fuels (E100, E85, etc.) as a function of speed, ambient temperature, and mileage accumulation. Emission strengths and speciations suitable for estimating impact on air quality (i.e., O<sub>3</sub>, NO<sub>2</sub>, CO, and particles) and on other issues such as global climate change and toxic compound exposure are needed. (Priority 2 for the next 2 to 4 years.)

### **4.3.1.2 Environmental Fate**

#### **4.3.1.2.1 Air Fate**

As with methanol, the chemistry of ethanol is fairly well understood. Acetaldehyde and hydroxyacetaldehyde are expected products from the homogeneous oxidation. Peroxyacetyl nitrate and possibly hydroxyPAN are expected products in the presence of NO<sub>x</sub>. Multiday smog-chamber and modeling studies are needed to establish the importance of second- and third-day effects, both locally and regionally. If large concentrations of PAN are produced, then second-day effects may be important because PAN-type compounds temporarily store NO<sub>x</sub> and can make NO<sub>x</sub> available for photochemistry on subsequent days. Also, PAN is a strong phytotoxicant. If PAN levels with ethanol use are significantly higher than those

observed with gasoline use, then plant-damage studies using a phytotron coupled to a smog chamber/dynamometer facility are recommended. Mutagenicity studies should also be performed on both the exhaust gases emitted and the photochemical oxidation products from these gases. Brazil uses ethanol to power many vehicles, so a study of the air quality in one of the major cities in Brazil should be undertaken. Particular attention should be given to ambient levels of acetaldehyde and PAN. Some basic kinetic studies are also needed to determine if ethyl and diethyl sulfate are produced.

#### Research Objectives:

1. Evaluate the photochemical reactivity of ethanol exhaust. (Priority 2 for the next 2 to 4 years.)
2. Determine the influence of irradiation of exhaust from ethanol-fuel vehicles on mutagenicity potency. (Priority 2 for the next 2 to 4 years.)
3. Characterize the formation of organic acids and carbonyls through heterogeneous UV-induced reactions with aerosols. (Priority 3 for the next 2 to 4 years.)
4. Determine the impact of ethanol fuel use on air quality in Rio de Janeiro. (Priority 3 for the next 2 to 4 years.)

#### ***4.3.1.2.2 Soil and Groundwater Fate***

Because ethanol and methanol are expected to behave similarly in the subsurface, the key research questions and the experimental approach will be the same for these alcohols. Some differences are anticipated in the magnitude of transport and fate parameters, so both solvents must be investigated. Research on the behavior of ethanol in the subsurface should parallel similar research for methanol (see Section 3.3.1.2.2).

Research Objective:

1. Assess the potential for groundwater contamination resulting from the use of ethanol as a replacement fuel. (Priority 3 for the next 2 to 4 years.)

#### ***4.3.1.2.3 Surface Water Fate***

Surface water (fresh and marine) transport and fate of ethanol is expected to have mechanisms similar to those of methanol, with ethanol-specific factors resulting in some differences. Therefore, research is needed on common mechanisms as well as fuel-specific factors. Findings from methanol research should be used to guide decisions on ethanol research. For example, if methanol is shown not to influence the bioavailability of neutral organic compounds, comparable ethanol studies should be scaled back or eliminated.

Research Objectives:

1. Develop a state-of-the-science surface water (marine and fresh) transport and fate methodology for use in comparative exposure-assessment analyses of catastrophic ethanol (and gasoline) spills. (Priority 2 for the next 2 to 4 years.)
2. Determine the influence of ethanol on the bioavailability of neutral organic compounds in the marine environment. (Priority 3 for the next 2 to 4 years.)

#### **4.3.1.3 Exposures**

##### ***4.3.1.3.1 Human Exposures***

The exposure research program for ethanol will be similar to that discussed for methanol, except that the specific target pollutants of concern will change based upon emissions testing. The research program will include (1) developing the necessary sampling and analytical procedures, (2) conducting measurement studies in locations impacted by mobile source emissions, and (3) exposure modeling. Because other routes of exposure add to total exposures, especially through ingestion, specific studies to document the total

1 exposures possible and the percentage directly resulting from mobile source emissions will be  
2 required.

3  
4 Research Objectives:

- 5
- 6 1. Exposure assessment of the identified pollutants that are primarily, if not  
7 specifically, related to use of ethanol fuel, including ethanol and acetaldehyde.  
8 (Priority 2 for the next 2 to 4 years.)  
9
  - 10 2. Development and application of validated human exposure models to predict  
11 changes in exposure resulting from ethanol fuels. (Priority 2 for the next  
12 2 to 4 years.)  
13

14 ***4.3.1.3.2 Biota Exposures***

15 Research needs are the same as those described for terrestrial and aquatic biota within  
16 the methanol section (see Section 3.3.1.3.2).  
17

18 Research Objectives:

- 19
- 20 1. Exposure assessment of ethanol-fuel pollutants (e.g., ethanol, acetaldehyde, and  
21 acetic acid) to terrestrial ecosystems within the South Coast Air Basin, CA.  
22 (Priority 3 for the next 2 to 4 years.)  
23
  - 24 2. Develop example cases for ethanol fuel spills and leakages to freshwater and  
25 estuarine ecosystems that include characterizations of system morphometry,  
26 organism types and locations, and physical/chemical properties that regulate fate  
27 and effects. Apply source scenarios and fate/transport models to these test cases to  
28 develop exposure time series for target organisms. (Longer term priority.)  
29

#### 4.3.1.4 Analytical Methodology

Analytical methods will be developed, upgraded, and/or evaluated for measurement of source emissions, atmospheric transport and transformation of the emissions, and population (human and ecosystem) exposure to the emissions and transformation products, as necessary, to support assessments of the impact of varied fuel formulations on risk to public health and welfare.

Procedures suitable for certification of regulated source emissions (THC, NMHC, CO, NO<sub>x</sub>, and particles) at levels mandated by the CAAAs and for the detailed speciation necessary to support estimation of impact on O<sub>3</sub> and toxics air quality will be required. The procedures must permit accurate and precise determination of large numbers of compounds in very complex mixtures.

Ambient air monitoring and microenvironmental monitoring will require methods development for the measurement of ethanol and acetaldehyde. In addition, development of personal monitors will also be required for population characterization studies, if undertaken in later years.

Ambient air monitoring techniques are needed for measuring unburned ethanol, acetic acid, acetaldehyde, ethyl nitrite, PAN, and hydroxyPAN. Standard instrumentation such as GCs equipped with FIDs and electron capture detectors, ion chromatographs, and high performance liquid chromatographs can be used to monitor most of the emissions and transformation products. Some developmental work may be needed to measure low levels of these compounds and any other compounds that may be produced with the use of ethanol as a fuel.

#### Research Objectives:

1. Develop/upgrade/evaluate analytical procedures for measurement of source emissions potentially associated with ethanol fuels (e.g., ethanol, acetaldehyde, ethyl nitrite, and acetic acid). (Priority 2 for the next 2 to 4 years.)

2. Validate classical procedures for certification of organic carbon, CO, NO<sub>x</sub>, particulate, and CO<sub>2</sub> emissions from ethanol-fueled vehicles; identify problems, provide corrective actions, and/or develop new, more simplistic, lower cost acceptable procedures. (Priority 2 for the next 2 to 4 years.)
3. Develop/upgrade/evaluate analytical procedures for measurement of ambient air concentrations of compounds potentially associated with ethanol fuels (e.g., ethanol, acetaldehyde, ethyl nitrite, acetic acid, diethyl sulfate, and PAN). (Priority 3 for the next 2 to 4 years.)
4. Develop/upgrade/evaluate analytical procedures for measurement of exposure to compounds potentially associated with ethanol fuels (e.g., O<sub>3</sub>, ethanol, acetaldehyde, ethyl nitrite, acetic acid, and diethyl sulfate), including passive personal and microenvironment monitors. (Priority 3 for the next 2 to 4 years.)

### **4.3.2 Effects Assessment**

#### **4.3.2.1 Human Health Effects**

##### **4.3.2.1.1 Overview**

The general strategy for health research for ethanol is similar to that for methanol (see Section 3.3.2.1); therefore, this section only highlights the differences in strategies between the two fuels, and states the research objectives applicable to ethanol. Information on health effects of ethanol is derived from both human and nonhuman species and primarily by the oral route of exposure. Relative to the other fuels of interest, a great deal is already known about ethanol. Based on the existing ethanol literature, endpoints of particular concern are for developmental effects and carcinogenesis. The relevance of these concerns to possible fuel-related environmental exposures is unclear. The most important research areas for ethanol (E85 and E100) are as follows: (1) pharmacokinetic evaluation to facilitate oral-to-inhalation and animal-to-human extrapolation, (2) ethanol developmental effects, (3) ethanol as a carcinogen or co-carcinogen, and (4) potential carcinogenicity and/or toxicity of ethanol



combustion and transformation products associated with both whole mixtures and specific mixture components, such as acetaldehyde.

#### **4.3.2.1.2 Primary Fuel-Ethanol**

Research efforts for ethanol should focus initially on evaluation of existing pharmacokinetic data and models as a basis for extrapolating the large body of existing oral data to human inhalation exposures. Studies should evaluate important metabolic pathways, develop metabolic constants and estimate dose to target tissue(s) across routes of exposure and species. If ethical concerns can be resolved, additional human data, using inhalation of ethanol, could be collected to facilitate this extrapolation. In addition, alterations in the metabolism of ethanol, induced by co-exposure to the ethanol and gasoline (E85), will need to be evaluated. Pharmacokinetic research and model development should be coupled to health effects research and dose-response model development, as warranted.

An additional high priority research need is the evaluation of the potential for developmental effects, such as fetal alcohol syndrome, via inhalation exposures. Critical activities include: (1) evaluation of existing human data on effects of fetal alcohol syndrome associated with oral exposure, (2) development of an animal model of effects by the inhalation route, and (3) evaluation of the implications of observed effects for low-dose extrapolation and predicted human inhalation exposures. This research should focus on linking the large, ongoing oral consumption/fetal alcohol syndrome research effort to understanding potential risks from inhalation exposures. If the research described above indicates that fetal alcohol syndrome could be induced or exacerbated by vehicle-related ethanol exposures, then consideration also should be given to issues associated with low-dose extrapolation (in the context of population dose-response modeling) and additivity to background incidence. The existence of a background incidence has been used, in other circumstances, to argue for linear, no-threshold models for population dose-response assessment.

Research into the carcinogenic or co-carcinogenic potential of ethanol is needed. The initial efforts should focus on evaluating the large oral exposure and effects data base. This evaluation, if inadequate to address current concerns, could focus additional studies on

specific differences in metabolism and/or mechanisms of action between oral versus inhalation and high-dose versus low-dose exposures. Because of the potential role of acetaldehyde in ethanol-induced carcinogenesis, differences in metabolism of ethanol to acetaldehyde could form the nucleus of initial efforts. Studies examining the interactions of ethanol with other fuel-associated carcinogens (e.g., benzene, POM) also would be important. Screening approaches, similar to those proposed for assessing combustion and transformation products by using short-duration in vitro and in vivo assays, could be used to focus on particular combinations of carcinogens that appear important. In the longer-term it is likely, given the complexity of this problem, that chronic inhalation bioassays of E85 and/or E100 would be necessary to make any definitive statement concerning the potential carcinogenic potency of these fuels. Consideration of the potential for market penetration of ethanol fuels (E85 and E100) and vehicle-related ethanol exposures should precede any such chronic bioassay.

#### ***4.3.2.1.3 Combustion and Atmospheric Transformation Products***

Research proposed for ethanol combustion and transformation products is similar to that described for methanol combustion and transformation products (Section 3.3.2.1.3). The proposed research is reiterated briefly here. Examination of the carcinogenicity and the respiratory system toxicity is of primary concern. In particular, the whole mixtures and specific components, such as acetaldehyde, are of interest. Screening studies, using short-term in vitro and in vivo methods should be conducted first. The results of these screening studies can be used to determine and compare the potency of these ethanol-related mixtures and individual compounds to the combustion and transformation products of other fuels of interest, and determine the need for more detailed chronic bioassays.

#### ***4.3.2.1.4 Research Objectives:***

1. Utilizing existing ethanol data where possible for the following: (1) evaluate important metabolic pathways, including in vivo and in vitro metabolic constants for humans and laboratory animals, and estimate dose to target tissue(s),

(2) develop physiologically-based pharmacokinetic models for the experimental species relevant to humans (and potentially relevant to human subpopulations), and (3) validate these models with experimental data. This effort is key to facilitating extrapolation (species-to-species, route-to-route, etc.) and estimating dose to target tissue, including dose to the fetus. (Priority 1 for the next 2 to 4 years.)

2. Utilizing existing ethanol data to the extent possible, assess the exposure-response relationships for developmental effects and cancer, including development of appropriate quantitative models. Focus will be on the extrapolation of oral data to evaluate potential inhalation exposures, using the pharmacokinetic model noted in Objective 1. (Priority 1 for the next 2 to 4 years.)

3. Evaluate the potential ability of combustion and transformation products to induce cancer or respiratory toxicity. Initially use in vitro and short-term in vivo assays to target vehicle types and operating conditions of concern, then compare estimates of potency for ethanol products to similar estimates of potency conventional fuels and other alternative fuels. These comparative potency estimates will determine the need for chronic bioassays for ethanol combustion and transformation products, in conjunction with improved estimates for emissions, exposure and market penetration. If needed, use bioassay-directed fractionation to identify particularly potent components of these mixtures. (Priority 1 for the next 2 to 4 years.)

4. Investigate potential acetaldehyde-induced effects: pulmonary inflammation, increased susceptibility to infectious and allergic diseases, and the potential for long-term respiratory impairment with recurrent acute exposures. Also, improve the cross-species estimates of dose to target tissues, understanding of mechanisms of action, and a biologically-based dose-response model. (Priority 1 for the next 2 to 4 years.)

5. Conduct chronic inhalation bioassays of ethanol fuel (E85 and/or E100), assessing both cancer and noncancer endpoints, if warranted. The bioassays should be conducted pending outcomes of data generated by Objectives 1 and 4, and improved estimates for emissions, exposure, and market penetration. (Priority 2 for the next 2 to 4 years.)

#### **4.3.2.2 Ecosystem Effects**

##### ***4.3.2.2.1 Terrestrial Effects***

Ethanol, acetaldehyde, and acetic acid (exhaust products from ethanol fuel combustion) deposition and exposure have the potential to impact terrestrial ecosystems. Several research projects to obtain information not available in the scientific literature are proposed. The research projects presented in the methanol chapter (Section 3.3.2.2.1) are also appropriate to evaluate ethanol ecosystem effects.

#### **Research Objectives:**

1. Evaluate the responses of plants to acetaldehyde, acetic acid, and ethanol exposures (dry and wet/fog), individually and in binary combinations with O<sub>3</sub>, at various concentrations to assess the sensitivity of plant process functions. (Priority 3 for the next 2 to 4 years.)
2. Evaluate the effects of acetaldehyde and ethanol binary exposures (dry and wet/fog) on plants to assess the sensitivity of plant process functions. (Priority 3 for the next 2 to 4 years.)
3. Evaluate the effects of acetaldehyde and ethanol on plant growth within mesocosms in relationship to altering temperature and water stress. (Longer term priority.)

4. Evaluate the effects of ethanol combustion emission/transformation products on plant growth and development using various exposure scenarios. (Longer term priority.)
5. Evaluate the use of biomarkers to monitor the effects of ethanol-fuel pollutants on plant growth and development as ethanol fuels gain prominence in the South Coast Air Basin, CA. (Longer term priority.)

#### ***4.3.2.2.2 Fresh Water Effects***

The research needs are the same as for methanol (see Section 3.3.2.2.2).

#### **Research Objective:**

1. Evaluate the toxic effects of ethanol and its joint toxicity with other fuel-blend components and hydrophobic contaminants on various freshwater aquatic organisms. Develop dose-response models suitable for application to various exposure situations. Include capability to add effects of suppressed dissolved oxygen levels as well. (Priority 3 for the next 2 to 4 years.)

#### ***4.3.2.2.3 Marine Effects***

The same studies that were proposed for methanol would be conducted using ethanol (see Section 3.3.2.2.3).

#### **Research Objective:**

1. Determine the effects of ethanol added to marine mesocosms. (Priority 2 for the next 2 to 4 years.)

### 4.3.3 Global Warming

The research described on source characterization, environmental fate in the ambient air, and risk reduction/control technology will result in identification of changes in RITGs due to the manufacture and combustion of various alternative fuels; therefore, the research description will not be repeated here. Ethanol from biomass should receive substantial quantification attention because of its potential as a mitigation measure.

#### Research Objective:

1. Identify and characterize RITGs affected by ethanol fuel production and use. This information will be used as input to global climate models being developed and applied under EPA's Global Climate Research Program. (Priority 3 for the next 2 to 4 years.)

### 4.3.4 Risk Prevention/Mitigation

#### 4.3.4.1 Stationary Sources

Risk reduction research will need to focus on (1) areas that are current problems for conventional fuels, (2) new areas of uncertainty brought about by the alternative fuels, and (3) areas likely to be aggravated by use of alternative fuels (specifically ethanol).

The research effort must ensure that the existing O<sub>3</sub>-nonattainment problem is not further aggravated through introduction of ethanol into the energy infrastructure. This means an examination of the adequacy of existing controls will be necessary. Existing combinations of emission sources and typically applied controls must be evaluated to determine applicability and effectiveness of add-on control technology. Opportunities for applying prevention technologies and strategies must be identified. Existing information on VOC rule effectiveness seems to indicate poor performance of controls in areas such as gasoline distribution. Relative to global warming, ethanol has much potential to reduce CO<sub>2</sub> emissions via the use of biomass as its feedstock. Obstacles and barriers to the use of ethanol for this purpose are an important part of the recommended research.

For USTs, the research needs relating to ethanol are essentially the same as those described for methanol in Section 3.3.4.1. The physicochemical properties of methanol and ethanol (especially when compared to gasoline) are quite similar, and, if warranted by projected use, research projects on these two alternative fuels could proceed in tandem in the same project. Alternatively, the most likely alcohol could be selected and the research results used to represent, generally, the results for the other alcohol.

#### Research Objectives:

1. Perform an overall assessment of the opportunities to increase effectiveness of the biomass-to-ethanol conversion process. Two specific areas are known to be important: (Priority 2 for the next 2 to 4 years.)
  - Higher yields and more effective conversion of the total biomass (crop material), including sugars, starches, cellulose, hemicellulose, and other carbohydrates.
  - More energy-efficient concentration of ethanol to fuel-grade ethanol (removal of water).
2. Assess and optimize the control/compliance effectiveness of stationary-source controls for ethanol production and utilization, and develop new or improved control systems to maximize emissions/discharge reduction. (Priority 3 for the next 2 to 4 years.)
3. Develop user-oriented accidental-release prevention reference manuals for ethanol storage, transportation, and marketing. (Priority 3 for the next 2 to 4 years.)
4. Confirm low emission potential (reduced hydrocarbons, CO, and NO<sub>x</sub>) for neat methanol used for power generation (including utility boilers and gas turbines), heat generation sources (such as industrial/commercial boilers), cogeneration units, and stationary IC engines; evaluate the barriers to application of ethanol to stationary combustion sources; and extend the evaluation of aldehyde emissions

from certain combustion sources utilizing ethanol for which exposure will be important (e.g., stationary IC engines and other nonhighway vehicles). (Longer term priority.)

5. For USTs, the research objectives are essentially the same as those for methanol, and research projects on these two alternatives fuels could be combined. (Priority 2 for the next 2 to 4 years.)

#### 4.3.4.2 Mobile Sources

The performance of motor vehicle emission control systems must be monitored as a function of consumer mileage accumulation. With ethanol fuels, special emphasis needs to be given to acetaldehyde, because engine-out emissions of this compound are projected to increase significantly with ethanol fuels. The impact of this technology on urban O<sub>3</sub> will weigh heavily on the effectiveness of control systems to reduce photochemically reactive emissions.

##### Research Objective:

1. Assess the effectiveness of motor vehicle emissions control systems for reduction of acetaldehyde as a function of consumer mileage accumulation. (Priority 2 for the next 2 to 4 years.)

#### 4.3.4.3 Fuel Transport Sources

Research needs for risk prevention/mitigation of major fuel spills from tankers, barges, pipelines, etc., are the same as described for methanol (see Section 3.3.4.3). Since many of the scientific issues for alcohols are similar, the methanol research should be completed first to provide guidance or directions for ethanol work.



Research Objectives:

1. Evaluate adequacy of transport system containment of ethanol fuels for preventing major spills and leaks. (Longer term priority.)
2. Assess clean-up options to reduce the impact of an ethanol fuel spill on sensitive biota and ecosystems. (Longer term priority.)

## 5.0 COMPRESSED NATURAL GAS

### 5.1 RISK ASSESSMENT RESEARCH FRAMEWORK

Compressed natural gas (CNG) has a limited degree of current use in this country as a transportation fuel and has been used in some other countries to fuel motor vehicles. Like other proposed alternative fuels, CNG may have the potential to reduce atmospheric pollution because of its composition and combustion properties. In particular, CNG could offer substantial ozone (O<sub>3</sub>) air quality improvement because the fuel itself is low in photochemical reactivity (Alson et al., 1989). The EPA has released a special report providing perspectives on CNG as an alternative fuel (U.S. Environmental Protection Agency, 1990c) and is preparing regulations for emissions certification of vehicles using CNG fuel. Available data suggest the potential for substantially reduced photochemically reactive nonmethane hydrocarbon (NMHC) emissions relative to gasoline, due primarily to the fuel being 90 to 95% methane. Furthermore, the nonmethane components of CNG include large fractions of relatively low reactivity paraffins such as ethane and propane. Additionally, because CNG vehicle fuel systems are not ventilated, evaporative emissions are essentially eliminated. Expanded understanding of associated emissions, atmospheric chemistry, target population exposures, health/ecosystem effects, and possibilities for risk reduction/control will be necessary to assess the potential impact of CNG on public health and the environment.

This chapter first highlights some key points of information and issues about CNG in a risk-assessment research format. The risk-assessment research framework section takes Section 1.4, Introduction to Risk Assessment Framework for Fuels, as its point of departure, but focuses only on those facets of the generic framework that are specific to CNG. The next section (Section 5.2) contains the background and rationale for research. This is intended to provide guidance for the research, rather than serve as a complete review of all CNG topics. The last section (Section 5.3) contains a discussion of research needed to provide the foundation for a quantitative risk assessment of this fuel.

## 5.1.1 Exposure Assessment

### 5.1.1.1 Source Characterization

#### 5.1.1.1.1 Emissions from Feedstock and Fuel Production, Storage, and Distribution

**Feedstocks.** Natural gas is the primary feedstock for CNG, although other feedstocks such as coal, biomass, oil shale, and petroleum crudes could be used. North American reserves amount to about 20% of world reserves; approximately 19% of world reserves are in Middle South Asia, and about 43% are in the U.S.S.R. Concerns about emissions (primarily methane and carbon dioxide [CO<sub>2</sub>]) and discharges have been discussed in Chapter 3. It should be restated that extraction of natural gas involves very large quantities of CO<sub>2</sub>, for which a good material balance is needed. Considering resource availability, CNG (methane) might need to be derived from coal in the near future; therefore, a coal-based methane assessment is needed.

**Production.** The manufacturing of CNG involves compression of the natural gas to suitable pressures (about 3,000 psi). The major potential emissions would be methane and other RITGs, and depending upon the fuel, sulfur oxides (SO<sub>x</sub>) from related power requirements. The fugitive and transient emissions need to be identified and quantified. Accidental large releases of methane have the potential for causing fires or explosions and global climate impact. The compression operation does present a hazard of concern because it may be located near populated areas. An accidental-release hazard-assessment study is, therefore, needed to identify specific areas of concern that may need prevention-oriented risk reduction work. Potential hazards could be greatest in the compression facility, where good industrial prevention/control approaches might not be widely practiced.

**Storage and Distribution.** Potential air quality problems would primarily be methane emissions related both to conventional, transient, or accidental releases from transportation of the natural gas to the compression facility and to the distribution, storage, and handling of CNG at the end-use facility. Large accidental releases of CNG could result in fires and explosions, causing serious concern.

1       Leaks and spills of natural gas or CNG will probably not pose a significant threat to  
2       terrestrial and aquatic ecosystems because of the volatility of the fuel; however, release of  
3       methane could contribute to global warming.

#### 5       ***5.1.1.1.2 Emissions Related to Fuel Use***

6       ***Stationary Source Emissions.*** Compressed natural gas could be used in internal  
7       combustion (IC) engines, such as construction equipment and other vehicles not used on  
8       roadways. Conventional natural gas, not CNG, would be used in stationary combustors,  
9       boilers, and turbine engines. Emissions may be quite low where dirtier fuels (e.g., gasoline  
10      and diesel fuel) are displaced. Radiatively important trace gas emissions from boilers and  
11      turbines have been fairly well quantified; however, the emissions of radiatively important  
12      trace gases (RITGs), especially methane, need to be determined. An assessment of the  
13      overall energy efficiency changes for stationary source IC engine end-use applications is  
14      needed. An accidental-release hazard assessment is needed for CNG to identify specific  
15      areas of concern that may need prevention-oriented risk-reduction work.

16  
17      ***Mobile Source Emissions.*** Natural gas provides an option to petroleum-based fuels for  
18      motor vehicles. The most fundamental difference between natural gas and conventional  
19      motor fuels is that natural gas, unless cryogenically stored under pressure, is gaseous rather  
20      than liquid. Therefore, transition "dual-fuel" vehicles must use two fuel tanks, unlike  
21      methanol and ethanol, which can be commingled with conventional fuels. The primary  
22      hydrocarbon component of natural gas, methane (generally greater than 90% of the mixture),  
23      is considered photochemically nonreactive for O<sub>3</sub> formation. Octane performance in  
24      Otto-cycle engines is very good, with (R+M)/2  $\approx$  120. This octane rating permits higher  
25      compression ratios than with conventional gasolines, with associated improved engine  
26      efficiencies; and CNG engines can be operated at higher air/fuel ratios (leaner combustion).

27      Two general categories of light- and heavy-duty motor vehicles are being considered for  
28      CNG fuels: dual-fuel (compatible with both conventional fuels and CNG), and dedicated  
29      (optimized for CNG). The dedicated category vehicles are further defined as those designed  
30      for fuel-lean combustion and those designed for stoichiometric combustion (chemically

1 correct amounts of air and fuel for complete combustion). Stoichiometric combustion is  
2 necessary for three-way catalyst control of tailpipe emissions.

3 Dual-fuel configurations suffer performance penalties relative to dedicated  
4 configurations, because they are not able to take full advantage of natural gas fuel  
5 characteristics (e.g., they must have compression ratios compatible with lower octane  
6 gasolines). When operated on CNG, however, dual-fuel vehicles generally have reduced  
7 carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>) emissions, and the impact on hydrocarbon  
8 emissions is varied. Methane, the primary component of natural gas, is not as easily reduced  
9 by catalysts as most gasoline hydrocarbons, but it is more environmentally benign (except for  
10 its potential contribution to global climate warming). Nonmethane hydrocarbon (NMHC)  
11 emission rates can be lower with CNG, and the composition can be substantially different  
12 from those of conventional fuels. Natural gas NMHCs are typically dominated by low  
13 molecular weight paraffins such as ethane and propane; the emission rate of toxics such as  
14 benzene and 1,3-butadiene should be reduced by CNG fuel.

15 Dedicated CNG vehicles typically have lower CO emissions than conventional gasoline  
16 fuel vehicles, but they may have elevated NO<sub>x</sub> if compression ratios are increased and  
17 fuel-lean combustion is utilized (preventing use of three-way catalysts). Heavy-duty engines  
18 using CNG fuel should have lower particulate emissions than typical diesel engines. The  
19 cetane characteristics of natural gas prevent its use in conventional compression ignition  
20 engines. Some form of ignition assist (spark plugs, glow plugs, etc.) must be used. Relative  
21 to conventional diesel engines, catalyst equipped Otto-cycle CNG engines in heavy-duty  
22 applications, operated near stoichiometry, offer substantially reduced NO<sub>x</sub> and particulate  
23 emissions, somewhat higher CO emissions, and lower NMHC emissions. The EPA is  
24 preparing a rulemaking for regulation of emissions from vehicles using CNG fuel.

25 The global warming implications of motor vehicles using CNG fuel are varied,  
26 depending upon contrasts with heavy-duty diesel or light-duty gasoline engines. Considering  
27 methane, CO<sub>2</sub>, and emissions associated with fuel production and use, the contribution to  
28 global warming is projected to be elevated relative to heavy-duty diesels (+10 to 25%) and  
29 reduced relative to light-duty gasoline engines (–20 to 25%).  
30

1 Available data generally consider emissions only under the operating conditions of  
2 Federal emissions certification (19.6 mph, 70 °F). Comprehensive assessment of the impact  
3 of CNG fuel on air quality will require research on both emissions strength (g/mi) and  
4 composition under driving conditions typical of U.S. fleets during periods when air quality  
5 problems prevail.

#### 6 7 **5.1.1.2 Environmental Fate**

##### 8 ***5.1.1.2.1 Air Fate***

9 Methane reacts very slowly with hydroxyl (OH) radicals, the principal removal process  
10 in the atmosphere. The photooxidation product is formaldehyde. Very little O<sub>3</sub> is expected  
11 from atmospheric reactions. Photochemical models predict that ambient levels of methane  
12 (approximately 1.6 ppm) can produce low ppb levels of O<sub>3</sub> when NO<sub>x</sub> is also present at  
13 background levels. At higher NO<sub>x</sub> levels, in the absence of other volatile organic  
14 compounds (VOCs), very little O<sub>3</sub> is expected because of nitric oxide (NO)-inhibition effects  
15 (not enough RO<sub>2</sub> radicals are produced to completely oxidize NO to nitrogen dioxide [NO<sub>2</sub>]  
16 to produce O<sub>3</sub>). If significant levels of formaldehyde are also emitted with methane in  
17 vehicle exhaust, then the photochemical reactivity may be significant.

18 Another concern with methane emissions is its contribution to the greenhouse effect.  
19 Methane is not only an RITG, but it also acts as a sink for OH radicals when NO<sub>x</sub> levels are  
20 low. If OH radicals are depleted, most pollutants will have a longer lifetime in the  
21 atmosphere, which could have severe consequences to air quality and global warming.  
22 Interestingly, a rough analysis on the use of methane as a fuel suggests that it is preferred  
23 over other fossil fuels to minimize the greenhouse effect if its leakage can be kept below 6%.  
24 Research in this area needs to center on studies with exhaust gases and modeling to  
25 determine effects on air quality and global warming.

##### 26 27 ***5.1.1.2.2 Soil, Groundwater, and Surface Water Fate***

28 Since CNG exists as a gas, it is expected to have limited exposure to the surface or  
29 subsurface environment. Even if released, CNG would readily volatilize, resulting in

1 minimal residence times in the subsurface. Therefore, CNG is not expected to pose a  
2 significant threat to soil, groundwater, and surface water resources.

### 4 **5.1.1.3 Exposures**

#### 5 ***5.1.1.3.1 Human Exposure Assessment***

6 The impact of CNG on air quality and/or human exposures cannot be quantitatively  
7 assessed because of a lack of data. Because of the possibility of substantially increased  
8 emissions of methane, CNG use could result in increased levels of transformation  
9 by-products, such as formaldehyde. Actual direct exposures of consequence will need to be  
10 estimated after better emissions data become available.

11 As with all mobile source-generated pollutants, studies of the important  
12 microenvironments, activities, and populations exposed will be required if significant  
13 emissions are observed. Large-scale accidental releases could pose significant risk because  
14 methane is an asphyxiant.

#### 16 ***5.1.1.3.2 Biota Exposure Assessment***

17 Due to its volatility, CNG is not expected to produce a significant exposure threat to  
18 terrestrial and aquatic biota; however, as with the human exposure assessment, exposure  
19 patterns and transformation products (e.g., formaldehyde) must be considered as more  
20 information becomes available. Exposure research may then be needed.

### 22 **5.1.1.4 Analytical Methodology**

23 Analytical methodologies for measuring source emissions, for monitoring the ambient  
24 air transport and transformation of these emissions, and for monitoring the exposure of target  
25 populations (human and ecosystem) to the pollutants of interest are prerequisites for  
26 determining the relative impacts of varied motor fuels on risk to public health and welfare.

27 Source emissions characterization requires accurate and precise analytical procedures.  
28 Qualified certification procedures exist for measuring currently regulated THC, CO, NO<sub>x</sub>,  
29 CO<sub>2</sub>, and total particulate emissions, as well as for measuring some unregulated toxic  
30 emissions of interest, such as benzene, formaldehyde, and 1,3-butadiene, from motor

1 vehicles using conventional fuels. With CNG fuel, measurement of organic emissions is  
2 complicated by methane's domination of the composition (the fuel is generally greater than  
3 90% methane). The adequacy (accuracy and precision) of classical certification procedures  
4 will need to be examined at concentrations associated with the reduced emissions permitted  
5 by the CAAAs. Measurement of NMHC emissions will be difficult with CNG due to the  
6 predominance of methane in the emissions. Procedures for direct measurement of NMHC  
7 (versus determination by THC – methane difference) will be required for CNG fuel.  
8 Because available procedures are often costly and complex to implement, efforts to improve  
9 methodology performance and to simplify procedures, permitting application by lesser skilled  
10 analysts, are required. Many of the analytical procedures provide only integrated data for  
11 transient driving periods; therefore, conditions favoring emission of a particular toxic  
12 substance are difficult to isolate. Continuous "real time" measurement procedures must be  
13 developed for this purpose. Validated chromatographic procedures are required for  
14 determining the composition of organic emissions for both O<sub>3</sub> and toxics air quality impact  
15 assessments.

16 Analytical procedures employed with other fuels can also be employed for the analyses  
17 of transformation products arising from the use of CNG. The principal products expected  
18 are formaldehyde, CO, and unburned methane. All of these can be monitored with ease, and  
19 no further analytical work is needed.

20 Improvements to NO<sub>2</sub> monitors for indoor monitoring to account for potential  
21 interferences due to nitric and nitrous acids will be required. Ambient methodology should  
22 be adequate to measure any changes resulting from emissions from vehicles fueled by CNG.  
23 New methods may be required for measuring emissions of impurities in the CNG, such as  
24 arsenic, if they cannot be filtered out of the fuel supply before combustion.  
25

## 26 **5.1.2 Effects Assessment**

### 27 **5.1.2.1 Human Health Effects**

28 Considerable anecdotal information on human inhalation exposures to CNG is available.  
29 Compressed natural gas appears to be a simple asphyxiant and is not likely to produce general  
30 systemic effects. Only very limited additional evaluation of CNG is needed to verify



its apparent low toxicity. This is not high priority research. Considering the health and chemical characterization data available for CNG, this fuel should pose a lower potential for toxicological concerns compared to conventional fuels.

The major research for CNG should focus on complex mixtures of combustion and transformation products. This complex mixture research will be similar to that provided in the description of research in the introduction (Section 1.2). Some specific data on the transformation of gas combustion emissions already exist. Recent studies of natural gas combustion emissions show that nitrous acid can be produced at sufficiently high levels to react readily with methane and other hydrocarbons and to produce genotoxic and potentially carcinogenic mixtures containing compounds such as peroxyacetylnitrate (PAN). More studies of this nature are required to assess health risks associated with CNG use.

### **5.1.2.2 Ecosystem Effects**

#### ***5.1.2.2.1 Terrestrial Ecosystem Effects***

The use of CNG fuel will release methane into the atmosphere. Methane is a nontoxic gas that has minimal direct toxicity to plants and animals. Terrestrial effects should be minimal, and at present, no significant research needs exist. If direct and indirect formaldehyde atmospheric concentrations are significant, plant effects research may be justified.

#### ***5.1.2.2.2 Aquatic Ecosystem Effects***

The most likely effects of large scale CNG use may be related to its production (i.e., offshore drilling), but this risk can be assessed, rather than be the subject of research within this Strategy. Any CNG released into aquatic systems will rapidly move to the atmosphere; therefore, such releases of CNG itself are unlikely to produce major problems in these systems.

### **5.1.3 Risk Prevention/Mitigation**

#### **5.1.3.1 Stationary Sources**

If the Global Climate Research Program determines that widespread introduction of CNG into the energy infrastructure aggravates global warming, the adequacy of existing prevention and control technologies and practices for stationary sources will need to be evaluated. Guidance would be needed to develop new or improved control systems, design methods, and operating procedures that would minimize emissions/discharges from the recovery of feedstocks, production, transportation, distribution, and use of CNG. This is especially true for minimizing methane emissions associated with those steps unique to the handling and use of CNG. Accidental release hazards that are specific to stationary source processes and utilization aspects unique to CNG would need to be evaluated. Also, user-oriented accidental-release reference manuals/guidelines for prevention of accidental releases of CNG from storage, production, transportation, and marketing would need to be developed.

#### **5.1.3.2 Mobile Sources**

Motor vehicle risk reduction programs will focus on the long-term durability of production emission control technology for limiting the emissions of compounds associated with CNG that are considered detrimental to the environment.

## **5.2 BACKGROUND AND RATIONALE**

### **5.2.1 Exposure Assessment**

#### **5.2.1.1 Source Characterization**

##### ***5.2.1.1.1 Stationary Source Characterization***

***Production.*** The United States consumes about 20 trillion cubic feet of natural gas per year; about 4 trillion cubic feet of natural gas is imported from Canada and Mexico.

***Feedstocks.*** Natural gas (methane) is produced from on-shore and off-shore wells. With the passage of the 1978 Natural Gas Policy Act and the foreign oil price increases that

1 stimulated gas production, supplies began to increase. Natural gas is present in, and  
2 recovered from, petroleum crudes and, to a more limited extent, from coal seams.  
3 Degradation of biomass also produces methane. In several locations, methane is recovered  
4 from municipal landfill sites. Methane also can be produced from coal; for example, the  
5 Great Plains Coal Gasification Plant in North Dakota produces 150 million cubic feet of  
6 methane per day (The Washington Post, Feb. 18, 1990).

7  
8 ***Processes.*** Natural gas processing involves removal of the gas from the well,  
9 separation of gas oils, and removal of acid gases. Manufacturing from coal would involve  
10 catalyzed reaction of synthesis gas (CO and hydrogen) into methane. This mechanism was  
11 discussed in Chapter 3 (Figure 3-2). Petroleum liquids can be cracked to produce methane,  
12 or the synthesis-gas route can be used. Oil shale produces a crude oil that could be used as a  
13 feedstock to petroleum refineries.

14 The primary concerns are the sources and levels of emissions and discharges that will  
15 result at all stages of processing, from the extraction of feedstocks through the refining and  
16 production of the fuels and the storage, transfer, and distribution of natural gas. Broadened  
17 distribution of natural gas is likely to result in increased opportunities for leakage or release  
18 of methane.

19 Methane is a key global climate gas. Fugitive emissions/leaks and releases have not  
20 been estimated with any reasonable degree of certainty. Extraction of natural gas and  
21 degradation of biomass materials results in substantial methane releases (waste gases, leaks,  
22 etc.). The extraction of coal is also a source of methane release.

23 Organic emissions from coal-based synthesis would be similar to coal-based alcohol  
24 production and would be dependent on the type of coal-conversion system utilized. Air  
25 toxics would follow the trend of organics.

26 Carbon monoxide and CO<sub>2</sub> emissions will result primarily from the combustion of fuel  
27 for power and steam and from the processes for the production of other feedstocks. Because  
28 CO is a primary reactant, high efficiencies of operations would result in very low emissions.  
29 The synthesis of methane from coal or other fossil-fuel feedstocks would increase RITG

CO<sub>2</sub> emissions significantly, unless economically feasible recovery/use of this CO<sub>2</sub> could be developed.

Nitrogen oxides are related to combustion activities of boilers/heaters and incinerators. These sources have been fairly well documented (U.S. Environmental Protection Agency, 1990g).

**Discharges.** Discharges to water would be minimal, but drilling new wells would involve effluents from the drilling muds. Discharges from coal- or petroleum-based processes would be similar to those from coal conversion or petroleum refining (Ghassemi et al., 1978).

**Accidental Releases.** Due to methane's flammability and its gaseous state, the possibility of an accidental release is a concern. Leakage of CNG in a confined space (e.g., private garage) can pose an explosion hazard, but unconfined leaks will disperse quickly to a concentration below the lower flammability limit. Large releases of methane, however, can result in large explosions and fires. Methane requires a higher concentration in air than gasoline to burn or detonate (5.3% vs. 1% to burn; 6.3% vs. 1.1% to detonate). If transported as liquified natural gas (LNG), safety concerns include receiving terminals and storage facilities (DeLuchi et al., 1988). The option to distribute domestic natural gas via pipeline with liquification and storage at local service stations also exists. The initial research would focus on the natural gas storage/distribution and compression systems and on consumer safety.

#### **5.2.1.1.2 Mobile Source Characterization**

Natural gas is an attractive fuel that is well suited for use in spark ignition engines. The inherent advantages of natural gas relative to gasoline are high octane, broader flammability limits permitting leaner air-fuel ratios, and generally lower NMHC and CO emissions (DeLuchi et al., 1988). Being a gas at normal ambient temperatures, natural gas does not present cold-start problems, as is the case with methanol- and ethanol-fuel vehicles (DeLuchi et al., 1988; Alson et al., 1989). An inherent disadvantage of this fuel relative to

1 gasoline is less power. The gas displaces more air than gasoline, thereby reducing the  
2 amount of charge available for burning. This disadvantage can be mitigated by using  
3 turbochargers or superchargers, increasing compression ratios, and adjusting spark timing.  
4 Natural gas also has less volumetric energy density, about 20% that of gasoline (when stored  
5 as CNG), thereby limiting driving range. Because CNG cannot be stored in the same tank  
6 with liquid fuels such as gasoline, transition or dual-fueled vehicles require two fuel tanks.  
7 Dual-fueled CNG-gasoline vehicles cannot be designed to take complete advantage of CNG  
8 fuel characteristics and, therefore, suffer performance penalties when operated on CNG.  
9 Dedicated CNG vehicles have been designed for stoichiometric and lean-burn combustion.  
10 The EPA's Office of Mobile Sources is preparing a rulemaking for regulation of emissions  
11 from vehicles using CNG fuel. The permitted emission rates will be the same as with  
12 gasoline fuels, with the possible exception of THC. Current-technology CNG vehicles have  
13 difficulty limiting the emissions to 0.41 g/mi due to the fuel being dominated by methane, a  
14 hydrocarbon that resists catalytic oxidation.

15 Nonmethane hydrocarbon emissions are reduced with CNG vehicles relative to gasoline  
16 vehicles, due in part to the nature of the fuel (generally greater than 90% methane) and in  
17 part to elimination of evaporative categories of emissions. The composition of the NMHC  
18 emissions will depend upon the characteristics of the fuel. Table 5-1 provides an example of  
19 fuel and emissions characteristics reported by the California Air Resources Board (1989).  
20 These data were developed with a dual-fuel CNG-gasoline vehicle operated on commercially  
21 available natural gas. Carbon monoxide emissions from light-duty vehicles can be reduced  
22 with CNG fuel by a factor of two or more (DeLuchi et al., 1988; Alson et al., 1989).

23 Generally, dual-fuel vehicles emit less NO<sub>x</sub> when using CNG because of lower flame  
24 temperatures (2,148 K for methane; 2,470 K for gasoline), but exceptions of increased  
25 emission rates by as much as a factor of two have been reported (DeLuchi et al., 1988;  
26 Alson et al., 1989). With dedicated CNG vehicles, NO<sub>x</sub> emissions can be elevated relative  
27 to gasoline because of higher compression ratios, advanced spark timing, and leaner  
28 combustion (eliminating the possibility for three-way catalysts).

29 The cetane characteristics of CNG prevent its use as a fuel in conventional compression  
30 ignition diesel engines; however, Otto-cycle spark-ignition CNG engines have been

**TABLE 5-1. COMPRESSED NATURAL GAS FUEL AND ASSOCIATED TAILPIPE EMISSIONS, DUAL-FUEL MOTOR VEHICLE**

| Component         | Fuel<br>Mole % | Tailpipe<br>Emissions<br>wt% <sup>a</sup> |
|-------------------|----------------|---|
| Methane           | 92.8           | 90.5                                      |
| Ethane            | 4.0            | 6.8                                       |
| Propane           | 0.82           | 0.8                                       |
| Isobutane         | 0.07           | 0.02                                      |
| <i>n</i> -Butane  | 0.08           | 0.05                                      |
| Isopentane        | 0.02           | 0.1                                       |
| <i>n</i> -Pentane | 0.02           | 0.07                                      |
| Ethylene          | --             | 0.16                                      |
| Propylene         | --             | 0.25                                      |
| Benzene           | --             | 0.09                                      |
| Toluene           | --             | 0.05                                      |
| Formaldehyde      | --             | 0.22                                      |

<sup>a</sup>Total organic emission rate is 1.99 g/mi.

Source: California Air Resources Board (1989).

1 developed for heavy-duty truck and bus applications. About 1,500 heavy-duty vehicles are  
2 currently being operated on CNG (43% dump trucks and pick-up trucks, 18% school buses),  
3 and plans are being developed for expanded use of this fuel during the next decade. A given  
4 volume of natural gas at 3,000 psi contains only about one-fifth the energy of the same  
5 volume of diesel fuel. On an energy equivalent basis, steel cylinders filled with CNG weigh  
6 about five times more than diesel or gasoline tanks and fuel. These observations are  
7 important to vehicle weight and fuel economy, although lighter weight composite CNG tanks  
8 are being developed. As with light-duty applications, heavy-duty applications involve both  
9 dual-fuel and dedicated (stoichiometric and lean-burn) configurations. The impact of CNG  
10 on heavy-duty vehicle emissions is similar to that described for light-duty vehicle emissions.

1 With heavy-duty vehicles, contrasts with diesels are of interest; NO<sub>x</sub> and particulate  
2 emissions are greatly reduced with stoichiometric heavy-duty CNG engines using catalysts,  
3 CO emissions are elevated, and NMHC emissions are reduced.

4 Most of the emissions data that exist for CNG vehicles are for older technology designs  
5 that are no longer relevant. Scant information is available on CNG engines designed to  
6 comply with post-1981 emission standards; information on advanced-technology CNG  
7 vehicles is practically nonexistent. To assess the impact of this technology on air quality,  
8 expanded efforts to characterize emissions as a function of varied driving scenarios must be  
9 undertaken. Available data suggest that CO and NMHC emissions are greatly reduced with  
10 CNG relative to gasoline and that NO<sub>x</sub> emissions are generally, but not always, elevated  
11 (U.S. Environmental Protection Agency, 1988, 1990c; Alson et al., 1989). Data on  
12 unregulated emissions and non-FTP driving conditions are very sparse. From the standpoint  
13 of RITGs, CNG presents the possibility for substantially increased emissions of methane;  
14 CO<sub>2</sub> emissions are projected to be reduced relative to gasoline technologies and elevated  
15 relative to diesel technologies.

## 17 **5.2.1.2 Environmental Fate**

### 18 **5.2.1.2.1 Air Fate**

19 Methane does not contribute significantly to the production of urban O<sub>3</sub>. Modeling  
20 studies have shown that geophysical levels of methane (about 1.6 ppm) can produce only low  
21 levels (5 to 10 ppb) of O<sub>3</sub> when NO<sub>x</sub> is at low ppb levels. When NO<sub>x</sub> levels are very low  
22 (mostly over oceans), methane can act as a sink for O<sub>3</sub>. When methane is used as a motor  
23 fuel, the air quality in urban areas should improve, although some O<sub>3</sub> will still be produced  
24 because exhaust gases will contain higher molecular weight compounds that are more  
25 reactive. This occurs through the high-temperature combustion process of the engine.  
26 Methane fractionates into free radicals that combine to form higher molecular weight  
27 compounds, including carbonyls. Methane is removed from the troposphere largely through  
28 its reaction with OH radicals. The reaction products of methane and OH will react with  
29 trace concentrations of NO<sub>x</sub> to form formaldehyde.

1       The lifetime of methane in the troposphere is about 8 years. Because its lifetime is  
2 quite long, it will contribute to global warming. Also, as stated above, depending upon the  
3 NO<sub>x</sub> present, methane may produce O<sub>3</sub>, which is an RITG. This, combined with the  
4 possibility that large releases of methane may affect the OH levels (Crutzen, 1987), implies  
5 that the lifetimes of many pollutants that are normally removed from the atmosphere through  
6 their reactions with OH radicals will increase and may exacerbate global warming.

#### 8       ***5.2.1.2.2 Soil, Groundwater, and Surface Water Fate***

9       Compressed natural gas should vaporize rapidly after accidental or fugitive releases and  
10 not pose a significant fate, transport, or exposure threat to soil or water pathways.

#### 12       **5.2.1.3 Exposures**

##### 13       ***5.2.1.3.1 Human Exposures***

14       The impact of changing to CNG-fuel vehicles on human exposure can be estimated after  
15 better emissions data become available. As for all mobile source-generated pollutants,  
16 studies of the important microenvironments, activity patterns, and populations exposed will  
17 be required if significant emissions, especially of unregulated pollutants, are observed.  
18 If formaldehyde becomes a significant atmospheric transformation product, future studies to  
19 determine the extent to which the public health risk will change with CNG-fuel vehicles may  
20 be required. Confined high-level releases could pose significant risk, because methane is an  
21 asphyxiant.

##### 23       ***5.2.1.3.2 Biota Exposures***

24       Compressed natural gas exposure to biota is expected to be minimal in the soil/water  
25 pathway. Atmospheric exposures to terrestrial biota should not be of concern.

#### 27       **5.2.1.4 Analytical Methodology**

28       A wide range of analytical procedures are required to facilitate examination of the  
29 impact of changes in motor fuels on risk to health and welfare. The procedures can  
30 generally be categorized according to procedures for characterizing source emissions,



1 procedures for monitoring the transport and transformation of the emissions in ambient air,  
2 and procedures for monitoring human and ecosystem exposure.

3 Procedures both for certification of regulated emissions and for comprehensive  
4 characterization of unregulated emissions are required for sources. Although rules for  
5 certification of emissions from vehicles using CNG fuel have not yet been promulgated, the  
6 primary concerns with analytical methodology will be the adequacy (accuracy and precision)  
7 of classical procedures for measurement of pollutant (THC, NMHC, CO, NO<sub>x</sub>, and  
8 particulate) concentrations at levels dictated by reduced emission standards of the CAAAs.  
9 All currently defined procedures will require evaluation.

10 Organic emissions certification will be complicated by methane's dominance of the  
11 composition. With organic emission standards requiring measurement of NMHC  
12 (a departure from current THC standards), analytical methodology will be required to  
13 determine methane, permitting calculation of NMHC by subtraction from THC, and/or to  
14 measure NMHC directly. The latter will probably be required with CNG fuels because of  
15 uncertainties associated with using a small difference in two large numbers (NMHC =  
16 THC - methane). Procedures for direct measurement of methane exist for motor vehicle  
17 emissions (Hoffman et al., 1987; Burch and Pembroke, 1973; Probst and Reschke, 1977;  
18 Society of Automotive Engineers, 1976), but procedures for direct measurement of NMHC  
19 emissions will require development.

20 Efforts to assess the impact of motor vehicles on O<sub>3</sub> and toxics air quality require  
21 detailed speciation of emissions. Historically, chromatography, infrared spectroscopy, and  
22 mass spectroscopy have been popular choices of methods for this purpose. The problems  
23 with CNG will be somewhat simplified because this fuel composition is typically much less  
24 complex compared to conventional fuels. Continuous or "real-time" analysis that provides  
25 information necessary to isolate driving conditions most responsible for emissions of interest  
26 will also be required. Efforts to develop such methods have been initiated for many toxics of  
27 interest and will continue as fuel formulations and compounds of interest change (Butler  
28 et al., 1985; Staab et al., 1985; Von Carlowitz et al., 1990; Heller et al., 1990).

29 Analytical procedures employed with other fuels can also be employed for the analyses  
30 of transformation products arising from the use of CNG. The principal products expected

are formaldehyde, CO, and unburned methane. All of these can be monitored with ease, and no further analytical development work is needed.

Improvements to NO<sub>2</sub> monitors for indoor monitoring to account for potential interferences due to nitric and nitrous acids will be required. Ambient methodology should be adequate to measure any changes resulting from emissions from vehicles fueled by CNG. New methods may be required for measuring emissions of impurities in the CNG, such as arsenic, if they cannot be filtered out of the fuel supply before combustion.

## **5.2.2 Effects Assessment**

### **5.2.2.1 Human Health Effects**

Methane is odorless (or has a mild sweet odor at more than 200 ppm) and tasteless. Methane has no Threshold Limit Value; it is classified as an asphyxiant that can be tolerated at high levels, to the point at which oxygen is displaced and not sufficiently available for breathing (i.e., the oxygen level is less than 8%). Methane appears to be absorbed and readily metabolized by mammals. In some cases, inhaling very high levels (thousands of ppm) can sensitize the heart, causing fibrillation (Reinhardt et al., 1971). When inhaled, most methane is exhaled unchanged. One study that exposed pregnant mice to 5 to 8% (50,000 to 80,000 ppm) natural gas for 1 h on Day 8 of gestation resulted in brain abnormalities in the fetuses (Shepard, 1989).

### **5.2.2.2 Ecosystem Effects**

Methane is the primary constituent of CNG and represents the primary terrestrial ecological concern. Although formaldehyde is expected to be produced as an atmospheric transformation product, the potential ecological effects of formaldehyde were discussed in Chapter 3. Comparisons with conventional gasoline and diesel fuel combustion products (e.g., CO, CO<sub>2</sub>, lead, NO<sub>x</sub>, volatile hydrocarbons, and particulate matter) and transformation products (e.g., O<sub>3</sub> and PAN) will be made in the CNG ecosystem effects assessment to evaluate which fuel may pose the greatest hazard.

A review of several literature data bases produced one reference that showed that rice seedlings were not affected by methane at 1- or 100-ppm concentrations (Ku et al., 1970).

1 The primary effect on animals is through asphyxiation, as noted in the Health Effects  
2 Section 5.2.2.1. Because methane will rapidly move to the atmosphere, it is unlikely to  
3 cause any problems for aquatic ecosystems.  
4

### 5 **5.2.3 Global Warming**

6 Methane is a trace gas 10 to 30 times more radiatively efficient than CO<sub>2</sub> (Houghton  
7 and Woodwell, 1989). Considering atmospheric lifetime as an equal mass basis, methane  
8 produces about 10 times the climate effect of CO<sub>2</sub>. The extensive use of CNG may increase  
9 the atmospheric load of methane, resulting in an enhanced greenhouse effect. Atmospheric  
10 models developed and applied under the ORD Global Climate Program will be used to  
11 predict the impact of methane from CNG combustion on global warming.  
12

### 13 **5.2.4 Risk Prevention/Mitigation Technologies**

#### 14 **5.2.4.1 Stationary Sources**

15 Prevention and control techniques for many of the emission and discharge sources from  
16 recovery, storage, and transportation of natural gas are available. The effectiveness of their  
17 application to areas like venting and flaring is a substantial question, however. Aging  
18 distribution systems need attention in regard to prevention and control techniques. Coal mine  
19 methane recovery and landfill gas recovery can have a positive effect, if these resources can  
20 displace conventional natural gas recovery. Although the controls for natural gas will be  
21 applicable to synthesis methane from coal, coal gasification plants have many unsolved  
22 problems. The present gasification plants all experienced problems with various control  
23 systems. Control application to water discharges could be a problem and needs specific  
24 attention. Guidelines will be needed for safe consumer handling of this fuel.  
25

#### 26 **5.2.4.2 Mobile Sources**

27 Durability of vehicle emission-control technology should be monitored as mileage  
28 accumulates. With CNG, this process would be somewhat simplified because evaporative  
29 emissions are not considered a concern (the vehicle fuel-introduction system is closed  
30 because this fuel is a compressed gas).

### 5.3 RESEARCH NEEDS

Compared to previous discussions of methanol and ethanol, CNG presents a more dramatically variant option to petroleum-distillate fuels. This fuel, being a compressed gas, would require greater divergence from classical fuel-distribution practices. The worldwide abundance of natural gas and its characteristics as a motor vehicle fuel, however, suggest that CNG should be given serious consideration as a replacement for petroleum-distillate fuels. Because CNG is composed primarily of methane, a photochemically nonreactive compound, it offers large potential O<sub>3</sub> air quality benefits; however, as an RITG, increased emissions of methane could be detrimental to efforts to control global warming. Transition to a compressed-gas fuel would also offer experience that would be invaluable when considering the future use of noncarbon compressed-gas fuels such as hydrogen.

In this section, broad research objectives for each key element of risk assessment are described and priorities are assigned. The priorities across all fuels were considered with the understanding that future knowledge, technology changes, and market factors are likely to have some impact on them. One major difficulty in developing a prioritization scheme is that some research needs are contingent on others. For example, in many cases, dose-response information is a higher priority than hazard-identification information, but hazard-identification research must proceed first to guide the dose-response work. Due to the extent of the uncertainties about fuels, the approach chosen for prioritization would, in this example, rank hazard-identification research higher than dose-response research. Each research objective is coded with one of the following prioritization phrases.

- Priority 1 for the next 2 to 4 years. This is the highest priority research over the near term. The research generally entails resolution of major issues of known concern, identification of new issues likely to be critical to risk assessment/risk reduction, crucial methods development that paces much other work, and major mandates of the CAAAs. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.
- Priority 2 for the next 2 to 4 years. This is medium priority research over the near term. Work in this category generally entails pursuing key issues that have importance for either the exposure or effects phase of hazard identification or for evaluating key elements of risk reduction. Gaining

such information will certainly be important, but is less crucial than work under Priority 1. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.

- Priority 3 for the next 2 to 4 years. Although this research is of lower priority relative to other categories, it is still critical to development of comprehensive baseline information for all fuels. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished in that time frame.
- Longer term priority. This research is essential to developing comprehensive, quantitative risk assessments and/or risk reduction approaches. However, its initiation is paced by the completion of earlier research. When major elements of the earlier research are completed, it will be possible to more definitively prioritize this category of work.

### **5.3.1 Exposure Assessment**

#### **5.3.1.1 Source Characterization**

##### ***5.3.1.1.1 Stationary Source Characterization***

The production aspects of natural gas (methane) are covered in the section on methanol. The specific aspects for CNG that require further discussion are those related to distribution and use of this high-pressure alternative fuel. Because of compressed-gas safety concerns, attention must be given to factors related to accidental release. Also, because of methane's role as a greenhouse gas, extra attention must be placed on the potential for increased releases.

Research Objectives:

1. Develop emission factors and energy efficiency data for the natural gas handling steps unique to CNG. (Priority 1 for the next 2 to 4 years.)
2. Perform a catastrophic-release hazard assessment for CNG to identify specific areas of concern that may need prevention-oriented risk-reduction work. (Priority 1 for the next 2 to 4 years.)

3. Assess overall energy efficiency for stationary source applications. (Priority 2 for the next 2 to 4 years.)

The emissions problem addressed by the research must include continuous/routine emissions, short-term releases, and catastrophic-scale releases.

#### ***5.3.1.1.2 Mobile Source Characterization***

Although emphasis on CNG as a transportation fuel has been relatively limited in the United States, interest is expected to grow in future years, and vehicles designed to comply with current U.S. emission standards are expected to be available for evaluation. Both dual-fueled (gasoline-CNG) transition vehicles and dedicated CNG vehicles are likely to become available for light- and heavy-duty applications. The emissions characteristics of the varied designs will be different and will require examination to assess their potential impact on risk to public health and welfare. The structure of these studies will be similar to that described for methanol fuels. Experimental variables will include appropriate vehicles, fuels, and varied operating conditions. Tailpipe, evaporative, and refueling emissions will be characterized to permit evaluation of the potential impact of this technology on urban air quality (i.e., O<sub>3</sub>, CO, NO<sub>2</sub>, and particles) as well as on other environmental factors such as global climate change and toxic emissions exposure.

#### **Research Objective:**

1. Characterize (composition and rates, g/mi) emissions from motor vehicles fueled with CNG as a function of speed, ambient temperature, altitude, fuel composition, and age/mileage accumulation. Both light-duty and heavy-duty vehicles should be examined. (Priority 1 for the next 2 to 4 years.)

### 5.3.1.2 Environmental Fate

#### 5.3.1.2.1 Air Fate

Photooxidation reactions of methane with NO<sub>x</sub> are extremely slow; however, exhaust from vehicles powered with natural gas will contain some reactive hydrocarbons and carbonyls. Some measure of the reactivity of the exhaust gases should be made and is currently possible with the use of a smog chamber coupled to a dynamometer. Also, some modeling of urban-type and regional-type conditions is recommended. Because the lifetime of methane is so long, a concern is that increased emissions will contribute to global warming. This characteristic of methane will have a role in background O<sub>3</sub> formation if the global NO<sub>x</sub> levels are sufficiently large. An increase in background O<sub>3</sub> will contribute to global warming because it is an RITG. Regional transport models and global chemistry models must be used to establish the role of methane in both O<sub>3</sub> formation and global warming.

#### Research Objectives:

1. Characterize products from the photooxidation of motor vehicles fueled with CNG. (Priority 3 for the next 2 to 4 years.)
2. Use airshed and regional models to determine the effect of CNG usage on air quality. (Priority 3 for the next 2 to 4 years.)
3. Provide input to the Global Climate Program on the role of increased methane emissions in global warming. (Priority 3 for the next 2 to 4 years.)

#### 5.3.1.2.2 Soil, Groundwater, and Surface Water Fate

No research in this area is anticipated.

### 5.3.1.3 Exposures

#### 5.3.1.3.1 *Human Exposures*

The exposure research plan for CNG will include studies similar to those described for methanol. Studies of the important mobile source-impacted microenvironments, activity patterns, and populations exposed will be required only if significant emissions, especially of unregulated pollutants such as formaldehyde, are observed.

#### Research Objectives:

1. Exposure assessment of the identified pollutants related to use of CNG, including methane and formaldehyde. (Priority 3 for the next 2 to 4 years.)
2. Development and application of validated human exposure models to predict changes in exposure resulting from use of CNG. (Longer term priority.)

#### 5.3.1.3.2 *Biota Exposures*

No research in this area is anticipated.

### 5.3.1.4 Analytical Methodology

Analytical methods will be developed, upgraded, and/or evaluated for measurement of source emissions, atmospheric transport and transformation, and population (human and ecosystem) exposure as necessary to support assessment of the impact of varied fuel formulations on risk to public health and welfare. Procedures suitable for certification of regulated source emissions (THC, NMHC, CO, NO<sub>x</sub>, and particles) at levels mandated by the amended Clean Air Act and for the detailed speciation necessary to support estimation of impact on O<sub>3</sub> and toxics air quality will be required. The procedures must permit accurate and precise determination of large numbers of compounds in very complex mixtures.

Analytical procedures employed with either fuel can also be employed for the analyses of photooxidation and combustion products arising from CNG. Unburned methane, formaldehyde, CO, possibly formic acid, and some ethane and higher molecular weight



organics present as impurities along with their oxidation products can be expected from CNG consumption. All of these could probably be measured with existing methodologies; however, this should be tested.

Improvements to NO<sub>2</sub> monitors for indoor monitoring to account for potential interferences due to nitric and nitrous acids will be required. Ambient methodology should be adequate to measure any changes resulting from emissions from vehicles fueled by CNG, such as arsenic, if they cannot be filtered out of the fuel supply before combustion.

#### Research Objectives:

1. Develop/upgrade/qualify analytical procedures for speciation of O<sub>3</sub> precursor and toxic motor vehicle emissions. (Priority 1 for the next 2 to 4 years.)
2. Validate classical procedures for measurement of organic carbon, CO, NO<sub>x</sub>, and CO<sub>2</sub> emissions from CNG-fueled motor vehicles at certification emission rates (concentrations) permitted by the CAAAs; identify problems, provide corrective actions, and/or develop new, more simplistic, lower cost acceptable procedures. Emphasis will be placed on direct measurement of NMHC. (Priority 1 for the next 2 to 4 years.)
3. Develop procedures for continuous or "real-time" measurement of selected toxics in transient motor vehicle emissions. (Priority 3 for the next 2 to 4 years.)
4. Develop methodology for direct measurement of personal exposure to NO<sub>2</sub> at background levels (1 to 10 ppb). (Priority 3 for the next 2 to 4 years.)
5. Develop methodology for direct measurement of personal exposure to NO<sub>2</sub>. Develop microenvironmental monitors for use indoors free of nitric and nitrous acids and interferences. (Priority 3 for the next 2 to 4 years.)

6. Upgrade/evaluate analytical procedures for measuring of ambient-air concentrations of compounds potentially associated with the use of CNG fuels (formaldehyde, ethane, propane, formic acid, acetaldehyde, and other higher molecular weight compounds). (Priority 3 for the next 2 to 4 years.)

### **5.3.2 Effects Assessment**

#### **5.3.2.1 Human Health Effects**

Based on an evaluation of the health effects and chemical characterization data available for CNG, this fuel is assumed to pose a significantly lower potential for effects than other fuels of interest. Based on the relatively greater completeness of CNG combustion (compared to other fuels), the health risks posed by combustion and transformation products also are assumed to be lower relative to other fuels. Some research is necessary to validate these assumptions. Short-duration in vitro and in vivo screening studies of mutagenicity and respiratory toxicity of both CNG itself and the transformation and combustion products are proposed. If these studies (or emissions characterization or atmospheric chemistry studies) suggest the potential for carcinogenicity or toxicity, more detailed assessment should be conducted. Due to the projected early market penetration of CNG, these efforts have a moderate research priority in this Strategy, even though significant health effects are not anticipated. In the long-term, if CNG appears likely to have a significant market share, then a chronic inhalation bioassay of CNG, assessing both cancer and noncancer endpoints, may be prudent even if limited or no health effects are expected.

#### **Research Objective:**

1. Compare the mutagenicity and potential respiratory toxicity of CNG, and the combustion and atmospheric transformation products of CNG, to the mutagenicity and toxicity of conventional and other alternative fuels by using short-term in vitro and in vivo assays. Determine the need for additional evaluations, potentially including chronic bioassays, based on the results of these short-term tests and

improved estimates for emissions, exposure and market penetration. (Priority 2 for the next 2 to 4 years.)

#### **5.3.2.2 Ecosystem Effects**

Use of CNG as an alternative fuel will release methane into the atmosphere. Though methane is a nontoxic gas that has minimal direct toxicity to plants and animals, at high concentrations and in confined areas, it can induce animal asphyxiation. The environmental concern is that methane is a trace gas 20 times more radiatively efficient than CO<sub>2</sub>. Thus, an increase in the atmospheric load of methane could enhance the greenhouse effect and thereby affect ecosystems. However, because CNG does not currently pose a risk to terrestrial ecosystems, no research is proposed at this time.

Aquatic impacts attendant to accidental release are likely to be relatively unimportant compared to the explosive/reactive potential and off-site migration that result in human risk. The water immiscibility and extreme volatility of CNG will result in an aquatic exposure that is much more limited than that for all other fuels and exposure scenarios.

Because CNG compounds will rapidly move to the atmosphere, they are unlikely to cause any problems for the marine environment, and therefore, no research program is proposed for CNG relative to this ecosystem.

#### **5.3.3 Global Warming**

The research described on source characterization, environmental fate in ambient air, and risk reduction/control technologies will result in identification of changes in RITGs arising from the manufacture and combustion of various alternative fuels and will not be repeated here. Primary concerns relate to increased leakage of methane.

##### **Research Objective:**

1. Identify and characterize RITGs, especially methane, affected by CNG fuel production and use. This information will be used as input to global climate

models being developed and applied under the Global Climate Research Program.  
(Priority 2 for the next 2 to 4 years.)

### **5.3.4 Risk Prevention/Mitigation**

#### **5.3.4.1 Stationary Sources**

The important prevention and control areas to be addressed for CNG include methane emissions and hazards associated with the handling and use of CNG.

Research Objectives:

1. Provide guidance for minimizing methane emissions associated with those steps unique to the handling and use of CNG. (Priority 1 for the next 2 to 4 years.)
2. Provide guidance on accidental-release hazards that are specific to those stationary source processes and utilization aspects unique to CNG. (Priority 1 for the next 2 to 4 years.)

#### **5.3.4.2 Mobile Sources**

The performance of motor vehicle emission control systems as a function of consumer mileage accumulation needs to be evaluated. Emphasis should be given to methane, to emissions of importance to global climate change, and to others projected to be improved by this technology (e.g., O<sub>3</sub> precursors and particles).

Research Objective:

1. Evaluate changes in motor vehicle emissions with consumer mileage accumulation.  
(Priority 2 for the next 2 to 4 years.)

## 6.0 REFORMULATED GASOLINES

### 6.1 RISK ASSESSMENT RESEARCH FRAMEWORK

In addition to previously discussed replacements for petroleum-distillate fuels, reformulations of gasoline fuels have been proposed to reduce emissions (Keebler, 1989). These fuels, with advanced gasoline motor vehicle emissions control systems, may challenge the air quality benefits of previously discussed alternatives. The automobile and petroleum industries have undertaken cooperative efforts to identify optimum gasoline formulations for positive environmental impact and satisfactory vehicle performance. The following discussion emphasizes the impact of gasoline reformulation on emissions, atmospheric chemistry, exposure, health/ecosystem effects, and risk reduction/control, and identifies associated research needs.

A variety of reformulations of petroleum-based fuels are being examined by the motor vehicle and petroleum industries for potential to reduce the environmental hazards of associated emissions. The impact of changes in several fuel specifications is being evaluated with conventional gasoline. Consideration is being given to increased levels of octane-enhancing oxygenated organic compounds, such as ethanol and methyl- and ethyl-tertiary-butyl ethers (MTBE and ETBE, respectively), to reduced levels of aromatic (including benzene) and olefinic hydrocarbons, to reduced sulfur, and to reduced volatility. With diesel distillate, consideration is being given to reduced sulfur and aromatic hydrocarbon levels and to changes in fuel cetane number. Potential benefits to air quality levels of ozone (O<sub>3</sub>), carbon monoxide (CO), particulate matter (PM), and other toxics (e.g., benzene, formaldehyde, 1,3-butadiene, and gasoline vapors) are being considered. The EPA currently permits blending ethanol 10% by volume with gasoline, MTBE 15% by volume, and ETBE 13% by volume, corresponding to 3.7%, 2.7%, and 2.0% fuel oxygen by weight, respectively.

Waiver requests for a number of methanol-cosolvent blends have also been granted but have not gained significant market penetration, (e.g., 4.75% [by volume] methanol and

4.75% [by volume] gasoline grade tertiary butyl alcohol [ARCO], and 5% [by volume] methanol with 2.5% co-solvent alcohols having carbon number 1 of 4 or less [DuPont]). Also, the "substantially similar" rules permit aliphatic alcohols and ethers to be blended with gasoline, provided the oxygen content does not exceed 2.7% by weight.

This chapter first highlights some key points of information and issues about reformulated fuels in a risk assessment research format. This initial section uses Section 1.4, Introduction to Risk Assessment Framework for Fuels, as its point of departure, but it focuses only on those facets of the generic framework that are specific to reformulated fuels. The next section (Section 6.2) is intended to provide a background and rationale for the research. It is not intended to be a complete review of the literature. The last section (Section 6.3) describes research needed to provide the foundation for a quantitative risk assessment of these fuels.

## **6.1.1 Exposure Assessment**

### **6.1.1.1 Source Characterization**

#### ***6.1.1.1.1 Emissions from Feedstock and Fuel Production, Storage, and Distribution***

**Feedstocks.** Feedstock-related emissions and discharges would include those from recovery of petroleum crudes, natural gas (methanol and MTBE manufacture), and corn-based ethanol (direct use and ETBE manufacture). Each of these feedstocks has been discussed previously. Emissions of concern would be volatile organic compounds (VOCs) and radiatively important trace gases (RITGs) (especially methane and carbon dioxide [CO<sub>2</sub>]). Discharges of interest would be alcohols, ethers, and petroleum-related compounds.

Emissions and discharges from the recovery of crude oils and natural gas have been identified in a limited manner, but better quantification for the variety of crudes is needed. The greatest danger is accidental release, the loss of containment at the well head. Operational energy requirements will result in additional emissions of nonmethane RITGs. Development of an accurate carbon dioxide (CO<sub>2</sub>) budget for ethanol from biomass would be critical in this evaluation. Evaluation of the overall net change in RITGs, VOCs, and other stationary source multimedia emissions/discharges resulting from one or more key scenarios of market penetration by reformulated fuels is needed.

1       **Production.** The emissions and discharges from the production of methanol, ethanol,  
2 and conventional fuels have been discussed previously and will be dependent upon the  
3 crudes, blending agent, and processes used. Methyl-tertiary-butyl ether is produced from  
4 methanol and isobutylene (from petroleum refining). Ethyl-tertiary-butyl ether production is  
5 similar, using ethanol and isobutylene. Both can be produced either at a refinery or at a  
6 separate facility. Information on the quality and quantities of emissions and discharges from  
7 the manufacture of MTBE and ETBE is lacking. The changes in emissions/discharges and  
8 control effectiveness at the refinery that are brought about by modification of the  
9 conventional fuels to make reformulated fuels must be determined. A further issue is using  
10 the low boiling fractions and aromatic fractions removed from the base gasoline in a way that  
11 would minimize impacts on O<sub>3</sub> nonattainment and global warming. Effects on equipment  
12 and potential releases of methanol-base reformulated fuels need to be evaluated. Emissions  
13 of concern are VOCs, RITGs, alcohols, and ethers. Effluents would contain a variety of  
14 organic pollutants and require treatment prior to discharge. Solid waste consists of solids  
15 (coke), spent catalysts, and water treatment sludges.

16  
17       **Storage and Distribution.** Emissions and other releases of VOCs, RITGs, alcohols,  
18 and ethers from the transportation, storage, and distribution of reformulated fuels are major  
19 concerns. A major technical issue to be resolved is the effect of reformulated fuels on VOC  
20 emissions in existing and new fuel handling systems. Such emissions include those  
21 previously discussed for the alcohols and conventional fuels. The major difference is that the  
22 reformulated fuel will have properties that are different from those of other fuels, and the  
23 effect of these properties on releases needs to be understood. For example, volatility and  
24 corrosiveness will be different for a reformulated fuel compared to fuels previously  
25 discussed, and their influence on leakage from underground and aboveground storage tanks is  
26 not known. Very little is known about emissions and releases from MTBE and ETBE  
27 storage and distribution, making this area an appropriate target for research. Effects on  
28 existing equipment and controls and their relationship to potential releases (especially for  
29 methanol-based reformulated fuels) need to be evaluated. The factors potentially causing

1 releases (transient and accidental) must be determined, and the probability for maximum  
2 credible releases must be identified as a function of prevention measures.

#### 3 4 **6.1.1.1.2 Emissions Related to Fuel Use**

5 **Stationary-Source Emissions.** Reformulated fuels could be used in stationary internal  
6 combustion (IC) engines and construction equipment, but they would not likely be used as a  
7 boiler or power generation fuel. Volatile organic compounds from storage and RITGs from  
8 the combustion of reformulated fuels are the dominant emissions. Large-scale accidental  
9 releases from storage at the utilization site are likely to be analogous to similar releases of  
10 conventional fuels, but they are still a concern.

11  
12 **Mobile-Source Emissions.** During recent years, increased emphasis has been given to  
13 the potential environmental benefits of petroleum-based motor fuel reformulations. Octane-  
14 enhancing lead additives are being phased out of gasoline (prohibited by the Clean Air Act  
15 Amendments [CAAAAs] after Dec. 31, 1995), significantly reducing the risk of exposure to  
16 lead; and oxygenated organics such as ethanol and MTBE are being blended with gasoline to  
17 reduce motor vehicle CO emissions, especially during low-temperature winter months.  
18 These oxygenated organics are also octane-enhancing, offering the possibility for changes in  
19 hydrocarbon formulations to smaller fractions of compounds that are octane-enhancing but  
20 also detrimental to the environment (e.g., smaller amounts of aromatic hydrocarbons such as  
21 benzene, toluene, and xylenes), as well as the possibility for less of the low molecular weight  
22 paraffins (e.g., butanes and pentanes), which elevate fuel volatility and associated evaporative  
23 emissions. The presence of oxygen in the fuel will reduce CO emissions during periods of  
24 fuel-rich combustion. Recent-technology vehicles equipped with closed-loop three-way  
25 catalysts experience less of this CO emissions benefit than older-technology vehicles because  
26 they have fewer periods of fuel-rich operation. The potential benefit of fuel reformulation  
27 for O<sub>3</sub> reduction is currently being studied. Reformulations of lower volatility are known to  
28 result in reduced parking and running-loss evaporative emissions, which contribute  
29 significantly to the atmospheric burden of O<sub>3</sub> precursor organics during hot summer months.  
30 Gasoline formulations resulting in emissions with reduced photochemical reactivity (e.g.,



1 lower olefinic fractions) are expected to be developed. Fuel formulations favoring reduced  
2 toxic-compound emissions could also be developed. The 1990 CAAAs require that in  
3 selected O<sub>3</sub> nonattainment areas, gasolines be reformulated to provide a 15% reduction of  
4 O<sub>3</sub>-forming VOCs and toxic component emissions by 1995, and a 25% reduction by 2000  
5 (relative to a 1990 baseline condition). It is not clear what benefit these changes will provide  
6 for O<sub>3</sub> air quality and cancer risk from mobile source toxics. Associated changes in VOC  
7 photochemical reactivity are unclear, and the relative cancer potencies of the varied toxic  
8 compounds are uncertain. Most of the toxic compound emissions reduction from gasoline  
9 reformulation will be with benzene.

10 The automobile and petroleum industries recently initiated a cooperative effort to  
11 investigate a number of gasoline reformulations. The primary emphasis of the program is on  
12 O<sub>3</sub> and toxics air quality impact. The initial program is examining tailpipe, parking, and  
13 running-loss evaporative emissions composition using Federal Emissions Certification driving  
14 simulations (19.6 mph, 70 °F average temperature, 60 to 84 °F diurnal temperature ramp,  
15 95 °F running-loss temperature), with about 20 recent-technology automobiles and 23 fuel  
16 formulations. Fuel formulations are to be varied and include aromatic (20 to 45%), olefinic  
17 (5 to 20%), MTBE (0 to 15%), and T<sub>90</sub> °F (280 to 360 °F) specifications. The fuel  
18 volatility will be maintained at 9 psi RVP. Changes in the formulation of diesel distillates  
19 (e.g., reduced aromatic hydrocarbon and sulfur) and changes in cetane number are also being  
20 examined, with emphasis on heavy-duty engine NO<sub>x</sub> and particulate emissions. Preliminary  
21 results from this program have been published by the Coordinating Research Council, and  
22 suggest that both O<sub>3</sub> and toxic air quality can potentially be improved by gasoline  
23 reformulation. The degree of improvement will depend on the marketplace composition of  
24 reformulated gasoline. The developing regulations require fuel formulations providing  
25 percentage reductions (15% by 1995, 25% by 2000) of aggregate O<sub>3</sub>-forming VOC mass and  
26 aggregate toxic mass. Since the O<sub>3</sub>-forming potential and cancer potency of organic  
27 compounds vary, estimates of benefits will have to await the development of marketplace  
28 gasoline formulations.

29 This data base will need to be expanded to include other ambient temperatures and  
30 average speed driving conditions to provide more complete assessment of potential

1 environmental impact. The initial effort will permit selection of optimum fuel formulations  
2 for a further, more comprehensive study of associated emissions. Air quality benefits for  
3 O<sub>3</sub>, CO, and some air toxics are expected. The reformulations will probably have little  
4 impact on the emission rates of global climate RITGs such as CO<sub>2</sub>, nitrous oxide (N<sub>2</sub>O), and  
5 methane.

#### 6 7 **6.1.1.2 Environmental Fate**

##### 8 **6.1.1.2.1 Air Fate**

9 The chemistry of the exhaust gases from vehicles powered with MTBE and ETBE  
10 reformulated gasolines has not been reported in detail. The exhaust in a smog chamber study  
11 that substituted synthetic methanol in gasoline never resulted in an increase in the  
12 O<sub>3</sub> maximum when compared to the exhaust from conventional fuel (Jeffries et al., 1985).  
13 However, 10% substitution of methanol in gasoline has shown very little O<sub>3</sub> benefit at  
14 modest VOC/nitrogen oxides (NO<sub>x</sub>) ratios (approximately 10/1). At lower VOC/NO<sub>x</sub> ratios,  
15 the methanol substitution showed significant benefit. Similar results can be expected from  
16 ethanol-gasoline mixtures and from MTBE- and ETBE-gasoline mixtures.

17 A recent modeling study by Morris et al. (1989) presents results on the role of ethanol  
18 blends on O<sub>3</sub> formation. The two cities studied were New York and St. Louis. A scenario  
19 with 100% penetration of 10% ethanol showed almost no effect on O<sub>3</sub> for New York.  
20 In St. Louis, a 50% penetration with 10% ethanol showed a slight (approximately 3%)  
21 decrease in maximum O<sub>3</sub>. A 100% penetration of ETBE in St. Louis showed a 4% decrease  
22 in O<sub>3</sub>. Apparently, no effects were observed in New York because of confounding regional  
23 transport of O<sub>3</sub> and its precursors.

24 The primary atmospheric removal process for the ethers is through hydroxyl (OH)  
25 radical reactions. Some preliminary kinetic studies with MTBE/OH reactions show tertiary  
26 butyl formate to be the major product. The chemistry of the ethyl ether should be more  
27 complex, but some preliminary studies have shown that tertiary butyl formate is the principal  
28 product. In the presence of NO<sub>x</sub>, as in auto exhaust, organic nitrate products can be  
29 expected.

1 Reformulated gasolines containing reduced aromatics may have their own peculiarities.  
2 Aromatic VOCs act as sinks for NO<sub>x</sub>. Thus, they remove NO<sub>x</sub> from a photochemical  
3 reactive system. Downwind rural sites are presently NO<sub>x</sub>-poor but VOC-rich.  
4 If reformulated gasolines do not contain aromatics, part of the NO<sub>x</sub> sink is removed and NO<sub>x</sub>  
5 may be transported farther downwind. This could produce more O<sub>3</sub> on the second day or  
6 move the O<sub>3</sub> maximum farther downwind.

7 Monitoring all possible reactants present in auto exhausts and their transformation  
8 products from the many types reformulated gasolines will be a major research task. Risks to  
9 health and ecosystems associated with the use of such fuels cannot be ascertained until basic  
10 kinetic and applied chemistry studies are performed.

#### 11 12 **6.1.1.2.2 Soil and Groundwater Fate**

13 The extent to which releases of reformulated, petroleum-based fuels impact  
14 groundwater quality is determined by the rate at which these hydrocarbon mixtures move  
15 through the subsurface, and by the degree to which they are attenuated during migration.  
16 Because these fuels are complex mixtures of chemicals having a broad range of  
17 physicochemical properties, subsurface transport may occur via several mechanisms. These  
18 include aqueous phase liquid, nonaqueous phase liquid (NAPL), and gaseous phase transport.  
19 The importance of each of these mechanisms in a specific situation will be determined by the  
20 nature of the contaminant source (composition, rate, and duration of the release) and by the  
21 properties of the soil or aquifer. The influence of these transport mechanisms on the  
22 behavior of the fuels and the aqueous-organic-vapor phase dynamics for the immiscible  
23 systems must be understood.

24 Because of the disparity in physicochemical properties, individual components of  
25 reformulated fuels will be chromatographically separated during migration through the soil.  
26 Our current knowledge base permits reasonable predictions of chemical transport in  
27 predominantly aqueous systems; however, much less is known about contaminant transport  
28 and fate in the organic phase. Because important research questions concerning the physics  
29 and chemodynamics of these complex mixtures remain unanswered, current conceptual and

1 mathematical models of contaminant mixing, transport, dissolution, and transformation in  
2 multiphase flow systems are suspect.

3 Both contaminant transport and transformation can be influenced by the chemical  
4 composition of the solution phase in which it resides; therefore, compositional changes  
5 resulting from conventional fuel reformulation could alter groundwater contamination  
6 potential from fuel releases. A quantitative description of these compositionally induced  
7 effects would be limited by our current understanding of the physical, chemical, and  
8 biological processes controlling the activity of these complex mixtures.

#### 9 10 ***6.1.1.2.3 Surface Water Fate***

11 Reformulated gasolines present an array of fate problems for freshwater and estuarine  
12 spill scenarios that are very similar to those of conventional fuels. In the case of  
13 reformulated gasoline, the fuels are a complex mixture of individual compounds within the  
14 base stock to which some individual components have been added. The reformulated mixture  
15 will exhibit multiple fate profiles. Some components will degrade rapidly, whereas others  
16 are much more persistent. Degradation will produce other products that, in turn, display  
17 different fate and effects properties. Reformulated gasolines will separate into multiple  
18 phases in the water column, complicating the transport as well as the fate of each phase.  
19 At least three distinct phases result: the product phase, emulsions formed as the fuel  
20 disperses, and product dissolved in the water. The three phases move at different rates,  
21 interact as concentration and turbulence fields change, and degrade at different rates and by  
22 different mechanisms. Surface slicks form at even very low concentrations, further  
23 complicating the subsequent effects (i.e., effects may be much more subtle than direct  
24 toxicity).

25 Fate processes requiring study include the identification of individual fuel components  
26 and subsequent transformation in water systems. If relatively high amounts of additives or  
27 alternate fuels have been added, the fate of the added products must be determined alone and  
28 in combination with the base gasoline. Biological degradation is especially important, and  
29 oxygen depletion is expected to be a major impact. Related processes of reaeration and  
30 volatilization are also important. Priority research for transport is the formation and

1 movement of emulsions. The total, multiphase transport will require additional study to  
2 establish the expected spatial extent, duration, and volume of spills.

### 3 4 **6.1.1.3 Exposures**

#### 5 ***6.1.1.3.1 Human Exposure Assessment***

6 Characterization of emissions from vehicles operating on reformulated gasolines is  
7 fragmentary, with data needed to estimate emissions for specific emission control systems  
8 and operating conditions. Once these data become available, comparisons with conventional  
9 fuel emissions and methanol and ethanol fuel emissions can be described, which will serve as  
10 input to comparative exposure models. In addition, if significant transformation products  
11 (e.g., acetaldehyde, formaldehyde, and acetone) are likely to result, future exposure studies  
12 to determine the impact of these changes on estimates of public health risk may be required.

#### 13 14 ***6.1.1.3.2 Biota Exposure Assessment***

15 The biota of terrestrial and aquatic ecosystems will potentially be exposed to pollutants  
16 related to reformulated fuels (e.g., methanol, ethanol, formaldehyde, acetaldehyde, acetic  
17 acid, MTBE, ETBE, and O<sub>3</sub>) that are derived from fugitive emissions during fuel  
18 manufacture, transportation, storage, vehicle refueling, fuel combustion, and atmospheric  
19 transformation. Terrestrial and aquatic ecosystems will be exposed to the pollutants through  
20 airborne deposition and accidental spills/leaks from barges, tankers, and storage tanks.  
21 Of all the possible sources, airborne pollutant deposition represents the greatest potential  
22 threat to terrestrial ecosystems, whereas accidental spills/leaks will have the greatest potential  
23 impact on aquatic ecosystems. Such exposures could be acute or chronic, frequent or  
24 infrequent, high level or low level, and local or regional. Scenario modeling efforts will  
25 determine whether significant exposures are likely to occur and pose a threat to terrestrial or  
26 aquatic biota.

27 As explained in the generic fuel risk assessment in Section 1.4.2.2, final exposure  
28 assessments for aquatic ecosystems involve integration of efforts on source characterization  
29 and environmental fate with information on the populations of organisms at risk to produce  
30 appropriate exposures that can be used in effects assessments discussed below. For

1 reformulated gasolines, considerations are similar to those for conventional fuels. Exposures  
2 are heavily influenced by the different fates of the different fuel components and by the  
3 specific microenvironments of the organisms at risk. The mix of fuel components to which  
4 the organisms actually are exposed must be characterized so appropriate effects information  
5 can be applied. Compared to conventional fuels, additional considerations include the  
6 potential diversity of reformulations and the effects on exposure and mixture toxicity of new  
7 extenders that characterize these reformulations.

#### 9 **6.1.1.4 Analytical Methodology**

10 Analytical methodologies for measuring source emissions, for monitoring the ambient  
11 air transport and transformation of these emissions, and for monitoring the exposure of target  
12 populations (human and ecosystem) to the pollutants of interest are prerequisites for  
13 determining the relative impacts of varied motor fuels on risk to public health and welfare.

14 Source emissions characterization requires accurate, precise analytical procedures.  
15 Qualified certification procedures exist for measuring currently regulated total hydrocarbons  
16 (THCs), CO, NO<sub>x</sub>, CO<sub>2</sub>, and total particulate emissions, as well as for measuring some  
17 unregulated toxic emissions of interest (such as benzene, formaldehyde, and 1,3-butadiene)  
18 from motor vehicles using conventional fuels. With reformulated gasolines, the primary  
19 certification uncertainty is the response of the THC flame ionization detection (FID)  
20 methodology to the oxygenated additives, such as MTBE, ETBE, and ethanol, that may  
21 constitute 10 to 15% of the fuel by volume. The adequacy (accuracy and precision) of  
22 classical certification measurement methods will require evaluation at the lower pollutant  
23 concentrations associated with the reduced standards of the CAAAs. Validated sampling and  
24 analysis procedures will be required for selective determination of MTBE, ETBE, and  
25 ethanol. Because available procedures are often costly and complex to implement, efforts to  
26 improve methodology performance and to simplify procedures, permitting application by  
27 lesser skilled analysts, are required. Many of the analytical procedures provide only  
28 integrated data for transient driving periods; therefore, conditions favoring emission of the  
29 toxic substance of interest are difficult to isolate. Continuous "real-time" measurement  
30 procedures must be developed for this purpose. Validated chromatographic procedures are

1 required for determining the composition of organic emissions, for both O<sub>3</sub> and toxics air  
2 quality impact assessments. Gasoline reformulation will likely include reduced aromatic and  
3 olefinic hydrocarbon fractions, placing increased emphasis on these categories of compounds.

4 Ambient air containing MTBE and ETBE can be analyzed with gas chromatographs  
5 (GCs) equipped with FID. The formates and acetates produced in the photooxidation of  
6 these ethers are also measured with GC. New methodology may be needed if any unusual  
7 products are produced from the photooxidation of complex mixtures arising from the use of  
8 oxygenated fuels.

9 Methods development for measuring MTBE, ETBE, and ethanol may be required for  
10 adequate characterization of ambient and exposure patterns. Determination of this need will  
11 depend upon emissions characterization studies and exposure calculations based upon  
12 estimated exposure levels.

## 14 **6.1.2 Effects Assessment**

### 15 **6.1.2.1 Human Health Effects**

16 Research on reformulated gasolines, as on other alternative fuels, involves study of the  
17 inhaled vapors and combustion products, with and without atmospheric transformation. The  
18 health effects resulting from conventional fuels relative to reformulated fuels are important in  
19 this assessment. The health effects of reformulated gasolines may be generally similar to  
20 those of current gasolines, with additional effects due to extenders and no effects from  
21 components that may be removed (e.g., certain aromatics).

22 Much of the research for reformulated fuels must await exposure assessment research  
23 that is described in Section 6.1.1.3.1. Given the number of different reformulated gasolines  
24 that currently exist and are anticipated to be developed, prioritizing the study of blends will  
25 be necessary. This ordering should be based on the results of mobile source  
26 characterization, atmospheric fate, and exposure assessment research as well as on estimates  
27 of market penetration and knowledge of individual components (e.g., MTBE, ethanol). Until  
28 the work on reformulated gasolines as a complex mixture can begin, efforts should focus on  
29 the potential effects of the primary extenders themselves (i.e., MTBE and ETBE).

1 In addition, delineation of the pharmacokinetic behavior of MTBE and ETBE should be  
2 conducted, both in isolation and in the reformulated mixtures.

3 The peer-reviewed literature contains little information on MTBE human health effects,  
4 primarily case reports on the use of MTBE in the dissolution of cholesterol gallstones.  
5 Based on these human data, target organs for high-priority MTBE research include the  
6 nervous system, liver, kidney, immune system, and hematopoietic system. Most of the  
7 available animal data come from unpublished reports submitted to EPA in accordance with  
8 Section 4 TSCA test rules. Reports covering the pharmacokinetics, mutagenicity,  
9 neurotoxicity, and developmental and reproductive toxicity (principally from inhalation  
10 exposure) have been completed, and a chronic inhalation oncogenicity study is due to be  
11 finished in 1992. The EPA has derived an inhalation Reference Concentration (RfC) for  
12 MTBE of  $0.5 \text{ mg/m}^3$ , which is a lifetime exposure level (within an order of magnitude)  
13 thought to have negligible risk of adverse noncancer health effects in sensitive human  
14 subpopulations.

15 The animal studies completed thus far indicate that inhaled MTBE has the potential to  
16 cause neurotoxicity and developmental toxicity. Rats exposed intermittently for up to  
17 14 weeks to 800, 4,000, and 8,000 ppm MTBE showed no evidence of changes upon light  
18 microscopic evaluation of the respiratory tract. However, a number of hematological and  
19 organ weight and length changes were observed at the two higher exposure levels.  
20 An absolute decrease in brain length was observed in male rats exposed to 4,000 ppm and in  
21 both sexes at the 8,000 ppm exposure level. Several other neurotoxicological indices were  
22 also altered; however, concentration-response relationships were not clear. Concentration-  
23 related increases in liver, kidney, and adrenal weights (both absolute and relative to body  
24 weight) were observed in both sexes at 4,000 and 8,000 ppm.

25 Acute inhalation exposures as brief as 50 min to 8,000 ppm caused significant  
26 alterations in the motor activity of rats. Six-hour exposures to 800 ppm caused similar but  
27 less severe changes. Effects on motor activity were transient.

28 The effects of MTBE on reproduction and development have been examined in several  
29 animal species. Reproductive parameters were not affected in either of two generations of  
30 male and female CD rats exposed to 400, 3,000, or 8,000 ppm MTBE for 8 to 10 weeks



1 prior to gestation and during gestation and lactation. Pup survival was reduced in the  
2 8,000 ppm F2 litters on Postnatal Day 4, and reduced body weights and body-weight gains  
3 were observed in both generations of pups at 3,000 and 8,000 ppm. In a one-generation  
4 reproductive toxicity study, exposure of male and female rats for 16 or 28 weeks,  
5 respectively, to levels as high as 3,000 ppm did not affect the pregnancy rate. However,  
6 viability of the pups from parents exposed to about 1,200 and 3,000 ppm was slightly  
7 decreased. In a third rat study, developmental toxicity was not observed at levels up to  
8 3,300 ppm MTBE. Levels up to 8,000 ppm also did not cause developmental toxicity in  
9 rabbits. However, roughly equivalent levels of MTBE increased the number of dead fetuses,  
10 reduced the number of implantations, and caused skeletal variations in mouse fetuses. Some  
11 of the skeletal variations occurred at approximately 4,100 ppm.

12 A search of the literature produced no information on ETBE. As a consequence,  
13 standard toxicity testing is appropriate for this chemical, beginning with pharmacokinetic,  
14 acute, and subchronic studies. This should be followed by a comparison with preliminary  
15 exposure assessment data to determine the appropriateness of additional study. Research on  
16 ETBE could potentially benefit from structure-activity research once more MTBE data are  
17 available. The only research proposed in this Strategy for the primary fuel or its components  
18 is the pharmacokinetic evaluation of ethers, until more information becomes available to  
19 better guide research directions.

20 No health research on the combustion and transformation products of the ethers or  
21 reformulated gasolines has been published. This is high priority research, as described in  
22 Chapter 1, and includes the primary endpoints of concern (i.e., cancer, respiratory toxicity,  
23 and immunotoxicity).

## 24 25 **6.1.2.2 Ecosystem Effects**

### 26 ***6.1.2.2.1 Terrestrial Ecosystem Effects***

27 Terrestrial ecosystems might be affected through airborne deposition of pollutants  
28 associated with reformulated fuels, especially MTBE and ETBE. The biological and  
29 ecological effects of MTBE and ETBE have not been studied, particularly in relation to  
30 likely ambient exposure levels and in combination with O<sub>3</sub>. Research on the environmental

1 effects of methanol and ethanol are described in Sections 3.2.2.2 and 4.2.2.2, respectively.  
2 Knowledge of conventional-fuel effects is necessary to provide a background for the  
3 assessment of reformulated fuels. Research needs for conventional fuels are presented in  
4 Chapter 2. Given the number of existing reformulated fuels and potential reformulated fuel  
5 mixtures, prioritizing research to maximize resources will be necessary. Given that  
6 conventional fuel mixtures vary regionally and seasonally, a "standard fuel" must be  
7 established for research purposes. This information will be based on mobile source  
8 characterization research.

9 The effects of MTBE and ETBE on terrestrial biota are not known and, therefore,  
10 hazard identification studies are needed. Exposure-response research is needed to identify  
11 plant species sensitivity to MTBE and ETBE, individually and in binary exposures with  
12 O<sub>3</sub>. Microcosm/mesocosm studies will be beneficial in identifying the environmental fate of  
13 the ethers and their potential ecological effects in relationship to various temperature and  
14 water stress regimens. Finally, field biomonitoring is necessary to evaluate ecosystem  
15 responses under natural conditions as reformulated fuels gain prominence in urban areas.  
16 The animal toxicology studies described in Section 6.1.2.1 will provide information from  
17 which to judge the need for wildlife research.

#### 18 19 ***6.1.2.2.2 Aquatic Ecosystems Effects***

20 Reformulated fuel mixtures have a considerable formulation range. The behavior and  
21 effects of reformulated fuels on aquatic systems will depend on many factors, including the  
22 physical/chemical properties of the fuel, the amount released, its release rate, its persistence,  
23 and the toxicity of the mixture.

24 Little is known about behavior, persistence, or toxicity of the proposed mixtures. The  
25 alcohols or ethers present in these mixtures may act to rapidly disperse many of the  
26 hydrophobic compounds found in fossil fuels into the water column. This could enhance the  
27 bioavailability and, hence, the toxicity of the petroleum compounds. Shifts in the relative  
28 amounts of aromatic, olefinic, and aliphatic hydrocarbons will also affect the nature and  
29 toxicity of the mixture of chemicals to which aquatic organisms are exposed.

1        Because of the widely different aquatic release scenarios (for both fresh and marine  
2        waters) that are possible and the lack of aquatic toxicity data, hazard identification research  
3        on the acute and chronic effects of these mixtures is needed. The current use of MTBE as a  
4        gasoline additive in some regions of the United States may result in research to provide some  
5        hazard information. Also, due to the likely transient nature of the exposures, kinetic-based  
6        toxicity models will need to be developed and tested. In addition, studies on the influence of  
7        alcohols or ethers and on the bioavailability of petroleum hydrocarbons are needed.  
8        Mesocosm experiments should also be conducted to determine potential community-level  
9        effects of these mixtures. This should include the testing of a variety of aquatic community  
10       types, which may vary greatly in their responses and sensitivities. Integrative system  
11       measurements, such as oxygen consumption and nutrient fluxes, should be included to assess  
12       the state and health of these systems.

### 14       **6.1.3 Risk Prevention/Mitigation**

#### 15       **6.1.3.1 Stationary Sources**

16       Opportunities for taking advantage of reformulations as a means of shifting hydrocarbon  
17       fractions in production/utilization to minimize total emissions will be examined. The impact  
18       of reformulated fuels on control system effectiveness during storage, distribution, and  
19       marketing needs to be determined. Guidance is needed to develop new or improved control  
20       systems, design methods, and operating procedures that would minimize emissions/discharges  
21       from the recovery of feedstocks, production, transportation, distribution, and the use of  
22       reformulated petroleum-based fuels.

23       Carbon-based controls are especially important for hydrocarbon recovery. Research is  
24       needed to optimize the effectiveness of carbon-based technology; however, existing  
25       oxygenates (ethanol and MTBE) in conventional fuels may impact adversely the  
26       control-effectiveness of existing carbon-based controls. Research should be undertaken to  
27       quantify this potential adverse effect and to develop improved carbon-absorption technology  
28       for minimizing or eliminating this effect.

1 To reduce the occurrence and severity of releases, user-oriented accidental-release  
2 reference manuals/guidelines for prevention of accidental releases of conventional fuels from  
3 storage, production, transportation, and marketing need to be developed.

4 Improved means to reduce RITGs, VOCs, and other stationary source multimedia  
5 emissions/discharges resulting from one or more key scenarios of reformulated fuels market  
6 penetration need to be determined.

7 The compatibility of fabrication materials and the internal corrosion and reactive  
8 potential with reformulated gasolines must be compared to conventional fuels and,  
9 subsequently, must be examined vis-à-vis both current and future designs of underground  
10 storage tank (UST) systems (tanks and piping). Guidance documents on site investigations  
11 (where leaks are suspected) are based on our understanding of the fate and transport of  
12 gasoline in the soil/groundwater environment. Guidance documents on soil cleanup and  
13 aquifer restoration are based primarily on the properties of, and experience with, gasoline.  
14 A switch to reformulated gasolines, with somewhat different properties, will require  
15 expanding upon this work. Certain soil cleanup technologies that may have somewhat  
16 limited applicability to gasoline-contaminated soils may find, for example, a much greater  
17 applicability to reformulated-gasoline-contaminated soils. Leak prevention standards and  
18 protocols that may be suitable for gasoline and fuel oil may be quite unsuitable for  
19 reformulated gasolines.

#### 21 **6.1.3.2 Mobile Sources**

22 A number of material compatibility and related drivability problems have been noted  
23 with oxygenate-gasoline blends, especially those involving methanol and ethanol (American  
24 Petroleum Institute, 1988). The problems have been related to corrosion of fuel system  
25 metals and deterioration and swelling of elastomers and plastics. These problems are more  
26 pronounced with older vehicles, manufactured prior to industry efforts to improve the  
27 material compatibility of vehicles with oxygenate-gasoline blends. Because of the solvent  
28 nature of the alcohol, gas tank residue and debris can be released and transported through the  
29 fuel system, plugging the fuel filter and causing drivability problems. Although the sources  
30

of many of these problems have been identified and corrected, uncertainties about the durability of emission control technology (catalyst, fuel management systems, etc.) remain.

Motor vehicle risk reduction programs will focus on the long-term durability of production emission control technology for limiting environmentally damaging emissions associated with use of reformulated petroleum-based fuels.

### **6.1.3.3 Fuel Transport Sources**

Control technology development for fuel tankers, barges, and pipelines to reduce accidental spills and leakage will reduce the entry of reformulated fuels into terrestrial and aquatic ecosystems. Accidents are inevitable, however, and insofar as spills pose a significant adverse risk, cleanup technologies must be improved through research.

## **6.2 BACKGROUND AND RATIONALE**

### **6.2.1 Exposure Assessment**

#### **6.2.1.1 Source Characterization**

##### ***6.2.1.1.1 Stationary Source Characterization***

Gasoline is presently being extended with methanol, ethanol, or MTBE. The alcohol blends may contain up to 90% of either alcohol or gasoline. The MTBE-extended gasoline will contain between 5 and 20% MTBE (American Petroleum Institute, 1988). Methanol and ethanol have been discussed previously. In the last several years, MTBE production has increased rapidly, from 846,000 tons in 1987 to 1,172,000 tons in 1988, an increase of 38.5%. Interest in the use of ETBE as an extender has also been shown.

***Production.*** Commercial alcohols are produced from ethylene synthesis, synthesis gas reactions, or biomass fermentation, as were previously discussed. Methyl-tertiary-butyl ether is produced by reacting isobutylene with methanol. Ethyl-tertiary-butyl ether is the product of an isobutylene and ethanol reaction.

1       **Feedstocks.** Gasoline can be produced from crude oil, coal, oil, shale, and biomass.  
2 Biomass feedstocks are not currently attractive, but research is underway. Feedstocks for  
3 alcohols were discussed previously in Chapters 3 and 4.

4  
5       **Processes.** Production of alcohols was discussed previously. Gasoline produced from  
6 petroleum crudes involves separation of the gasoline components by distillation and blending  
7 to obtain the desired composition. Gasoline and the alcohol are then blended to obtain the  
8 final fuel.

9  
10       **Cost of Production.** Gasoline is the cheapest fuel per BTU; however, the price of  
11 gasoline is governed by the cost of crude oil. Because about 45% of the U.S. crudes are of  
12 foreign origin, gasoline cost will vary. The cost of ethanol would normally be higher than  
13 the cost of methanol (U.S. Department of Energy, 1990).

14  
15       **Emissions.** The primary concerns are the sources and levels of emissions and  
16 discharges that will result at all stages of processing, from the extraction of feedstocks  
17 through the refining, storage, distribution, and marketing of the reformulated gasolines. The  
18 most important problem is the likelihood that the effectiveness of existing gasoline VOC-  
19 control systems will be affected by the addition of oxygenates. This problem may already  
20 exist, considering the market penetration that oxygenates have made. Although many of  
21 these discharges have been quantified, or qualitatively described to various degrees, data are  
22 not now available to support the valid characterization needed to quantitatively estimate risks  
23 to public health or potential ecological impacts. The release of RITGs, such as methane, has  
24 not been fully evaluated. In reformulated gasolines, the emissions from direct leaks and  
25 spills would be based on the primary constituent of the blend. Evaporative emissions are a  
26 complex function of the gasoline volatility and composition along with the characteristics and  
27 amounts of the specific oxygenate added for blending. The primary question in each case is:  
28 "How are existing controls affected?"

29       Emissions from recovery of crude oil have been fairly well documented, and numerous  
30 regulations have been enacted to reduce emissions. These previous studies did not include an

1 in-depth evaluation of RITGs; thus, few data on the emissions of CO<sub>2</sub> at all stages, from  
2 crude oil recovery through refining, distribution, and marketing, are available. Carbon  
3 dioxide emissions from fermentation are large and equal the molecular quantity of alcohol  
4 produced, or 0.96 lbs of CO<sub>2</sub> for 1 lb of alcohol. The generation of steam and energy would  
5 produce additional CO<sub>2</sub>. Extraction of petroleum is normally accompanied by natural gas  
6 (methane) emissions. Worldwide recovery of methane results in substantial releases (waste  
7 gases, leaks, etc.), with important implications for global climate change. The extraction of  
8 coal for synthetic gasoline production would also be a source of releases of methane. These  
9 methane releases require quantification.

10 Nitrogen oxides are related to combustion activities of boilers/heaters and incinerators.  
11 These sources have been fairly well documented. Air toxics would follow the trend of  
12 organics.

13  
14 **Discharges.** The types of discharges to water and current treatment/control methods  
15 for fermentation processes have been discussed. Discharges from coal- or petroleum-based  
16 processes would be similar to those from coal conversion or petroleum refining. The present  
17 gasification plants have all experienced problems with various control systems. Control  
18 application to water discharges could be a problem and needs specific attention.

19  
20 **Accidental Releases.** Due to reformulated gasoline's high flammability factor and its  
21 potential toxicity, accidental release is a serious concern. Accidental releases related to  
22 conventional petroleum refining facilities are a concern; in the hundred largest property  
23 losses worldwide, petroleum refining represented 38% of the accidents (Marsh & McLennan,  
24 1985).

#### 25 26 **6.2.1.1.2 Mobile Source Characterization**

27 Reformulated gasolines will likely contain alcohol and/or ether additives because of  
28 their octane-enhancing qualities and their positive impact on emissions (American Petroleum  
29 Institute, 1988; U.S. Environmental Protection Agency, 1988). The use of oxygenated  
30 blends in conventional cars typically results in reduced emission rates of CO and, to a lesser

1 extent, of hydrocarbons (U.S. Environmental Protection Agency, 1988). For this reason,  
2 some cities have mandated the use of oxygenated fuels during winter months to alleviate high  
3 ambient CO levels (Anderson, 1987). The 1990 CAAAs require the use of oxygenated  
4 gasolines in selected O<sub>3</sub>- and CO-nonattainment areas during the periods of the year when  
5 these air quality problems are most prevalent. A fuel oxygen level of 2.7% is required by  
6 1992 in 44 cities with severe CO air pollution, and 2.0% by 1995 in 9 cities with severe  
7 O<sub>3</sub> air pollution. The CAAAs also provide for "opt-in" of other areas in nonattainment.  
8 Potentially, about 50% of the nation's unleaded gasoline could require reformulation by  
9 1995.

10 The reduction of CO exhaust emissions from automobiles burning oxygenated blends  
11 occurs because the blend combusts at air-fuel ratios leaner (more oxygen, less fuel) than  
12 those of straight gasoline. Oxygen contained in the alcohol or ether supplements oxygen in  
13 the intake air to cause a leaner, more complete combustion. Even newer vehicles with  
14 "closed-loop control" (air-fuel ratios are held at constant, near stoichiometric values) benefit  
15 from reduced CO emissions when burning blends. During engine warm-up and heavy  
16 acceleration modes, the control loop is disabled and the blend provides a fuel-lean shift that  
17 effectively reduces the high CO emissions associated with these modes. The extent of CO  
18 reduction with blend usage will require periodic reassessment because fuel control systems  
19 that regulate air-fuel ratios more effectively, even during cold start and engine warm-up, are  
20 being developed. Available data suggest that use of a 3.7% oxygen blend will reduce CO  
21 emissions by as much as 20 to 35%, depending upon the type of fuel control system being  
22 utilized.

23 Fuel-lean combustion also results in modest reductions in exhaust hydrocarbon and  
24 slight increases in NO<sub>x</sub> emissions. Hydrocarbon emissions are reduced by about 2 to 15%  
25 and NO<sub>x</sub> emissions are elevated 4 to 8% (U.S. Environmental Protection Agency, 1988).  
26 The octane-enhancing characteristics of the added oxygenated organics will permit changes in  
27 the hydrocarbon composition of gasoline that can offset the elevated NO<sub>x</sub> emissions  
28 associated with leaner combustion (e.g., aromatic hydrocarbons can be reduced, lowering  
29 peak combustion temperatures [i.e., aromatics have higher flame temperatures than  
30 oxygenates] and thus NO<sub>x</sub>). Less is known about the impact of oxygenated blends on



1 unregulated tailpipe emissions (e.g., aldehydes, benzene, 1,3-butadiene, and methyl or ethyl  
2 nitrites) or on vehicles operating under conditions such as low winter and high summer  
3 temperatures and varied average speeds. Preliminary examination of tailpipe emissions from  
4 ethanol blends suggests elevated acetaldehyde emissions relative to the base case of gasoline,  
5 but little impact on other toxic emissions of interest (1,3-butadiene and benzene) (Stump  
6 et al., 1990). In general, aldehyde emissions are expected to be elevated somewhat with  
7 oxygenated blends.

8 Ethanol blends have been granted a vapor pressure waiver of 1 psi under the current  
9 volatility regulation. This enables ethanol to be splash-blended with gasoline because  
10 resultant gasohol (90% gasoline, 10% ethanol) vapor pressure increases only about 1 psi  
11 above that of the base gasoline. From an air pollution standpoint, this increase in fuel  
12 volatility causes increased evaporative and running-loss emissions relative to those with  
13 gasoline (American Petroleum Institute, 1988). The data base examining evaporative  
14 emissions with these fuels and current- or future-technology vehicles is limited, especially at  
15 the elevated summer temperatures often associated with high-O<sub>3</sub> episodes.

16 The two ethers receiving most attention in automobile fuel blends are MTBE and ETBE  
17 (Piel, 1988; Anderson, 1988). Methyl-tertiary-butyl ether is produced by reacting methanol  
18 with isobutylene over an acid catalyst; ETBE is similarly produced, using ethanol in lieu of  
19 methanol. Use of MTBE as a gasoline additive has been steadily gaining importance during  
20 the past 5 years, primarily as an unleaded gasoline octane enhancer. It has also gained favor  
21 in metropolitan areas such as Denver, where oxygenated-fuel mandates have expanded its  
22 usage. The petroleum industry favors MTBE because its blending properties (MTBE has  
23 little solubility or affinity for water and causes little change in volatility when blended with  
24 gasoline [American Petroleum Institute, 1988]) allow it to be transported and marketed like  
25 gasoline. Ethyl-tertiary-butyl ether, which possesses fuel qualities similar to those of MTBE,  
26 may gain importance as an oxygenate-blending component if the ethanol used in its  
27 production can qualify for a federal subsidy. Ethanol used in the production of gasohol  
28 currently receives a tax exemption of \$0.60 per gallon, which translates to a \$0.06 tax break  
29 at the pump.  
30

1 Ethanol-, MTBE-, and ETBE-gasoline blends are currently permitted by EPA to 10%  
2 ethanol, 15% MTBE, and 13% ETBE by volume, corresponding to 3.7%, 2.7%, and 2.0%  
3 fuel oxygen contents, respectively. Future waivers to permit somewhat greater percentages  
4 may be requested (Anderson, 1988). The EPA has been petitioned by the Oxygenated Fuels  
5 Association to allow 2.7% oxygen (instead of current 2.0% oxygen) under the "substantially  
6 similar" rules. Various methanol-gasoline blends have also been approved by EPA but are  
7 not being widely marketed because of their inability to qualify for a fuel-volatility waiver.  
8 The 1990 CAAAs require that gasoline marketed in the nine worst O<sub>3</sub> nonattainment areas be  
9 reformulated to provide 15% reductions of O<sub>3</sub>-forming VOC and toxics by 1995, and 25%  
10 reductions by 2000 (relative to a 1990 baseline condition). The EPA has issued a proposed  
11 rulemaking in response to those requirements (Federal Register, 1991).

12 The automobile and petroleum industries have initiated a cooperative effort to examine  
13 a number of possible gasoline formulations in the Auto/Oil Air Quality Improvement  
14 Research Program (Kiskis et al., 1989). The initial program (in 1989 to 1990) examined  
15 emissions from 20 recent-technology vehicles with 22 gasoline formulations. Fuel aromatics,  
16 olefins, T<sub>90</sub>, and oxygenate content were varied. Federal Test Procedure tailpipe and  
17 evaporative emissions tests were completed at 75 °F, along with running-loss evaporative  
18 emissions tests at 95 °F. Twenty flexible-fueled vehicles also will be studied with M85,  
19 M10, and M0 fuels. Detailed emission compositional characterization was completed, and  
20 models applied to estimate impact on urban O<sub>3</sub>. Preliminary results from the Auto/Oil  
21 Program have been published in a series of Technical Bulletins (Auto/Oil Air Quality  
22 Improvement Research Program, 1990, 1991a, 1991b, 1991c, 1991d, 1991e; Carter et al.,  
23 1991). Ozone benefit will be sensitive to the actual gasoline formulations reaching the  
24 marketplace. A range of formulations is possible under the proposed rulemaking (Federal  
25 Register, 1991). The preliminary results from the Auto/Oil Program suggest that for the  
26 reformulated gasolines studied, the contribution of light-duty vehicles to peak O<sub>3</sub> can be  
27 reduced up to 26%, primarily the result of reducing fuel olefin content (Auto/Oil Air Quality  
28 Improvement Research Program, 1991b). An evaluation of optimum fuels under other varied  
29 motor vehicle operating conditions should also be done.  
30

1 Significant expansion of the data base will be required to fully examine the impact of  
2 these fuels on air quality and the public health and environment. Carbon monoxide benefit is  
3 expected, especially with older technology motor vehicles, but the impact on tailpipe  
4 O<sub>3</sub>-precursor emissions cannot be estimated until formulations are selected. Because of  
5 oxygenate octane-enhancing properties, fuel aromatic and olefinic hydrocarbon fractions are  
6 likely to be reduced, which should result in lower emissions of photochemically reactive  
7 organic compounds. Possibilities for increased isobutylene and aldehyde emissions exist,  
8 however, somewhat offsetting the O<sub>3</sub> benefit of the fuel improvements (Stump et al., 1990).  
9 Ozone benefit will also be derived from reduced evaporative emissions from formulations  
10 having reduced volatilities (volatilities will be adjusted downward by reducing the amounts of  
11 C<sub>4</sub> and C<sub>5</sub> paraffins in the fuel). Reduced fuel aromatics will provide benefit in the form of  
12 reduced emissions of hazardous aromatics such as benzene. The impact of these fuels on  
13 RITG emissions such as CO<sub>2</sub>, methane, and N<sub>2</sub>O is largely unknown and will require further  
14 examination.

#### 16 **6.2.1.2 Environmental Fate**

##### 17 **6.2.1.2.1 Air Fate**

18 The photochemical activity of ether-gasoline blends should be greater compared to  
19 methanol-gasoline, but less compared to pure gasoline. Like the alcohols, however, the  
20 photochemical reactivity of ether blends will largely depend upon aldehydes present in the  
21 exhaust gases. High aldehyde levels will increase photochemical reactivity. Modeling and  
22 experimental data show little difference in smog manifestations when up to 10% of the VOC  
23 (as carbon) is replaced with methanol at VOC/NO<sub>x</sub> ratios of approximately 10:1. Similar  
24 results were obtained with ethanol. Both blends have a strong dependence on the VOC/NO<sub>x</sub>  
25 ratio. At lower VOC/NO<sub>x</sub> ratios (approximately 3:1), the methanol-blend exhaust showed  
26 much lower reactivity, producing about one-third less O<sub>3</sub> (Jeffries et al., 1985). Again,  
27 ethanol showed a similar effect. With many days of sunlight, however, the exhaust may  
28 produce more O<sub>3</sub> because the lower O<sub>3</sub> levels observed at the lower VOC/NO<sub>x</sub> ratio  
29 probably result from nitric oxide (NO) inhibition.

1       An urban airshed modeling study of an air pollution episode in Los Angeles has shown  
2       that a 10% ethanol/gasoline blend improved air quality, not only on the first day but also on  
3       subsequent days (Whitten, 1989). Whitten ascribes the multiday improvements to influences  
4       of the boundary conditions and initial inputs. The inputs and boundary conditions did not  
5       allow the VOC/NO<sub>x</sub> ratio to increase; thus, O<sub>3</sub> production was inhibited because of the low  
6       ratio.

7       Methyl nitrite has also been observed in gasoline-methanol exhaust (Jonsson and  
8       Bertilsson, 1982). This compound is important because OH radicals are produced from  
9       photodissociation of methyl nitrite. Ethyl nitrite should be produced from ethanol-containing  
10      fuels. This, like methyl nitrite, will produce OH radicals when photodissociated in air.

11      The chemistry of MTBE and ETBE has not been sufficiently studied. Some  
12      preliminary work on MTBE suggests that OH attack leads to tertiary butyl formate (Northrop  
13      Services, Inc., 1989). The OH rate constant has been measured for MTBE, but not for  
14      ETBE. The atmospheric lifetime of MTBE is about 6 days through its reaction with OH.  
15      Ethyl-tertiary-butyl ether should have a slightly shorter lifetime. Products expected from the  
16      photooxidation-type reactions with these compounds are acetaldehyde, formaldehyde, and  
17      possibly acetone. Ethers are generally not very soluble in water, so their wet deposition  
18      rates should be low.

#### 19 20      **6.2.1.2.2 Soil and Groundwater Fate**

21      When used as fuel additives or extenders, consideration must be given to the effects  
22      that alcohols will have on the environmental fate of other compounds in the fuel. Subsurface  
23      contamination by petroleum-based fuels often results in multiphase contaminant plumes;  
24      however, the presence of fuel extenders such as methanol or ethanol could significantly alter  
25      the chemodynamics of the system. For example, the addition of alcohol to a biphasic  
26      solution of gasoline and water would likely increase the solubility of the partially miscible  
27      organic compounds present (e.g., benzene and xylene) and could, at some fraction of  
28      alcohol, change the solution to a single-phase mixed solvent. As discussed in  
29      Section 6.1.1.2.2, the subsurface behaviors of single- and multiphase systems can be very

different. Additional research to assess the utility of existing approaches for describing and predicting the chemodynamics of these complex solutions is required.

Research has shown that alcohols enhance the mobility of hydrophobic organic chemicals (HOCs) in laboratory soil columns (Nkedi-Kizza et al., 1987; Wood et al., 1990). This increased mobility is primarily a result of the increased solubility of these HOCs in aqueous solvents containing organic cosolvents. A theoretical approach for quantitatively describing this phenomenon has been formulated and tested in the laboratory (Rao et al., 1985; Nkedi-Kizza et al., 1985; Fu and Luthy, 1986).

As described previously, contaminant plumes are often complex mixtures of solvents and solutes, with the chemical composition constantly changing as the plume migrates through the subsurface. Currently available contaminant transport theories focus on the behavior of the dissolved constituents (solute) of these solutions and typically assume an aqueous solvent phase. Even when the effects of organic cosolvents (i.e., methanol and MTBE) are incorporated into these theories, the dynamic nature of the solvent phase is not addressed. Preliminary results from current research suggest that gradient-elution chromatography theory and techniques may be useful in assessing contaminant transport in these temporally variable solutions (Wood et al., 1990).

Compared to gasoline, the ethers MTBE and ETBE have relatively large aqueous solubilities and would likely leach more rapidly through soil and groundwater. Also, limited data suggest that ethers may be persistent in subsurface environments. The paucity of experimental data makes conclusions concerning the transport and fate of ethers speculative; however, recent research has shown that even partially miscible organic solvents (PMOSs), such as MTBE and ETBE, can significantly alter the solubility, sorption, and mobility of slightly soluble organic compounds. Thus, the addition of these solvents to gasoline could enhance the mobility of the less-soluble components of gasoline and increase their potential for groundwater contamination. Substantial research must be done, however, before the cosolvency effects of these PMOSs can be conceptually and mathematically described in the context of complex mixtures such as gasoline. Predicting *a priori* the impact of fuel extenders on microbial degradation of fuel mixtures is difficult. As discussed in Section 6.1.1.2.2, the presence of low concentrations of alcohols may stimulate microbial

1 activity and enhance transformation of susceptible compounds, whereas higher concentrations  
2 may inhibit biotransformations. The specific conditions under which inhibition or stimulation  
3 occurs cannot be established with the current knowledge base.

#### 5 ***6.2.1.2.3 Surface Water Fate***

6 Reformulated gasolines present an array of fate problems for freshwater and estuarine  
7 spill scenarios that are very similar to those of conventional fuels. In the case of  
8 reformulated gasoline, the fuels are a complex mixture of individual compounds within the  
9 base stock to which some individual components have been added. The reformulated mixture  
10 will exhibit multiple fate profiles. Some components will degrade rapidly, whereas others  
11 are much more persistent. Degradation will produce other products that, in turn, display  
12 different fate and effects properties. Reformulated gasolines will separate into multiple  
13 phases in the water column, complicating the transport as well as the fate of each phase.  
14 At least three distinct phases result: the product phase, emulsions formed as the fuel  
15 disperses, and product dissolved in the water. The three phases move at different rates,  
16 interact as concentration and turbulence fields change, and degrade at different rates and by  
17 different mechanisms. Surface slicks form at even very low concentrations, further  
18 complicating the subsequent effects (i.e., effects may be much more subtle than direct  
19 toxicity).

20 Fate processes requiring study include the identification of individual fuel components  
21 and subsequent transformation in water systems. If relatively high amounts of additives or  
22 alternate fuels have been added, the fate of the added products must be determined alone and  
23 in combination with the base gasoline. Biological degradation is especially important, and  
24 oxygen depletion is expected to be a major impact. Related processes of reaeration and  
25 volatilization are also important. Priority research for transport is the formation and  
26 movement of emulsions. The total, multiphase transport will require additional study to  
27 establish the expected spatial extent, duration, and volume of spills.

### 6.2.1.3 Exposures

#### 6.2.1.3.1 *Human Exposures*

Because the regulated air emissions are affected by ether-gasoline blends in much the same way as they are affected by ethanol-gasoline blends and the unregulated emissions are not yet fully characterized for reformulated gasolines, the impact on health risk and ecosystems is unknown. If acetaldehyde, formaldehyde, and acetone become significant atmospheric transformation products, future studies to determine the impact of these changes on estimates of public health risks may be required.

Effects of inhalation exposures to alcohol-gasoline blends will likely vary little from effects of exposures to current gasoline; however, these blends may change concentration levels of aldehydes, benzene, 1,3-butadiene, and methyl or ethyl nitrites. If laboratory studies report significant concentration changes for evaporative or running-loss emissions, the resulting change to human exposure effects for these compounds may require documentation to understand the impact on air quality and risk to public health.

Adding oxygenates such as methanol and ethanol to current fuels would obviously increase the potential for soil and water contamination by these organic solvents. When used as fuel extenders, the impact of these solvents on groundwater contamination/human exposure by constituents of currently used fuels is less apparent. The relative proportion of these constituents (and thus the total quantity) would be reduced; however, their mobility in the subsurface could increase. Further, these extenders could affect the chemical and microbial transformation processes that attenuate pollutant levels. Additional environmental data on the fate of ethers (Section 6.2.1.2.2) in the subsurface are required before reliable predictions can be made about the effects of these fuel extenders on pollutant exposures.

#### 6.2.1.3.2 *Biota Exposures*

***Terrestrial Exposures.*** Terrestrial biota will be exposed to reformulated-fuel pollutants (e.g., MTBE, ETBE) primarily through the atmosphere. Exposure via the air depends upon numerous factors such as emission patterns, concentrations, and season. Such exposures could be acute or chronic, frequent or infrequent, high level or low level, and local or regional, depending upon pollutant source and atmospheric processes. Chemical

transformation within the atmosphere must also be considered. Terrestrial biota exposures will impact urban and agricultural ecosystems. Remote ecosystems will be exposed to pollutants via long-range atmospheric transport and deposition. Modeling scenarios using multimedia compartmental models can be used to estimate terrestrial ecosystem exposure to MTBE and ETBE.

***Aquatic Exposures.*** Considerations for making final aquatic exposure assessments for reformulated fuels are generally the same as those discussed in the conventional fuels chapter (Section 2.2.1.3). The addition of oxygenates will somewhat change the water-soluble fraction, but behavior should still be largely similar to gasoline. Altering the aromatic fraction will also change the water-soluble fraction, but this will be an extension of the effects of current variability in fuel composition.

#### **6.2.1.4 Analytical Methodology**

A wide range of analytical procedures are required to facilitate the examination of the impact of changes in motor fuels on risk to health and ecosystems. The procedures can generally be categorized according to procedures for characterizing source emissions, procedures for monitoring the transport and transformation of the emissions in ambient air, and procedures for monitoring human and ecosystem exposure.

Both procedures for certification of regulated emissions and for comprehensive characterization of unregulated emissions are required for sources. The primary concerns with reformulated-gasoline fuel-certification methodology are (1) the adequacy (accuracy and precision) of classical procedures for measuring pollutant (THC, nonmethane hydrocarbons [NMHC], CO, NO<sub>x</sub>, and PM) concentrations at levels dictated by lowered emission standards required by the CAAAs, and (2) the impact of oxygenated additives such as MTBE, ETBE, and ethanol on determination of total organic carbon. All currently defined procedures will require evaluation.

As previously discussed (Section 2.2.1.4), the Coordinating Research Council has examined the adequacy of procedures for certification of heavy-duty engine particulate emissions at the reduced standards of 1991 and 1994. The project identified factors



1 contributing to the variability of particulate-mass emission-rate measurements in the heavy-  
2 duty transient test procedures used in certification, and suggested possibilities for method  
3 improvement. Similar activities will be required with other procedures for measuring  
4 regulated emissions if proposed standards are enacted.

5 With organic emission standards requiring measurement of NMHC (a departure from  
6 current THC standards), analytical methodology will be required for determination of  
7 methane, permitting calculation of NMHC by subtraction from THC, and/or direct  
8 measurement of NMHC. The latter will probably be required for the lowest standards  
9 because of uncertainties associated with using a small difference in two large numbers  
10 (NMHC = THC - methane). Procedures for direct measurement of methane have been  
11 developed for motor vehicle emissions (Hoffman et al., 1987; Burch and Pembroke, 1973;  
12 Probst and Reschke, 1977; Society of Automotive Engineers, 1976), but not for direct  
13 measurement of NMHC emissions. The added complication of determining the contribution  
14 of oxygenated additives (MTBE, ETBE, and ethanol) to organic carbon emissions will be  
15 required with reformulated gasolines. Oxygenated organics typically do not have the same  
16 carbon response in THC FIDs as hydrocarbon compounds. Available procedures for  
17 selective measurement of the oxygenated additives of interest involve complex  
18 chromatographic methods (American Society for Testing and Materials, 1988). Simplified  
19 procedures will be required for certification.

20 Efforts to assess the impact of motor vehicles on O<sub>3</sub> and toxics air quality require  
21 detailed speciation of emissions. Because of the very complex nature of the mixtures, many  
22 studies have used chromatography (California Air Resources Board, 1989; Crews and Stump,  
23 1988; Lipari, 1990; Sigsby et al., 1987; Stump and Dropkin, 1985; Stump et al., 1989;  
24 Black et al., 1980; Williams et al., 1990). Efforts to provide standardized uniform  
25 chromatographic methods and quality assurance procedures across the user community will  
26 be useful, and such activities have been initiated in the Auto/Oil Air Quality Improvement  
27 Research Program (Schuetzle, 1990). Chromatographic procedures generally involve  
28 collection of an integrated sample of transient emissions in a container (generally a teflon  
29 bag) during the test period, with subsequent analysis. Continuous or "real-time" analysis  
30 provides the additional information necessary to isolate the driving conditions most

1 responsible for emissions of interest. Efforts to develop such methods have been initiated for  
2 many toxics of interest, and will continue as fuel formulations and compounds of interest  
3 change (Butler et al., 1985; Staab et al., 1985; Von Carlowitz et al., 1990; Heller et al.,  
4 1990).

5 Ambient air containing MTBE and ETBE can be analyzed with a GC equipped with  
6 FID. The formates and acetates produced in the photooxidation of these ethers are also  
7 measured with GC. New methodology may be needed if any unusual products are produced  
8 from the photooxidation of complex mixtures arising from the use of oxygenated fuels.

9 Methods development for measuring MTBE, ETBE, and ethanol may be required for  
10 adequate characterization of ambient air exposure patterns. Determination of this need will  
11 depend upon emissions characterization studies and exposure calculations based upon  
12 estimated exposure levels.

## 14 **6.2.2 Effects Assessment**

### 15 **6.2.2.1 Human Health Effects**

16 The health effects of reformulated gasolines may be generally similar to current  
17 gasolines, with additional effects due to any extenders (e.g., MTBE) and no negative effects  
18 from any components that may be removed (e.g., certain aromatics). No major health  
19 effects studies of these reformulated fuels or their combustion products have been reported.  
20 Reformulated fuels are complex mixtures, and their resulting combustion and transformation  
21 products are even more complex. Despite the lack of health studies reported on reformulated  
22 gasolines, a general view of the importance of conducting such studies can be seen from the  
23 relatively large and important health studies conducted on synthetic fuels by the Department  
24 of Energy (DOE) and the National Laboratories as well as from the EPA and DOE studies  
25 on diesel fuels and combustion emissions. These studies generally show that fuel  
26 composition does affect the toxicology of the fuel itself and the combustion products. The  
27 combustion particle emissions from different formulations of diesel fuel, including alcohol  
28 blends, and the aromatic, nitrogen, and sulfur contents showed significant differences in  
29 comparative genetic toxicology studies.

1 General background information on complex mixtures of the fuels themselves and of  
2 products resulting from alternative fuel combustion and atmospheric transformation can be  
3 found in the discussion of the health effects of gasoline, methanol, and ethanol fuels  
4 (Sections 2.2.2.1, 3.2.2.1, and 4.2.2.1). The extenders used in reformulating fuels (e.g.,  
5 MTBE) are discussed below.

#### 6 7 **6.2.2.1.1 Methyl-Tertiary-Butyl Ether**

8 Toxic effects data on MTBE are now becoming available, but the combustion and  
9 transformation products of MTBE still require identification. The available human  
10 information comes from case reports on the use of MTBE in the dissolution of cholesterol  
11 gallstones. During this procedure, MTBE is injected, typically into the gallbladder, and  
12 aspirated. The signs and symptoms of toxicity are apparently due to leakage or escape of  
13 MTBE from the biliary systems and subsequent systemic absorption (Thistle et al., 1985).  
14 With such MTBE treatment in humans, the following effects have been observed: transient  
15 nausea with or without emesis, duodenitis, confusion, sedation, transient intravascular  
16 hemolysis, reversible coma, reversible acute renal failure, and altered levels of serum  
17 enzymes and leukocytes (Thistle et al., 1989; Di Padova et al., 1986; Ponchon et al., 1988).

18 Several pharmacokinetic studies (Bio-Research Laboratories Limited, 1990a, 1990b,  
19 1990c, 1990d) in Fischer 344 rats have been conducted by the MTBE Task Force, in  
20 response to EPA's TSCA Section 4 Testing Consent Order. Difficulties with mass balance  
21 were encountered, perhaps due to the volatility of MTBE. Keeping this difficulty in mind,  
22 several apparent conclusions may be drawn from this data. Methyl-tertiary-butyl ether was  
23 rapidly absorbed following oral exposure. Absorption from the skin was limited, with  
24 greater absorption at the higher (400 mg/kg) than at the lower (40 mg/kg) dosage; however,  
25 dermal bioavailability was lower at the higher dosage. The respiratory system appeared to  
26 the principal route of elimination of MTBE, followed by the kidney. Methyl-tertiary-butyl  
27 ether, as the parent chemical, was the predominant form in expired air, while metabolites of  
28 tert-butyl alcohol, a metabolite of MTBE, predominated in the urine. Expressed as  
29 percentage of administered dose, more MTBE was eliminated by the lungs following an oral  
30 high (400 mg/kg) than an oral low (40 mg/kg) exposure, while the percentage eliminated in

1 the urine was higher after the low dose, suggesting saturation of metabolism. Apparent  
2 saturation of metabolism also occurred at the high (8,000 ppm) relative to the low (400 ppm)  
3 inhalation exposure of MTBE. Elimination of MTBE occurred within 48 h of exposure.  
4 The data suggested gender differences in the pharmacokinetics (e.g., decreased plasma  
5 concentrations in female rats) that warrant further exploration. Data from repeated inhalation  
6 exposure suggested possible induction of metabolism of MTBE. This finding warrants  
7 further investigation.

8       Animal studies indicate that inhaling MTBE has the potential to cause neurotoxicity and  
9 developmental toxicity. In a subchronic inhalation study (Dodd and Kintigh, 1989), Fischer  
10 344 rats (25/sex/group) were exposed to 800, 4,000, or 8,000 ppm MTBE vapors for  
11 6 h/day, 5 days/week for 13 weeks. No treatment-related findings were noted for the  
12 respiratory tract upon gross and light microscopy evaluations. Necropsy examination of  
13 nervous system tissue showed no evidence of treatment-related changes in exposed animals  
14 compared to the controls. However, at both the 8,000- and 4,000-ppm exposure levels, an  
15 absolute decrease in the brain length was observed in male rats only. Reductions in absolute  
16 brain weight in both sexes were noted following exposure to 8,000 ppm. The authors  
17 evaluated the neurobehavioral effects of MTBE using a functional observational battery  
18 (FOB) and a test of motor activity. The 4,000- and 8,000-ppm exposure groups deviated  
19 from controls with respect to several FOB endpoints. However, a clear concentration-  
20 response relationship was not evident for any of these endpoints. Slight hematologic  
21 alterations were observed in the male and female rats exposed to 4,000 and 8,000 ppm.  
22 However, deviations were of marginal statistical significance and did not demonstrate a  
23 concentration-response relationship. The most noteworthy biochemical finding was a  
24 significant increase in corticosterone levels for the 8,000-ppm group, which is consistent with  
25 the observed increase of relative adrenal weight and may reflect a direct action of MTBE on  
26 the neuroendocrine system (e.g., at the hypothalamus, pituitary or adrenal glands). Body  
27 weight gains were depressed in both male and female rats of the 8,000-ppm group for the  
28 first 3 weeks of exposure. There were significant (>10%) concentration-related increases in  
29 liver, kidney, and adrenal weights relative to body weight in both the 4,000- and 8,000-ppm  
30 treatment groups compared to controls.

Greenough et al. (1980) exposed Sprague-Dawley rats (10/sex/group) to MTBE at concentrations of 250, 500, and 1,000 ppm, 6 h/day, 5 days/week for 13 weeks. There was evidence of a respiratory infection in control and exposed animals; however, the lack of description of animal husbandry and any attempt to isolate causative organisms precludes any conclusions from this study regarding the respiratory effects of MTBE. While hematologic and clinical chemistry tests revealed some statistically significant changes, it could not be determined if any changes were concentration-related because the two low-concentration groups were not evaluated. Further, the effects were not corroborated by the Dodd and Kintigh (1989) study at higher concentrations. Thus, no treatment-related effects were identified in this study.

Gill (1989) evaluated neurotoxicity of MTBE in an acute inhalation study. Fischer 344 rats (22/sex/group) were exposed to 0, 800, 4,000, or 8,000 ppm MTBE for 6 h. Transient increases in motor activity were observed for males in the 800 and 4,000 ppm exposure groups. One hour after termination of exposure, significant increases in the incidence of abnormal gait and lacrimation were observed in both males and females exposed to 8,000 ppm MTBE. Labored respiration pattern (females only), decreased muscle tone (males only), decreased mean performance on the treadmill (males only), decreased mean hindlimb grip strength (females only), and increased hind limb splay (males only) were also significant in rats exposed to 8,000-ppm MTBE, 1-h postexposure. None of these motor activity and function changes remained 6 h after termination of exposure. Increased time to tail flick (males only) was the only significant observation at 6-h postexposure in rats exposed to 8,000 ppm but was not observed in any group at 1-h postexposure. Results show that a 6-h exposure to 8,000 ppm MTBE significantly affected the motor activity and function of rats, and that these effects are largely reversible within 6 h.

A nine-day inhalation study was performed (Bio/dynamics Incorporated, 1984) on Sprague-Dawley rats (20/sex/group) exposed to concentrations of 101, 300, 1,020, and 2,970 ppm MTBE vapors, 6 h/day, 5 days/week. Lacrimation, conjunctival swelling, and/or corneal changes were observed in both treated and control animals; however, statistical significance was not reported. A significant increase in the relative liver weight was evident in rats exposed to 2,970 ppm MTBE. Microscopic examinations revealed a significant

1 increase in the incidence of chronic inflammation in the nasal mucosa and trachea at 1,020  
2 and 2,970 ppm compared to pretest controls, but lung weight was not different from  
3 controls.

4 Savolainen et al. (1985) exposed 3-mo-old male Wistar rats (20/group) to 50, 100, or  
5 300 ppm MTBE vapor 6 h/day, 5 days/week for 2 to 15 weeks. A significant concentration-  
6 dependent increase in microsomal UDP-glucuronosyltransferase activity in liver and kidney,  
7 as well as NADPH cytochrome c-reductase activity in kidney, occurred after 2 weeks of  
8 exposure. These effects were not observed after 15 weeks of exposure.

9 Conaway et al. (1985) exposed pregnant Sprague-Dawley rats (23 to 25/group) to mean  
10 concentrations of 0, 250, 1,000, or 2,430 ppm MTBE and pregnant CD-1 mice  
11 (24 to 29/group) to mean concentrations of 0, 280, 1,110, or 2,710 ppm MTBE 6 h/day  
12 during Gestational Days 6 to 15. No statistically significant results were obtained, although  
13 concentration-related skeletal variations per litter of the mice were found to be 2/27 (7.4%)  
14 in the control group and 3/26 (11.5%), 4/25 (16%), and 6/27 (22.2%) in the 280, 1,100, and  
15 2,710 ppm groups, respectively.

16 Pregnant CD-1 mice (30/group) were exposed to MTBE at concentrations of 0, 1,035,  
17 4,076, and 8,153 ppm 6 h/day on Gestational Days 6 to 15 (Tyl and Neeper-Bradley, 1989).  
18 There were indications of maternal toxicity at 4,076 and 8,153 ppm; at these concentrations,  
19 fetal body weight per litter (male and female) was significantly decreased, and concentration-  
20 related increases in skeletal variations indicative of reduced ossification occurred. Other  
21 significant measures of developmental toxicity were evident at 8,153 ppm.

22 Developmental toxicity was also investigated in rabbits at Bushy Run Research Center  
23 (Tyl, 1989). Pregnant New Zealand white rabbits (15/group) were exposed to 0, 1,021,  
24 4,058, and 8,021 ppm MTBE, 6 h/day, during Gestational Days 6 to 18. No developmental  
25 toxicity was evident, although maternal toxicity occurred at 4,058 and 8,021 ppm.

26 Biles et al. (1987) conducted a one-generation reproductive toxicity investigation of  
27 Sprague-Dawley rats (15 males, 30 females/group) exposed to MTBE concentrations of 0,  
28 290, 1,180, and 2,860 ppm (males) and 0, 300, 1,240, and 2,980 ppm (females), 6 h/day,  
29 5 days/week, during the premating interval (12 weeks for males, 3 weeks for females).  
30 Males (F0 generation) continued to be exposed during and between matings, while F0

1 females were exposed 7 days/week on Days 0 to 21 of gestation and 5 days/week on days  
2 5 to 20 of lactation. After unexposed litters (F1a) were weaned, the F0 males and F0  
3 females underwent another mating period with the same exposure regimen to produce a  
4 second litter (F1b). The F0 males were sacrificed after this mating period and females were  
5 sacrificed after the end of F1b weaning. Thus, F0 males were exposed overall to MTBE for  
6 approximately 28 weeks and F0 females for 16 weeks. Histopathologic examination revealed  
7 an increased incidence, although not concentration-dependent, of dilated renal pelvises in the  
8 dams. The pup viability indices at birth were slightly, but significantly, decreased in the  
9 second litters of the dams exposed to 1,240 (95.5%; 278/291) and 2,980 ppm (95.5%;  
10 234/245) groups compared to second litters of control dams (99%; 292/295).

11 Neeper-Bradley (1991) conducted a two-generation reproduction study in CD (Sprague-  
12 Dawley) rats. Male and female rats were exposed to mean MTBE concentrations of 0, 402,  
13 3,019, and 8,007 ppm over two generations. The F0 animals (25/sex/concentration) were  
14 exposed for 10 weeks, and then bred once to produce F1 litters. Reproductive parameters  
15 were not affected in either of the two parental generations despite evident parental toxicity at  
16 3,000 and 8,000 ppm.

17 Subacute and subchronic oral toxicity studies have been conducted in male and female  
18 Sprague-Dawley rats (Robinson et al., 1990). In the subacute portion of the study, rats were  
19 exposed for 14 consecutive days to 0, 357, 714, 1,071, or 1,428 mg MTBE/kg/day.  
20 Exposure to 1,428 mg/kg resulted in profound anesthesia, with recovery within 2 h.  
21 Significantly decreased body weight gain occurred at 714 mg/kg in males and in both males  
22 and females at 1,071 and 1,428 mg/kg. In females, relative lung weight was decreased at all  
23 dosage groups, and relative thymus weight was decreased at the highest dosage, while  
24 relative kidney and brain weights were increased at the highest dosage. In males, relative  
25 liver weight was increased at the highest dosage, and relative kidney weight was increased at  
26 the highest two dosages. With the exception of an increase in renal tubular nephropathy  
27 characterized by increased hyaline droplets in proximal tubular epithelial cells, histologic  
28 examination did not reveal target organ toxicity. In the subchronic portion of the study, rats  
29 were exposed for 90 consecutive days to 0, 100, 300, 900, 1,200 mg MTBE/kg/day.  
30 Profound anesthesia, with recovery within 2 h occurred at 1,200 mg/kg. Final body weight

was decreased in females exposed to 1,200 mg/kg. Relative kidney weight was increased in both females and males at 900 and 1,200 mg/kg and in females at 300 mg/kg. Relative liver weight was increased in males at 1,200 mg/kg and in males and females at 900 mg/kg. In males and females, serum blood urea nitrogen was decreased; and in males serum creatinine levels were decreased at all dose levels. Small, but statistically significant increases in serum cholesterol levels were seen in females at all dose levels and in males at 900 mg/kg. Microscopically, tissues appeared normal with the exception of changes consistent with hyaline droplet nephropathy in treated male rats.

Mice exposed to 0.1 mL/kg gasoline plus MTBE by ip injection evidenced increased barbiturate-induced sleep time, reduced spontaneous motor activity, and slight disturbances in motor coordination (SNAMPROGETTI, 1980). These effects suggest possible neurotoxic, hepatotoxic, and nephrotoxic properties.

Chronic toxicity testing of MTBE, currently in progress under Section 4 of TSCA, is expected to provide information on its potential for carcinogenic effects.

#### **6.2.2.1.2 Ethyl-Tertiary-Butyl Ether**

No information on the health effects of ETBE was found by an extensive on-line search of the literature of all major automated biological and medical data bases and all accessible chemical industry data bases (1966 through 1989; all languages). Because it is the next higher homologue of MTBE, ETBE may produce effects similar to those produced with MTBE.

#### **6.2.2.2 Ecosystem Effects**

##### **6.2.2.2.1 Terrestrial Effects**

Ethanol, methanol, MTBE, and ETBE will serve as fuel extenders of gasoline. Exhaust products resulting from the combustion of ethanol-gasoline blends include ethanol, acetaldehyde, acetic acid, CO, and NO<sub>x</sub>. Products of ecological interest from ether blends include MTBE and ETBE. Anticipated atmospheric transformation products from photochemical reactions are PAN, O<sub>3</sub>, and formaldehyde. The ecological effects of CO, NO<sub>x</sub>, PAN, and O<sub>3</sub> are documented (Runeckles, 1986). The potential ecological effects of



methanol and ethanol pollutants are discussed in Chapters 3 and 4, respectively. The potential ecological effects of MTBE and ETBE are not known and need to be identified through research.

#### **6.2.2.2.2 Aquatic Effects**

Reformulated gasolines will involve addition of oxygenates (alcohols, ethers) and changes in the relative proportions of current gasoline components (especially the aromatic fraction). The toxicity of MTBE and ETBE to aquatic organisms has not been reported, but based on their hydrophobicity, these ethers probably have less toxicity than most gasoline components, but greater toxicity than alcohols. The aromatic fraction of gasoline is disproportionately represented in the water-soluble fraction that is often related to toxicity, so changes in the aromatic fraction also are expected to alter toxicity. The interaction of these changes on the availability and toxicity of fuel mixtures is uncertain.

### **6.2.3 Global Warming**

All the oxygenates considered have ethanol or methanol as the production product or serve as a feedstock (in the case of the ethers). Thus, the earlier discussion of RITGs related to ethanol and methanol is very pertinent to the extenders. The RITGs related to combustion of ethers are largely unknown.

### **6.2.4 Risk Prevention/Mitigation**

#### **6.2.4.1 Stationary Sources**

Control techniques for most of the stationary gasoline VOC emission and discharge sources are available. The primary concern, however, is the lack of knowledge of the impact of the oxygenate blends on control-device effectiveness for stationary VOC emission points associated with gasoline storage, distribution, and marketing. Oxygenates may have a substantial adverse impact on existing conventional control-system capacities/capabilities (e.g., carbon adsorption and add-on controls).

As with methanol, the concerns about loss of containment of reformulated gasolines in USTs apply. Even though these fuels are more closely related to conventional petroleum

1 fuels, differences in the physicochemical properties may warrant an evaluation of specific  
2 leak prevention, leak detection, and corrective action technologies, as discussed in  
3 Section 3.2.4 under methanol risk prevention/mitigation technologies.

4 A potential benefit of reformulated gasolines is the opportunity for using the displaced  
5 gasoline hydrocarbon fractions in more efficient stationary combustors. For example, the  
6 volatile paraffins (butanes and pentanes) responsible for elevated motor vehicle evaporative  
7 emissions and the aromatics (benzene, toluene, and xylenes) responsible for toxic tailpipe  
8 emissions could be "clean-burning" fuels in high-efficiency, low-emission combustors such as  
9 power plant and industrial boilers.

#### 11 **6.2.4.2 Mobile Sources**

12 As discussed for methanol fuel, the durability of production motor vehicle emissions  
13 control systems that are important to air quality must be monitored as vehicle miles  
14 accumulate. The hazardous emissions of interest will depend upon the oxygenate blending  
15 component. For example, formaldehyde emissions could be important with methanol and  
16 MTBE blends, and acetaldehyde could be important with ethanol and ETBE blends.

#### 18 **6.2.4.3 Fuel Transport Sources**

19 Aquatic ecosystems will be impacted by water discharge of pollutants and accidental  
20 spills/leaks. Control technology development of fuel tanks, barges, and pipelines to reduce  
21 accidental spills and leakage will reduce the entry of reformulated fuels and their components  
22 into aquatic ecosystems. Insofar as spills pose adverse risks, then cleanup technologies must  
23 be improved through research and development.

### 26 **6.3 RESEARCH NEEDS**

27 In addition to previously discussed alternatives for replacement of petroleum distillates,  
28 a category of fuels, commonly referred to as "clean-burning" reformulated gasolines, is  
29 emerging. These fuels generally use oxygenated organic compounds (sometimes called  
30 gasoline extenders) to change the combustion characteristics of gasoline in spark-ignition

1 engines. These substances enhance gasoline octane and reduce tailpipe hydrocarbon and CO  
2 emissions in several vehicle categories. The impact on emissions is more pronounced with  
3 the older vehicles, which are typically noncatalyst and oxidation catalyst vehicles. Closed-  
4 loop three-way and adaptive-learning three-way vehicles, which represent the bulk of vehicles  
5 marketed today, have less emissions response, depending on operating conditions and the  
6 amount of fuel-rich combustion. Other fuel variables being manipulated include aromatic  
7 and olefinic hydrocarbon fractions and volatility. The octane-enhancing characteristics of the  
8 oxygenates permit reduction of fuel aromatic and olefinic hydrocarbons. Reduced volatility  
9 will result in reduced evaporative emissions (diurnal, hot soaks, and running-loss).  
10 Variations of possible formulations are currently being evaluated by the automobile and  
11 petroleum industries to optimize choices regarding both vehicle performance and positive  
12 environmental impact.

13 Methyl-tertiary-butyl ether has made the greatest market penetration in recent years,  
14 with ethanol of secondary importance. Ethyl-tertiary-butyl ether may gain market importance  
15 in the future. These reformulated fuels, with improved gasoline motor vehicle emissions  
16 control technology, are expected to compete with previously discussed alternatives for  
17 positive environmental impact. The following research needs address uncertainties that are  
18 important to the assessment of possible change to public health and the environment resulting  
19 from implementation of these advancing technologies.

20 In this section, broad research objectives for each key element of risk assessment are  
21 described and priorities are assigned. The priorities across all fuels were considered with the  
22 understanding that future knowledge, technology changes, and market factors are likely to  
23 have some impact on them. One major difficulty in developing a prioritization scheme is  
24 accounting for scientific pacing. For example, in many cases, dose-response information is a  
25 higher priority than hazard identification per se, but hazard-identification research must  
26 proceed first to guide the dose-response work. Due to the extent of the uncertainties about  
27 fuels, the approach chosen for prioritization would, in this example, rank hazard-  
28 identification research higher than dose-response research. Each research objective is coded  
29 with one of the following prioritization phrases:  
30

- Priority 1 for the next 2 to 4 years. This is the highest priority research over the near term. The research generally entails resolution of major issues of known concern, identification of new issues likely to be critical to risk assessment/risk reduction, crucial methods development that paces much other work, and major mandates of the CAAAs. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished within that time frame.
- Priority 2 for the next 2 to 4 years. This is medium priority research over the near term. Work in this category generally entails pursuing key issues that have importance for either the exposure or effects phase of hazard identification or for evaluating key elements of risk reduction. Gaining such information will certainly be important, but is less crucial than work under Priority 1. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished within that time frame.
- Priority 3 for the next 2 to 4 years. Although this research is of lower priority relative to other categories, it is still critical to development of comprehensive baseline information for all fuels. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished within that time frame.
- Longer term priority. This research is essential to developing comprehensive, quantitative risk assessments and/or risk reduction approaches. However, its initiation is paced by the completion of earlier research. When major elements of the earlier research are completed, it will be possible to more definitively prioritize this category of work.

### **6.3.1 Exposure Assessment**

#### **6.3.1.1 Source Characterization**

##### ***6.3.1.1.1 Stationary Source Characterization***

The primary concerns are the sources and levels of emissions/discharges that will result at all stages of processing, from the extraction of feedstocks through the refining, storage, and transportation of the reformulated fuels (alcohol, MTBE, or ETBE). Although many of these discharges have been quantified or qualitatively described to various degrees, data are not now available to develop quantitative health and ecosystem risk assessments.

The major issue at hand is the impact of the oxygenates on the existing stationary sources and their associated VOC-control systems. The limited data available indicate the

1 potential for greatly increased stationary source emissions stemming from a variety of causes,  
2 such as vapor pressure effects and modified adsorption characteristics in carbon adsorption  
3 control systems. Emissions of VOCs may have already increased substantially, considering  
4 the existing market penetration of the oxygenates and their use in existing storage,  
5 transportation, and marketing systems. Although some neat fuels will likely be handled in  
6 new, specially designed systems, the blends are not likely to utilize existing handling  
7 equipment. Existing control systems were not designed specifically for blends.

8 An additional issue is the need to evaluate and compare emerging fuel-reformulation  
9 options, contrasting their overall environmental emission characteristics. The new  
10 reformulated gasolines being advanced by industry may substantially enhance the  
11 environmental picture for gasoline by stripping out additional volatile and hard-to-burn  
12 high-molecular-weight compounds and by removing toxics such as benzene and other  
13 problem substances. For stationary sources, reduction in volatility and removal of toxic  
14 components will do much to reduce evaporative emissions of O<sub>3</sub> precursors and toxics.  
15 These substances can be shifted to other high-efficiency, continuous-combustion processes  
16 and be used there as clean fuel to displace dirtier fuels like fuel oil.

17  
18 Research Objectives:

- 19  
20 1. Develop modified emissions factors for production, distribution, and utilization for  
21 the sources listed in Chapter 3 for methanol fuels. (Priority 1 for the next  
22 2 to 4 years.)  
23
- 24 2. Determine the impact of reformulated gasolines on existing controls, where use of  
25 these fuels may result in increased emissions. (Priority 1 for the next  
26 2 to 4 years.)  
27
- 28 3. Determine the overall net change in VOCs and other multimedia emissions/  
29 discharges resulting from one or more key scenarios of market penetration.  
30 (Priority 1 for the next 2 to 4 years.)

**6.3.1.1.2 Mobile Source Characterization**

The only alcohol-gasoline blend currently being marketed in the United States is 10% ethanol, 90% gasoline by volume. Federal government policy permitting an ethanol blend to have a 1 psi volatility rise from the base gasoline and providing a price subsidy amounting to about \$0.60 per gallon of ethanol have been necessary for limited market penetration (i.e., 7% of 1988 national gasoline sales). Market penetration has been greater in select areas of the country. For example, ethanol blends accounted for 20 to 40% of gasoline sales in midwestern states such as Kentucky, Nebraska, Illinois, and Iowa.

Characterization of emissions from motor vehicles using this fuel will be structured similarly to that described for methanol (see Chapter 3). Because the impact of these fuels on emissions is very sensitive to the design of emissions control systems, a variety of vehicles representative of emissions control categories dominating U.S. fleets must be examined. Driving conditions (speed, ambient temperature, etc.) should be varied, and both regulated and selected unregulated emissions should be examined. Because this fuel is used primarily in light-duty vehicles (use in heavy-duty gasoline trucks is considered of little importance), only passenger cars and light-duty trucks should be examined. The emissions can then be contrasted with classical gasoline fuels.

As previously discussed, MTBE has enjoyed significant success in the market place as a gasoline-blending component, and with continued government ethanol subsidy or improved ethanol production economics, ETBE could grow in market importance. Gasoline reformulations are expected to have lower aromatic and olefinic hydrocarbon fractions as well as lower volatility (less C<sub>4</sub> and C<sub>5</sub> paraffinic hydrocarbon). As with ethanol-gasoline blends, the impact of these fuels on emissions will vary with the emission-control system design and operating condition. Tailpipe, evaporative, and refueling emissions from vehicles representative of the U.S. fleet must be examined under varied operating conditions (speed, ambient temperature, etc.). The emission rates of both regulated and selected unregulated compounds should be determined and contrasted with classical gasoline fuels.

Emissions characterization must be structured to provide the data base necessary to estimate the potential impact of these fuels on air quality (i.e., O<sub>3</sub>, CO, NO<sub>2</sub>, and particles),

as well as on other important environmental issues such as global climate change and toxic compound exposures.

Research Objective:

1. Characterize (composition and rate, in grams per mile) emissions from motor vehicles using oxygenate-gasoline blended fuels. Test fleets need to be varied to represent vehicle families most prevalent on U.S. roadways. Greater emphasis should be placed on recent, rather than older, vehicles. If gasoline composition is to be changed significantly (e.g., low aromatics), large amounts cannot be produced quickly. The most recent vehicles will better reflect the emission changes likely to be found in the future when large amounts of reformulated gasoline could be marketed. (Priority 1 for the next 2 to 4 years.)

### 6.3.1.2 Environmental Fate

#### 6.3.1.2.1 Air Fate

As stated earlier, when alcohol-gasoline blends are photooxidized in the presence of  $\text{NO}_x$ , they show a slight decrease in  $\text{O}_3$ -forming potential. At higher  $\text{VOC}/\text{NO}_x$  ratios, typically found in most cities ( $\text{VOC}/\text{NO}_x$  about 10/1), little difference is observed. Laboratory smog chamber and modeling experiments are needed to understand the  $\text{O}_3$ - $\text{VOC}/\text{NO}_x$  relationships. Additional needs include transformation product studies and testing the reaction of mixtures for mutagenic activity. The effects on CO reduction must also be considered.

Like alcohol-gasoline blends, ether blends are not expected to produce significant changes in  $\text{O}_3$ -forming abilities when irradiated in the presence of  $\text{NO}_x$ ; however, some unusual and perhaps new hazardous compounds may arise. Thus, smog-chamber studies to characterize both the smog-forming potential of exhaust gases from MTBE- and ETBE-gasoline-powered vehicles are recommended. Mutagenicity testing is also recommended. Urban and regional models should be used to note the effect of ether blends on air quality.

## Research Objectives:

1. Characterize products from the photooxidation of emissions from motor vehicles using oxygenate-gasoline blends. (Priority 1 for the next 2 to 4 years.)
2. Use airshed and regional models to determine effect on air quality. (Priority 1 for the next 2 to 4 years.)

**6.3.1.2.2 Soil and Groundwater Fate**

Significant advances have recently been made in our knowledge of the environmental dynamics of pollutants as components of complex mixtures. To date, the focus has been on mixtures of water and completely miscible organic solvents; however, this work has established a theoretical framework by which more complex mixtures (i.e., alcohol-gasoline-water) may be studied (Rao et al., 1985; Nkedi-Kizza et al., 1985; Fu and Luthy, 1986). In fact, limited research on the chemodynamics of hydrophobic pollutants in mixtures of completely and partially miscible organic solvents is currently in progress. Some of the results of this research will have direct application to alcohol-gasoline blends, but additional research that specifically targets these fuel reformulations should be conducted.

Because many constituents of petroleum-distillate fuels are only partially miscible in water, gasoline spills often result in subsurface contaminant plumes that consist of multiple liquid phases. Unlike miscible fluid flow, the physical processes controlling multiphase flow are not well understood. Anecdotal evidence suggests that partially miscible fluids may move through porous media as continuous phases or as discontinuous components of the bulk mobile phase. In both cases, an understanding of the physics of the total flow system as well as of the chemical-phase equilibria is essential if reasonable predictions are to be made about the environmental consequences of the use of these fuels. Several current research efforts are addressing the problem of multiphase contaminant flow; however, for the purposes of this research initiative, these efforts should be expanded to include the influence of fuel extenders on both the physics and chemistry of systems.



1 For even relatively simple waste mixtures, the pollutant carrier (bulk-fluid phase) is  
2 typically assumed to be compositionally constant over time. For many, if not most,  
3 subsurface contamination problems concerning fuels, this assumption is not realistic. The  
4 character of the solvent phase will change with time, and these changes may have a  
5 significant impact on the mobility and fate of individual pollutants, particularly when solvents  
6 covering a broad range of physical and chemical properties are present. Research to study  
7 the effects of changing fuel composition on the mobility of pollutants is needed.

8 Biological transformations have been shown to be important factors in the ultimate fate  
9 of many petroleum products in soil and ground water. The effect of methanol and ethanol on  
10 potential biotransformation of gasoline constituents in the subsurface should be investigated.

11 Because they are polar organic solvents having relatively high aqueous solubilities,  
12 MTBE and ETBE may be expected to significantly influence the sorption and transport of  
13 nonpolar organic chemicals. The environmental conditions and spatial range for which this  
14 effect could be expected when these ethers are included in mixtures of petroleum-based fuels  
15 are unknown. Research to quantify the magnitude and extent of this effect is needed.

16 Given the aqueous solubilities of these ethers, aqueous-phase transport of these  
17 compounds is expected to be rapid, even in the presence of multiphase plumes. Thus, if  
18 these chemicals are biologically recalcitrant, as suggested by limited experimental data, they  
19 could exhibit a substantial threat for groundwater contamination when released into the soil  
20 as a constituent of gasoline. Much of this scenario is speculative and requires further  
21 investigation for confirmation.

#### 22 Research Objectives:

- 25 1. Assess the impact of reformulated gasolines on the potential for groundwater  
26 contamination and resultant pollutant exposure. (Priority 2 for the next  
27 2 to 4 years.)
- 28 2. Characterize the impacts of oxygenates on the fate and transport of fuel  
29 components. (Priority 2 for the next 2 to 4 years.)  
30

### 6.3.1.2.3 *Surface Water Fate*

Surface water fate issues for reformulated gasolines are similar to those for conventional gasoline (Section 2.3.1.2.3) the primary difference being the unknown impact of oxygenates on the fate of other hydrocarbon fuel components. The addition of alcohols or ethers to petroleum products could influence the bioavailability of the hydrocarbons. Hydrocarbons are hydrophobic and less dense than water and, therefore, do not readily mix down into the water column; instead, they form surface slicks. This greatly influences both the fate and effects of the oil because some of the hydrocarbons rapidly evaporate from the surface and others are photochemically altered.

Alcohols and ethers that are added to petroleum could influence the behavior of the petroleum, possibly acting like dispersants, causing the fuel compounds to mix more readily with seawater. This will affect the transport and weathering of the compounds and will change the exposure of marine organisms in the area. A process such as this could make the oil more biologically available to some species. Studies to determine if the addition of oxygenates influences the bioavailability of petroleum and its toxicity to marine organisms are proposed.

#### Research Objectives:

1. Determine if the presence of ethers and alcohols alters the bioavailability of petroleum hydrocarbons to marine organisms. (Priority 1 for the next 2 to 4 years.)
2. Determine the fate of MTBE and other fuel oxygenates in marine mesocosms. (Priority 2 for the next 2 to 4 years.)

### 6.3.1.3 *Exposures*

#### 6.3.1.3.1 *Human Exposures*

The exposure research plan for ethers includes studies similar to those described for methanol (Chapter 3). If acetaldehyde, formaldehyde, and acetone become significant

1 transformation products, future studies to determine the impact of these changes on estimates  
2 of public health risks may be required.

3 The exposure research for alcohol blends will be similar to that discussed for methanol  
4 (and ethanol), except that the specific target pollutants and concentration levels of concern  
5 may change. The research program should include (1) developing the necessary sampling  
6 and analytical procedures, (2) conducting measurement studies in locations impacted by  
7 mobile source emissions, and (3) exposure modeling. The actual need for monitoring  
8 studies, except for transformation and fate, may not be of major importance if testing does  
9 not establish significant changes in emissions that could result in potential human exposures  
10 of concern.

11  
12 Research Objectives:

- 13
- 14 1. Exposure assessment of the identified pollutants that are related to reformulated  
15 gasoline, including MTBE and ETBE. (Priority 1 for the next 2 to 4 years.)  
16
  - 17 2. Development and application of validated human exposure models to predict  
18 changes in exposure resulting from reformulated gasoline. (Priority 1 for the next  
19 2 to 4 years.)  
20

21 **6.3.1.3.2 Biota Exposures**

22 Research on aquatic exposures to reformulated gasolines should involve studies similar  
23 to those described for conventional fuels. The exposure assessment for reformulated  
24 gasolines will differ from that for conventional fuels due to consideration of the effects on  
25 exposure concentrations of added oxygenates and changes to the relative amount of aromatics  
26 and other gasoline components.

27 Reformulated-fuel pollutants have the potential to impact terrestrial biota through  
28 atmospheric exposure. Biota effects will depend upon the pattern of exposure (e.g., rate,  
29 duration, season, and concentration), pollutant toxicity, and species sensitivity. Research  
30 should focus initially on questions regarding MTBE and ETBE deposition, exposure, and

1 toxicity. Wet/fog and gaseous deposition should be evaluated for importance relative to  
2 pollutant delivery to vegetation.

3  
4 Research Objectives:

- 5
- 6 1. Develop example cases for reformulated fuel spills and leakages to freshwater and  
7 estuarine ecosystems that include characterizations of system morphometry,  
8 organism types and locations, and physical/chemical properties that regulate fate  
9 and effects. Apply source scenarios and fate/transport models to these test cases to  
10 develop exposure time series for target organisms. (Priority 1 for the next  
11 2 to 4 years.)  
12
  - 13 2. Provide exposure assessments of MTBE, ETBE, and other reformulated-fuel  
14 pollutants to terrestrial biota within the South Coast Air Basin, CA. (Priority 1 for  
15 the next 2 to 4 years.)  
16

17 **6.3.1.4 Analytical Methodology**

18 Analytical methods must be developed, upgraded, and/or evaluated for measurement of  
19 source emissions, atmospheric transport and transformation, and population (human and  
20 ecosystem) exposure, as necessary, to support assessment of the impact of varied fuel  
21 formulations on risk to public health and welfare.

22 Procedures suitable for certification of regulated source emissions (THC, NMHC, CO,  
23 NO<sub>x</sub>, and particles) at levels mandated by the CAAAs and for the detailed speciation  
24 necessary to support estimation of impact on O<sub>3</sub> and toxics air quality will be required. The  
25 procedures must permit accurate and precise determination of large numbers of compounds in  
26 very complex mixtures.

27 Most of the analytical methods for ambient air monitoring are expected to be similar to  
28 those employed with conventional fuels. However, some additional methods development  
29 may be needed to monitor the oxidation products resulting from the degradation of MTBE  
30 and ETBE. Methods development for measuring MTBE, ETBE and ethanol may be required

1 to adequately characterize exposure patterns. Determination of this need will be dependent  
2 upon emission characterization studies and exposure calculations based upon estimated  
3 exposure levels.

4  
5 Research Objectives:

- 6
- 7 1. Develop/upgrade/qualify analytical procedures for speciation of O<sub>3</sub>-precursor and  
8 toxic motor vehicle emissions. (Priority 1 for the next 2 to 4 years.)  
9
  - 10 2. Validate classical procedures for measurement of organic carbon, CO, NO<sub>x</sub>, and  
11 CO<sub>2</sub> emissions from motor vehicles fueled with reformulated gasoline at  
12 certification emission rates (concentrations) permitted by the CAAAs; identify  
13 problems, provide corrective actions, and/or develop new, simpler, lower cost  
14 acceptable procedures. Study the impact of oxygenated organic additives (MTBE,  
15 ETBE, and ethanol) on THC and/or NMHC determination. (Priority 1 for the  
16 next 2 to 4 years.)  
17
  - 18 3. Develop/upgrade/evaluate analytical procedures for measurement of real-time  
19 ambient air toxics and ambient measurements of ethanol, methanol, and  
20 oxygenated blends for use in characterizing ambient patterns. (Priority 2 for the  
21 next 2 to 4 years.)  
22
  - 23 4. Develop/upgrade/evaluate analytical procedures for measurement of exposure to  
24 compounds potentially associated with reformulated fuels containing methanol and  
25 ethanol (e.g., O<sub>3</sub>, methanol, ethanol, formaldehyde, methyl nitrite, DMS,  
26 aldehydes, and ethyl nitrite), including personal and microenvironmental monitors.  
27 (Priority 2 for the next 2 to 4 years.)  
28
  - 29 5. Develop procedures for continuous or real-time measurement of selected toxics in  
30 transient motor vehicle emissions. (Priority 3 for the next 2 to 4 years.)

## 6.3.2 Effects Assessment

### 6.3.2.1 Human Health Effects

Like the assessments of other fuels, a risk assessment of reformulated fuels requires knowledge of the potential effects of the inhaled vapors and combustion products, with and without atmospheric transformation. However, the market penetration of reformulated fuels is of great importance. Given the number of different reformulated gasolines that are anticipated to be developed, health-related work on whole emissions of specific reformulated fuels must await the outcome of formulation decisions and research on emissions and exposure characterization. In the interim, efforts to understand more about the potential effects of the primary extenders (i.e., ethanol, MTBE, and ETBE) will be the focus of the strategy for reformulated fuels. Ethanol health research has been discussed earlier (see Section 4.3.2.1); the health research needs for ethers are presented here.

The high priority research needs for the ethers are: (1) the evaluation of pharmacokinetic and structure-activity data to facilitate interpretation of newly developed toxicity testing data and (2) the development of pharmacokinetic models to predict human tissue burdens under various exposure scenarios of concern. In the future, when the most likely blends of the reformulated fuels are determined, the evaluation of the mutagenic and toxicologic potential of the whole reformulated fuels and their combustion and transformation products will also be a high priority.

Few health effects data on the ethers are currently available. Comprehensive identification of research needs will require evaluation of health data currently being collected under a Toxic Substances Control Act (TSCA) rest rule. (Results of some of the shorter duration MTBE studies are currently available; however, all the studies have not been reported.) The limited available data on MTBE suggest the potential for toxicity. Human data on parenteral exposure to MTBE (used as a therapeutic agent) indicate that toxicity may be observed at high blood levels of MTBE, with the nervous system, liver, kidney, immune system, and hematopoietic system as target organs of concern. Animal toxicology studies with MTBE have been conducted by both the oral and inhalation routes of exposure and indicate the potential for neurotoxicity, reproductive and developmental toxicity, and hepatic and renal effects. Data from pharmacokinetic studies also suggest that possible gender

1 differences occur in the metabolism of MTBE, that saturation of metabolism occurs at high  
2 dose levels of MTBE, and that MTBE may induce its own metabolism. No data on ETBE  
3 are currently available.

4  
5 Research Objectives:

- 6  
7 1. Perform pharmacokinetic and structure-activity evaluations, using existing data  
8 where possible, to facilitate interpretation of the new TSCA data on MTBE.  
9 Develop pharmacokinetic models for acute and repeated short-term exposure to  
10 MTBE and ETBE to predict human tissue burdens under various exposure  
11 scenarios of concern. The possibility of saturation of metabolism at high  
12 concentrations and gender differences in metabolism should be evaluated as part of  
13 this effort. Subsequently, determine the impact of co-exposure to gasoline on the  
14 pharmacokinetic behavior of MTBE and ETBE. (Priority 1 for the next  
15 2 to 4 years.)  
16
- 17 2. Compare the mutagenicity of the combustion and atmospheric transformation  
18 products of reformulated fuels relative to conventional fuels and other alternative  
19 fuels using short-term in vitro and in vivo assays and then use this information to  
20 determine the need for chronic bioassays. (Priority 1 for the next 2 to 4 years.)  
21
- 22 3. Perform additional dose-response studies on MTBE and ETBE, if warranted, based  
23 on the results obtained from Objective 1 and the evaluation of new TSCA data.  
24 The design of additional health effects studies would be guided by the results from  
25 the pharmacokinetic studies and the evaluation of existing health data. (Priority 2  
26 for the next 2 to 4 years.)  
27
- 28 4. Conduct chronic inhalation bioassays of reformulated fuels, assessing both cancer  
29 and noncancer endpoints, if improved estimates for emissions, exposure, and  
30 market penetration warrant. (Priority 3 for the next 2 to 4 years.)

### 6.3.2.2 Ecosystem Effects

#### 6.3.2.2.1 Terrestrial Effects

The effects of MTBE and ETBE on terrestrial ecosystems are not known; therefore, ecosystem effects research is justified. The research projects are quite similar to those presented for methanol (Section 3.3.2.2.1) and, therefore, will not be repeated here.

#### Research Objectives:

1. Evaluate the responses of plants to MTBE and ETBE exposures (dry and wet/fog), individually and in binary combinations with O<sub>3</sub> at various concentrations, to assess the sensitivity of plant process functions. (Priority 1 for the next 2 to 4 years.)
2. Evaluate the effects of MTBE and ETBE on plant mesocosms with temperature and water stress variations. (Longer term priority.)
3. Evaluate the use of biomarkers for monitoring the effects of ETBE and MTBE on vegetation as the fuel additives gain prominence in the South Coast Air Basin, CA. (Longer term priority.)

#### 6.3.2.2.2 Fresh Water Effects

Research on reformulated gasoline will be an extension of research for conventional fuels. Attention will be given to a broader range of gasoline composition and to the addition of oxygenates on fuel bioavailability and toxicity. In the latter part of this research program, if warranted by earlier work, tests on these fuels will be conducted in experimental ecosystems to further establish and confirm ecological effects.



Research Objectives:

1. Evaluate the toxic effects on various freshwater aquatic organisms of oxygenates added to reformulated fuels and of a broader range of gasoline compositions. (Priority 2 for the next 2 to 4 years.)
2. Develop dose-response models suitable for application to various accidental release exposure scenarios. (Priority 2 for the next 2 to 4 years.)

#### **6.3.2.2.3 Marine Effects**

With the anticipated switch to alternative fuels or fuel mixtures, large amounts of different or new chemicals are likely to be transported through marine systems; therefore, a different suite of chemical compounds will be released to the marine environment. In general, the fate and effects of these compounds on marine ecosystems have not been tested. Methyl-tertiary-butyl ether is one of the compounds currently being used as a fuel extender, and its use is likely to increase. This is the first compound that should be tested. Other compounds would be selected for testing after consideration of their chemical properties and projected usage.

Each of the compounds to be tested should be added to marine mesocosms, and the fate and effects in these systems documented. This would provide information on the movement of these chemicals in marine ecosystems and measurements of their degradation rates. Any changes in the composition or functioning of the mesocosm communities would be documented.

Toxicity tests using sensitive marine species should be conducted, and marine water quality criteria for each compound developed. Bioaccumulation studies to determine if these chemicals can be accumulated by marine biota should also be undertaken.

A considerable body of literature on the fate and effects of the petroleum hydrocarbon fuels, such as No. 2 Fuel Oil, in the marine environment is available. Much of this information will be appropriate for assessing the potential impact of fuel blends. Additional

studies on the behavior and effects of petroleum-alcohol and petroleum-ether mixtures are needed, as the presence of the oxygenates could influence the behavior of the hydrocarbons.

Research Objectives:

1. Measure the toxicity of MTBE, other fuel oxygenates, and reformulated gasoline fuels to several marine species. (Priority 1 for the next 2 to 4 years.)
2. Measure the bioaccumulation of MTBE and other fuel oxygenates by marine organisms. (Priority 3 for the next 2 to 4 years.)

### 6.3.3 Global Warming

The research described on source characterization, environmental fate in ambient air, and risk reduction/control technology will result in identification of changes in RITGs resulting from the manufacture and combustion of reformulated gasolines. The research description will not be repeated here. Increased use of ethanol (from biomass) could reduce emissions of CO<sub>2</sub>. Defining means for dealing with methane emissions will be a high priority for cases in which emissions may be increased because of its use as a feedstock for MTBE and methanol.

Research Objective:

1. Identify and characterize RITGs affected by reformulated gasoline production and use. This information will be used as an input to global climate models being developed and applied under the Global Climate Research Program. (Priority 1 for the next 2 to 4 years.)

## 6.3.4 Risk Prevention/Mitigation

### 6.3.4.1 Stationary Sources

Risk reduction research will focus on specific stationary source prevention and control opportunities related to reformulated gasolines.

For USTs, much of the previously completed research on gasoline (in the areas of leak prevention, leak detection, and corrective action) will be directly pertinent. Research direction will depend upon an evaluation of the differences in physicochemical properties between gasoline and the reformulated gasolines. In some areas, existing research has already shown that differences may be small. For example, the solubility of hydrocarbons in water that is in contact with a MTBE/gasoline blend is not much different than with pure gasoline. Research projects to reevaluate in-tank and external-tank leak detection methods can likely be modest in scope because of the similarity in properties. The area of corrective action, however, has more uncertainty. Here, the highly soluble gasoline additives could significantly alter the scope and objectives of cleanup actions. Methyl-tertiary-butyl ether, for example, would be expected to travel more rapidly and further than hydrocarbon components.

#### Research Objectives:

1. Develop control technology design and operation information to optimize existing stationary source controls, especially for emissions from gasoline storage, distribution, and marketing. Research on carbon adsorption will be especially important because of the potential adverse impacts of oxygenates on the capacity of existing carbon-based controls. (Priority 1 for the next 2 to 4 years.)
2. Assess the overall potential for fuel reformulation options that will maximize stationary source environmental benefits at a reasonable cost. This will provide an evaluation of U.S. and worldwide opportunities for shifting certain hydrocarbon fractions to avoid environmentally damaging (misplaced) usage. For example, this would include evaluating the potential for removal of volatiles causing evaporative

emissions, of high molecular weight hydrocarbons causing tailpipe emissions, and of toxics such as benzene as a part of the refining process. These fractions should then be evaluated for other nonpolluting uses (e.g., at power plants or other high-efficiency continuous-combustion processes). (Priority 2 for the next 2 to 4 years.)

3. For USTs, leak detection research is needed to confirm that existing in-tank and external systems are sufficient; and site investigation and corrective action technologies must be reevaluated in light of the changed physicochemical properties, especially the greater groundwater mobility of the oxygenated additives. (Priority 1 for the next 2 to 4 years.)

#### **6.3.4.2 Mobile Sources**

Previously defined motor vehicle emissions effects associated with use of reformulated gasolines should be evaluated as consumer mileage accumulates. The CO benefit of oxygenate blends, compared to that of gasoline, could conceivably improve with control system deterioration. For example, if a closed-loop three-way catalyst oxygen sensor fails, the vehicle air-fuel ratio will likely experience a fuel-rich shift. This condition would favor CO benefit with oxygenated blends.

#### **Research Objective:**

1. Assess the impact of consumer mileage accumulation on motor vehicle emissions associated with the use of reformulated gasoline fuels. (Priority 1 for the next 2 to 4 years.)

#### **6.3.4.3 Fuel Transport Sources**

Research needed to improve containment during transport of liquid fuels is similar to that of other chapters (e.g., 3.3.4.3)

Research Objectives:

1. Evaluate adequacy of transport system containment of reformulated fuels for preventing major spills and leaks. (Priority 1 for the next 2 to 4 years.)
2. Assess clean-up options to reduce the impact of a reformulated fuel spill on sensitive biota and ecosystems. (Longer term priority.)

## 7.0 SCIENTIFIC ASSESSMENTS

Several interrelated scientific assessment tasks need to be undertaken, including development of comprehensive health and ecosystem assessments of each fuel class, Special Assessment Reports, and workshops/conferences.

The highest priority is to develop comprehensive health and ecosystem assessment reports on conventional fuels and each of the alternative fuels. Such a report on the health effects of diesel emissions is nearing completion (U.S. Environmental Protection Agency, 1990e), and a methanol document has been initiated by ORD's Office of Health and Environmental Assessment. These assessments are needed to provide a complete evaluation of the state of knowledge on each of the fuels so that potential or actual risks can be characterized and the most appropriate research directions can be identified. As discussed earlier, the current data base on health and ecosystem risks is too sparse for comprehensive quantitative assessments, but as research progresses, the preliminary assessments can be revised to incorporate advancements in knowledge.

Periodic Special Assessment Reports will also be prepared because they can be used to focus on specific topics and to transmit new knowledge gained from research more rapidly than can be attained in the Reports to Congress or the comprehensive health and ecosystem assessments. Although these Special Assessment Reports are intended for the EPA Program Offices, they can also provide guidance to research organizations. For example, it appears that adequate information exists to estimate the risks of accidental ingestion of methanol and ethanol fuels in comparison to conventional gasoline. Because even small amounts of ingested methanol can cause blindness and death in children, an assessment of the possibilities of such occurrences is quite important. As another example, source characterization, atmospheric fate, and exposure research are expected to identify changes in exposure to a chemical(s) for which substantial health exposure-response data are available (e.g., O<sub>3</sub>, NO<sub>2</sub>, CO). In such cases, the change in risk will need to be assessed in a Special Report. An ecological risk assessment report could be prepared to assess the current state of knowledge of methanol-fuel production and pollutants (e.g., methanol, formaldehyde) effects

on biota and ecosystems. The emission and atmospheric transport data bases and exposure and ecosystem effects data bases would be used for regional evaluations of potential ecological risks. A Geographic Information System (GIS)-generated framework would help to identify potentially sensitive ecosystems and ecologically adverse risks. Coordination and information flow would occur with other related EPA research programs (e.g., Ecological Risk Assessment Research Program and Global Climate Research Program) within governmental agencies, industry, and universities.

Considerable further efforts are required to gather more detailed information and to identify more specific additional research needs. A series of two to three workshops/conferences is needed. In these meetings, experts from EPA, other federal agencies, industry, academia, and other pertinent national and international groups would be brought together to discuss specific alternative fuels topics. The first workshop would include presentations/discussions of recent research findings, of the Research Strategy, of research priorities, and of the research programs at other institutions. The second workshop most likely would focus on newer scientific findings and future research.

Each research objective below is coded with one of the following prioritization phrases.

- Priority 1 for the next 2 to 4 years. This is the highest priority research over the near term. The research generally entails resolution of major issues of known concern, identification of new issues likely to be critical to risk assessment/risk reduction, crucial methods development that paces much other work, and major mandates of the CAAAs. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished within that time frame.
- Priority 2 for the next 2 to 4 years. This is medium priority research over the near term. Work in this category generally entails pursuing key issues that have importance for either the exposure or effects phase of hazard identification or for evaluating key elements of risk reduction. Gaining such information will certainly be important, but is less crucial than work under Priority 1. Characterizing this work as over the next "2 to 4 years" does not necessarily denote that it can be accomplished within that time frame.

Scientific Assessment Objectives:

1. Provide comprehensive health and ecosystem assessments of conventional fuels and methanol fuels. (Priority 1 for the next 2 to 4 years.)
2. Provide comprehensive health and ecosystem assessments of ethanol fuels, CNG, and reformulated gasoline. (Priority 2 for the next 2 to 4 years.)
3. Conduct expert workshops and conferences to provide a scientific forum for communicating new research findings and identifying issues for further research. Publish the Conference Proceedings. (Priority 1 for the next 2 to 4 years.)
4. Provide Special Assessment Reports to the Program Offices. (Priority 2 for the next 2 to 4 years.)



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