ESTIMATING EXPOSURE TO DIOXIN-LIKE COMPOUNDS

VOLUME I: Executive Summary

NOTICE

Exposure Assessment Group
Office of Health and Environmental Assessment
U.S. Environmental Protection Agency
Washington, D.C.

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FOREWORD

The Exposure Assessment Group (EAG) within the Office of Health and Environmental Assessment of EPA's Office of Research and Development has three main functions: (1) to conduct exposure assessments, (2) to review assessments and related documents, and (3) to develop guidelines for exposure assessments. The activities under each of these functions are supported by and respond to the needs of the various EPA program offices. In relation to the third function, EAG sponsors projects aimed at developing or refining techniques used in exposure assessments.

This document is the first of a three-volume set addressing exposure to dioxin related compounds. The purpose of this document is to provide an Executive Summary of Volumes II and III. Volume II describes the properties, sources, environmental levels and background exposures to dioxin-like Compounds. Volume III presents methods for assessing site-specific assessments of exposure to these compounds. The document is intended to be used as a companion to the health reassessment of dioxin-like compounds that the Agency is publishing concurrently. It is hoped that these documents will improve the accuracy and validity of risk assessments involving this important family of compounds.

Michael A. Callahan
Director
Exposure Assessment Group

PREFACE

In April 1991, the U.S. Environmental Protection Agency (EPA) announced that it would conduct a scientific reassessment of the health risks of exposure to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and chemically similar compounds collectively known as dioxin. The EPA has undertaken this task in response to emerging scientific knowledge of the biological, human health, and environmental effects of dioxin. Significant advances have occurred in the scientific understanding of mechanisms of dioxin toxicity, of the carcinogenic and other adverse health effects of dioxin in people, of the pathways to human exposure, and of the toxic effects of dioxin to the environment.

In 1985 and 1988, the Agency prepared assessments of the human health risks from environmental exposures to dioxin. Also, in 1988, a draft exposure document was prepared that presented procedures for conducting site-specific exposure assessments to dioxin-like compounds. These assessments were reviewed by the Agency's Science Advisory Board (SAB). At the time of the 1988 assessments, there was general agreement within the scientific community that there could be a substantial improvement over the existing approach to analyzing dose response, but there was no consensus as to a more biologically defensible methodology. The Agency was asked to explore the development of such a method. The current reassessment activities are in response to this request.

The scientific reassessment of dioxin consists of five activities:

1. Update and revision of the health assessment document for dioxin.
2. Laboratory research in support of the dose-response model.
3. Development of a biologically based dose-response model for dioxin.
4. Update and revision of the dioxin exposure assessment document.
5. Research to characterize ecological risks in aquatic ecosystems.

The first four activities have resulted in two draft documents (the health assessment document and exposure document) for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds. These companion documents, which form the basis for the Agency's reassessment of dioxin, have been used in the development of the risk characterization chapter that follows the health assessment. The process for developing these documents consisted of three phases which are outlined in later paragraphs.

The fifth activity, which is in progress at EPA's Environmental Research Laboratory in

Duluth, Minnesota, involves characterizing ecological risks in aquatic ecosystems from exposure to dioxins. Research efforts are focused on the study of organisms in aquatic food webs to identify the effects of dioxin exposure that are likely to result in significant population impacts. A report titled, *Interim Report on Data and Methods for the Assessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) Risks to Aquatic Organisms and Associated Wildlife* (EPA/600/R-93/055), was published in April 1993. This report will serve as a background document for assessing dioxin-related ecological risks. Ultimately, these data will support the development of aquatic life criteria which will aid in the implementation of the Clean Water Act.

The EPA had endeavored to make each phase of the current reassessment of dioxin an open and participatory effort. On November 15, 1991, and April 28, 1992, public meetings were held to inform the public of the Agency's plans and activities for the reassessment, to hear and receive public comments and reviews of the proposed plans, and to receive any current, scientifically relevant information.

In the Fall of 1992, the Agency convened two peer-review workshops to review draft documents related to EPA's scientific reassessment of the health effects of dioxin. The first workshop was held September 10 and 11, 1992, to review a draft exposure assessment titled, *Estimating Exposures to Dioxin-Like Compounds.* The second workshop was held September 22-25, 1992, to review eight chapters of a future draft *Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds.* Peer-reviewers were also asked to identify issues to be incorporated into the risk characterization, which was under development.

In the Fall of 1993, a third peer-review workshop was held on September 7 and 8, 1993, to review a draft of the revised and expanded Epidemiology and Human Data Chapter, which also would be part of the future health assessment document. The revised chapter provided an evaluation of the scientific quality and strength of the epidemiology data in the evaluation of toxic health effects, both cancer and noncancer, from exposure to dioxin, with an emphasis on the specific congener, 2,3,7,8-TCDD.

As mentioned previously, completion of the health assessment and exposure documents involves three phases: Phase 1 involved drafting state-of-the-science chapters and a dose-response model for the health assessment document, expanding the exposure document to address dioxin related compounds, and conducting peer review workshops by

panels of experts. This phase has been completed.

Phase 2, preparation of the risk characterization, began during the September 1992 workshops with discussions by the peer-review panels and formulation of points to be carried forward into the risk characterization. Following the September 1993 workshop, this work was completed and was incorporated as Chapter 9 of the draft health assessment document. This phase has been completed.

Phase 3 is currently underway. It includes making External Review Drafts of both the health assessment document and the exposure document available for public review and comment.

Following the public comment period, the Agency's Science Advisory Board (SAB) will review the draft documents in public session. Assuming that public and SAB comments are positive, the draft documents will be revised, and final documents will be issued.

Estimating Exposures to Dioxin-Like Compounds has been prepared by the Exposure Assessment Group of the Office of Health and Environmental Assessment, Office of Research and Development, which is responsible for the report's scientific accuracy and conclusions. A comprehensive search of the scientific literature for this document varies somewhat by chapter but is, in general, complete through January 1994.

AUTHORS, CONTRIBUTORS, AND REVIEWERS

The Exposure Assessment Group (EAG) within EPA's Office of Health and Environmental Assessment was responsible for the preparation of this document. General support was provided by Versar Inc. under EPA Contract Number 68-D0-0101. Dr. William Farland, as overall Director of the Dioxin Reassessment, provided policy guidance and technical comments. Matthew Lorber of EAG served as EPA task manager (as well as contributing author) providing overall direction and coordination of the production effort.

AUTHORS FOR VOLUME I
Primary authors for Volume I include all authors listed below.

AUTHORS FOR VOLUME II
Primary authors of each chapter are listed below in alphabetical order.

Jerry Blancato   Chapter 6
U.S. Environmental Protection Agency
Las Vegas, NV

Elizabeth Brown   Chapter 4
Versar, Inc.

David Cleverly   Chapter 3
U.S. Environmental Protection Agency
Washington, DC

Jeff Dawson   Chapter 3
Versar, Inc.

Keith Drewes   Chapter 4
Versar, Inc.

Carl D'Ruiz   Chapter 3
Versar, Inc.

Robert J. Fares   Chapter 4
Versar, Inc.

Geoffrey Huse   Chapters 2, 4, 5
Versar, Inc.

Tim Leighton   Chapters 3, 5
Versar, Inc.

Matthew Lorber   Chapters 3, 4
U.S. Environmental Protection Agency
Washington, DC

Nica Mostaghim   Chapter 4
Versar, Inc.

Linda Phillips   Chapter 3, 4, 5
Versar, Inc.

John L. Schaum   Chapter 1 - 5
U.S. Environmental Protection Agency
Washington, DC

Greg Schweer   Chapter 2 - 5
Versar, Inc.

AUTHORS FOR VOLUME III

Primary authors of each chapter are listed below in alphabetical order.

David H. Cleverly   Chapters 3, 7
U.S. Environmental Protection Agency
Washington, DC

Matthew Lorber   Chapter 1-7
U.S. Environmental Protection Agency
Washington, DC

John L. Schaum   Chapters 1, 2
U.S. Environmental Protection Agency
Washington, DC

Paul White   Chapter 7
U.S. Environmental Protection Agency
Washington, DC

CONTRIBUTORS AND REVIEWERS

An earlier draft of this exposure document was reviewed by the Science Advisory Board in 1988. A revised draft was issued in August 1992 and was reviewed by a panel of experts at a peer-review workshop held September 10 and 11, 1992. Members of the Peer Review Panel for this workshop were as follows:

M. Judith Charles, Ph.D.
University of North Carolina
Chapel Hill, NC

Dennis Paustenbach, Ph.D.
ChemRisk - A McLaren/Hart Group
Alameda, CA

Ray Clement, Ph.D.
Ontario Ministry of the Environment
Quebec, Canada

Richard Dennison, Ph.D.
Environmental Defense Fund
Washington, DC

Richard Reitz, Ph.D.
Dow Chemical
Midland, MI

In addition, the following experts outside of EPA have reviewed and/or contributed to this document:

Michael Bolger
US Food and Drug Administration
Washington, DC

James Falco, Ph.D.
Battelle Northwest
Richland, WA

Heidelore Fiedler, Ph.D.
University of Bayreuth
Federal Republic of Germany

Charles Fredette
Connecticut Department of Environmental Protection
Hartford, CT

George Fries, Ph.D
United States Department of Agriculture
Beltsville Agricultural Research Center
Beltsville, MD

Laura Green, Ph.D, D.A.B.T
Cambridge Environmental, Inc.
Cambridge, MA

Dale Hattis, Ph.D.
Clark University
Worcester, MA

Steven Hinton, Ph.D., P.E.
National Council of the Paper Industry for Air and Stream
    Improvement
Tufts University
Medford, MA

Kay Jones
Zephyr Consulting
Seattle, WA

George Lew
California Air Resources Board
Sacremento, CA

Thomas E. McKone, Ph.D.
Lawrence Livermore National Laboratory
Livermore, CA

Derek Muir, Ph.D
Freshwater Institute
Department of Fisheries and Oceans
Winnipeg, MB, Canada

Marvin Norcross, Ph.D.
Food Safety Inspection Service, USDA
Washington, DC

Vlado Ozvacic, Ph.D.
Ministry of the Environment
Toronto, ON, Canada

Thomas Parkerton, Ph.D
Manhattan College
Riverdale, NY

Christopher Rappe, Ph.D.
University of Umea
Institute of Environmental Chemistry
Umea, Sweden

Curtis C. Travis, Ph.D.
Oak Ridge National Laboratory
Oak Ridge, TN

Thomas O. Tiernan, Ph.D.
Wright State University
Dayton, OH

Thomas Umbreit, Ph.D.
Agency for Toxic Substances and Disease Registry
Atlanta, GA

G.R. Barrie Webster, Ph.D.
University of Manitoba
Winnipeg, Canada

The following individuals within EPA have reviewed and/or contributed to this document:

OFFICE	REVIEWERS/CONTRIBUTORS	
Office of Research and Development	Frank Black Brian Gullett Joel McCrady Philip Cook Donna Schwede Bill Petersen James Kilgroe	
Office of Air and Radiation	Pam Brodowicz Thomas Lahre Phil Lorang Dennis Pagano Dallas Safriet Joseph Wood	George Streit Anne Pope Walter Stevenson Jim Crowder Joe Somers
Office of Pollution, Pesticides and Toxic Substances	Joe Cotruvo Steven Funk Pat Jennings Leonard Keifer Robert Lipnick Tom Murray	
Office of Water	Ryan Childs Mark Morris Edward Ohanian Al Rubin Maria Gomez Taylor	
Office of General Counsel	Chuck Elkins	
Office of Policy, Planning and Evaluation	Dwain Winters	

I. INTRODUCTION

I.1. BACKGROUND

In May of 1991, the Environmental Protection Agency (EPA) announced a scientific reassessment of the human health and exposure issues concerning dioxin and dioxin-like compounds (56 FR 50903). This reassessment has resulted in two reports: a health reassessment document (EPA, 1994), and *Estimating Exposure to Dioxin-Like Compounds* [this three-volume report], which expands upon a 1988 draft exposure report titled, *Estimating Exposure to 2,3,7,8-TCDD* (EPA, 1988). The health and exposure reassessment documents can be used together to assess potential health risks from exposure to dioxin-like compounds. In a related area, EPA has also discussed the data and methods for evaluating risks to aquatic life from 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) (EPA, 1993).

The purpose of the exposure portion of the dioxin reassessment is to describe the causes and magnitude of background exposures, and provide site-specific procedures for evaluating the incremental exposures due to specific sources of dioxin-like compounds.

In September of 1992, EPA convened workshops to review the first public drafts of the health (EPA, 1992a) and the exposure documents (EPA, 1992b). The current draft of the exposure document incorporates changes as a result of that workshop as well as other review comments.

The exposure document is presented in three volumes. Following is a summary of the material contained in each of the three volumes:

Volume I - Executive Summary

> This volume includes summaries of findings from Volumes II and III. It also includes a unique section on research needs and recommendations for dioxin-like compounds.

Volume II - Properties, Sources, Environmental Levels, and Background Exposures

> This volume presents and evaluates information on the physical-chemical properties, environmental fate, sources, environmental levels, and background human exposures to dioxin-like compounds. It summarizes and evaluates relevant information obtained from published literature searches, EPA program offices and other Federal agencies, and published literature provided by peer reviewers of previous versions of this document. The data contained in this volume is current through 1993 with some new information published in early 1994.

Volume III - Site-Specific Assessment Procedures

This volume presents procedures for evaluating the incremental impact from sources of dioxin released into the environment. The sources covered include contaminated soils, stack emissions, and point discharges into surface water. This volume includes sections on: exposure parameters and exposure scenario development; stack emissions and atmospheric transport modeling; aquatic and terrestrial soil, sediment, and food chain modeling; demonstration of methodologies; and uncertainty evaluations including exercises on sensitivity analysis and model validation, review of Monte Carlo assessments conducted for dioxin-like compounds, and other discussions. The data contained in this volume is current through 1993 with some new information published in early 1994.

I.2. TOXICITY EQUIVALENCY FACTORS

Dioxin-like compounds are defined to include those compounds with nonzero Toxicity Equivalency Factor (TEF) values as defined in a 1989 international scheme, I-TEFs/89. This procedure was developed under the auspices of the North Atlantic Treaty Organization's Committee on Challenges of Modern Society (NATO-CCMS, 1988a; 1988b) to promote international consistency in addressing contamination involving CDDs and CDFs. EPA has adopted the I-TEFs/89 as an interim procedure for assessing the risks associated with exposures to complex mixtures of CDDs and CDFs (EPA, 1989). As shown in Table I-1, this TEF scheme assigns nonzero values to all chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) with chlorine substituted in the 2,3,7,8 positions. Additionally, the analogous brominated compounds (BDDs and BDFs) and certain polychlorinated biphenyls (PCBs, see Table I-2) have recently been identified as having dioxin-like toxicity (EPA, 1994) and thus are also included in the definition of dioxin-like compounds. However, EPA has not assigned TEF values for BDDs, BDFs, and PCBs. In the case of PCBs, research on the applicability of the TEF approach is ongoing but there is not yet any formal EPA policy. The nomenclature adopted here for purposes of describing these compounds is summarized in Table I-3.

Table I-1. Toxicity Equivalency Factors (TEF) for CDDs and CDFs.

Compound		TEF
Mono-, Di-, and Tri-CDDs		0
2,3,7,8-TCDD	1	
Other TCDDs		0
2,3,7,8-PeCDD		0.5
Other PeCDDs		0
2,3,7,8-HxCDD		0.1
Other HxCDDs		0
2,3,7,8-HpCDD		0.01
Other HpCDDs		0
OCDD		0.001
Mono-, Di-, and Tri-CDFs		0
2,3,7,8-TCDF	0.1	
Other TCDFs		0
1,2,3,7,8-PeCDF		0.05
2,3,4,7,8-PeCDF		0.5
Other PeCDFs		0
2,3,7,8-HxCDF		0.1
Other HxCDFs		0
2,3,7,8-HpCDF		0.01
Other HpCDFs		0
OCDF		0.001

Source: EPA, 1989.

Table I-2. Dioxin-Like PCBs.

IUPAC No.	Congener
77	3,3',4,4'-tetra PCB
81	3,4,4',5-tetra PCB
105	2,3,3',4,4'-penta PCB
114	2,3,4,4',5-penta PCB
118	2,3',4,4',5-penta PCB
126	3,3',4,4',5-penta PCB
156	2,3,3',4,4',5-hexa PCB
157	2,3,3',4,4',5'-hexa PCB
167	2,3',4,4',5,5'-hexa PCB
169	3,3',4,4',5,5'-hexa PCB
189	2,3,3',4,4',5,5'-hepta PCB

Source: EPA, 1992a.

Table I-3. Nomenclature for dioxin-like compounds.

Term/Symbol	Definition
Congener	Any one particular member of the same chemical family; e.g., there are 75 congeners of chlorinated dibenzo-p-dioxins.
Homologue	Group of structurally related chemicals that have the same degree of chlorination. For example, there are eight homologues of CDDs, monochlorinated through octochlorinated.
Isomer	Substances that belong to the same homologous class. For example, there are 22 isomers that constitute the homologues of TCDDs.
Specific congener	Denoted by unique chemical notation. For example, 2,4,8,9-tetrachlorodibenzofuran is referred to as 2,4,8,9-TCDF.
D	Symbol for homologous class: dibenzo-p-dioxin
F	Symbol for homologous class: dibenzofuran
M	Symbol for mono, i.e., one halogen substitution
D	Symbol for di, i.e., two halogen substitution
Tr	Symbol for tri, i.e., three halogen substitution
T	Symbol for tetra, i.e., four halogen substitution
Pe	Symbol for penta, i.e., five halogen substitution
Hx	Symbol for hexa, i.e., six halogen substitution
Hp	Symbol for hepta, i.e., seven halogen substitution
O	Symbol for octa, i.e., eight halogen substitution
CDD	Chlorinated dibenzo-p-dioxins, halogens substituted in any position
CDF	Chlorinated dibenzofurans, halogens substituted in any position
PCB	Polychlorinated biphenyls
2378	Halogen substitutions in the 2,3,7,8 positions

Source: EPA, 1989.

The procedure relates the toxicity of 210 structurally related individual CDD and CDF congeners and is based on a limited data base of in vivo and in vitro toxicity testing. By relating the toxicity of the 209 CDDs and CDFs to the highly-studied 2,3,7,8-TCDD, the approach simplifies the assessment of risks involving exposures to mixtures of CDDs and CDFs (EPA, 1989).

In general, the assessment of the human health risk to a mixture of CDDs and CDFs, using the TEF procedure, involves the following steps (EPA, 1989):

1.   Analytical determination of the CDDs and CDFs in the sample.
2.   Multiplication of congener concentrations in the sample by the TEFs in Table I-1 to express the concentration in terms of 2,3,7,8-TCDD equivalents (TEQs).
3.   Summation of the products in Step 2 to obtain the total TEQs in the sample.
4.   Determination of human exposure to the mixture in question, expressed in terms of TEQs.
5.   Combination of exposure from step 4 with toxicity information on 2,3,7,8-TCDD to estimate risks associated with the mixture.

Samples of this calculation for several environmental mixtures are provided in EPA (1989). Also, this procedure is demonstrated in Volume III of this assessment in the context of the demonstration of the stack emission source category. The seventeen dioxin-like congeners are individually modeled from stack to exposure site. TEQ concentrations are estimated given predictions of individual congener concentrations using Steps 2 and 3 above.

I.3. OVERALL COMMENTS ON THE USE OF THE DIOXIN EXPOSURE DOCUMENT

Users of the dioxin exposure document should recognize the following:

1. This document does not present detailed procedures for evaluating multiple sources of release. However, it can be used in two ways to address this issue. Incremental impacts estimated with procedures in Volume III can be compared to background exposure estimates which are presented in Volume II. This would be a way of comparing the incremental impact of a specific source to an individual's total exposure. If the releases from multiple sources behave independently, it is possible it model them individually and then add the impacts. For example, if several stack emission sources are identified and their emissions quantified, and it is desired to evaluate the impact of all sources simultaneously, then it may be possible to model each stack emission source individually and then sum the concentrations and depositions at points of

interest in the surrounding area.

2. The procedures and estimates presented in this three-volume exposure document best serve as an information source for evaluating exposures to dioxin-like compounds. This document was not generated for purposes of supporting any specific regulation. Rather, it is intended to be a general information source which Agency programs can adopt or modify as needed for their individual purposes. For example, the demonstration scenarios of Volume III were not crafted as Agency policy on "high end" or "central tendency" scenarios for evaluating land contamination, stack emissions, or effluent discharges. Rather, they were designed to illustrate the site-specific methodologies in Volume III.

3. The understanding of the exposure to dioxin-like compounds continues to expand. Despite being one of the most studied groups of organic environmental contaminants, new information is generated almost daily about dioxin-like compounds. This document is considered to be current through 1993, with some information published early in 1994 included as well. Section IV of Volume I, Executive Summary, discusses research needs for dioxin exposure evaluation.

REFERENCES FOR INTRODUCTION

NATO/CCMS (North Atlantic Treaty Organization, Committee on the Challenges of Modern Society). (1988a) International toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. Report No. 176.

NATO/CCMS (North Atlantic Treaty Organization, Committee on the Challenges of Modern Society). (1988b) Scientific basis for the development of international toxicity equivalency (I-TEF) factor method of risk assessment for complex mixtures of dioxins and related compounds. Report No. 178.

U.S. Environmental Protection Agency. (1988) Estimating exposure to 2,3,7,8-TCDD. U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, DC; EPA/600/6-88/005A.

U.S. Environmental Protection Agency. (1989) Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-p-dioxins and -dibenzofurans (CDDs and CDFs) and 1989 update. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC; EPA/625/3-89/016.

U.S. Environmental Protection Agency. (1992a) Health reassessment of dioxin-like compounds, Chapters 1-8. U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, DC. EPA/600/AP-92/001a through EPA/600/AP-92/001h. August 1992 Workshop Review Draft.

U.S. Environmental Protection Agency. (1992b) Estimating Exposure to Dioxin-Like Compounds. U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, DC. EPA/600/6-88/005B. August 1992 Workshop Review Draft.

U.S. Environmental Protection Agency. (1993) Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Risks to Aquatic Life and Associated Wildlife. Environmental Research Laboratory, Duluth, MN, Office of Research and Development, U.S. Environmental Protection Agency. EPA/600/R-93/055. March, 1993.

U.S. Environmental Protection Agency. (1994) Health Assessment for 2,3,7,8-TCDD and Related Compounds. Public Review Draft. EPA/600/EP-92/001.

VOLUME II. PROPERTIES, SOURCES, ENVIRONMENTAL LEVELS,
AND BACKGROUND EXPOSURES

II.1. CHEMICAL STRUCTURES AND PROPERTIES

Polychlorinated dibenzodioxins (CDDs), polychlorinated dibenzofurans (CDFs), and polychlorinated biphenyls (PCBs) are chemically classified as halogenated aromatic hydrocarbons. The chlorinated and brominated dibenzodioxins and dibenzofurans are tricyclic aromatic compounds with similar physical and chemical properties, and both classes are quite similar structurally. There are 75 possible different positional congeners of CDDs and 135 different CDF congeners. Only 7 of the 75 possible CDD congeners, and 10 of the 135 possible CDF congeners, those with chlorine substitution in the 2,3,7,8 positions, are thought to have dioxin-like toxicity. Likewise, there are 75 possible different positional congeners of BDDs and 135 different congeners of BDFs (see Table II-1). The basic structure and numbering of each chemical class is shown in Figure II-1.

There are 209 possible PCB congeners, only 11 of which are thought to have dioxin-like toxicity. These dioxin-like congeners have four or more chlorine atoms with

Figure II-1. Structure of Dioxins and Furans.

PCDDs   PCDFs
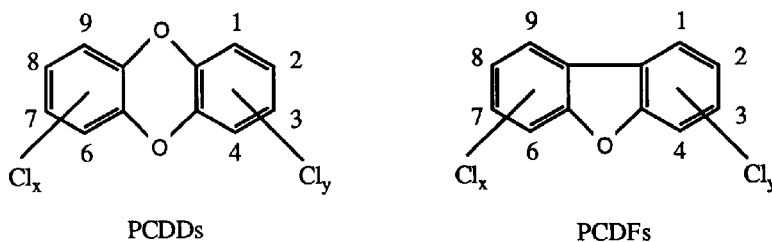
X = 1 to 4, Y = 1 to 4, X + Y $\geq$ 1

Table II-1. Possible number of positional CDD (or BDD) and CDF (or BDF) congeners

	Number of Congeners		
Halogen substitution	CDDs (or BDDs)	CDFs (or BDFs)	PCBs
Mono	2	4	3
Di	10	16	12
Tri	14	28	24
Tetra	22	38	42
Penta	14	28	46
Hexa	10	16	42
Hepta	2	4	24
Octa	1	1	12
Nona	0	0	3
Deca	0	0	1

no more than one substitution in the ortho positions (positions designated 2, 2', 6 or 6' in Figure II-2). Dioxin-like PCBs are listed in Table I-2. These compounds are sometimes referred to as coplanar PCBs, since the rings can rotate into the same plane if not blocked from rotation by ortho-substituted chlorine atoms. The physical/chemical properties of each congener vary according to the degree and position of chlorine substitution. The basic structure and numbering of each chemical class is shown in Figure II-2.

In general, these compounds have very low water solubility, high octanol-water partition coefficients, low vapor pressure and tend to bioaccumulate. Volume II presents congener-specific values for water solubility, vapor pressure, partition coefficients and photo quantum yields.

Despite a growing body of literature from laboratory, field, and monitoring studies

Figure II-2. Structure of dioxin-like PCBs.
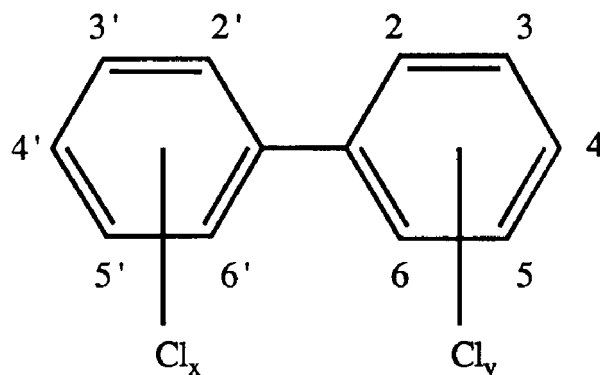
$$X = 1 \text{ to } 5, Y = 1 \text{ to } 5, X + Y \geq 1$$

examining the environmental fate and environmental distribution of CDDs and CDFs, the fate of these environmentally ubiquitous compounds is not yet well understood. In soil, sediment, and the water column, CDDs/CDFs are primarily associated with particulate and organic matter because of their high lipophilicity and low water solubility. In a detailed evaluation of ambient air monitoring studies in which researchers evaluated the partitioning of dioxin-like compounds between the vapor and particle phases, a principal conclusion was that the higher chlorinated congeners, the hexa through hepta congeners, were principally sorbed to airborne particulates, whereas the tetra and penta congeners significantly, if not predominantly, partition to the vapor phase. This finding is consistent with vapor/particle partitioning as theoretically modeled in Bidleman (1988). Dioxin-like compounds exhibit little potential for significant leaching or volatilization once sorbed to particulate matter. The available evidence indicates that CDDs and CDFs, particularly the tetra- and higher chlorinated congeners, are extremely stable compounds under most environmental conditions. The only environmentally significant transformation process for these congeners is believed to be photodegradation of nonsorbed species in the gaseous phase, at the soil-air or water-air interface, or in association with organic cosolvents. CDDs/CDFs entering the atmosphere are removed either by photodegradation or by deposition. Burial in-place, resuspension back into the air, or erosion of soil to water bodies appears to be the predominant fate of CDDs/CDFs sorbed to soil. CDDs/CDFs entering the water column primarily undergo sedimentation and burial. The ultimate environmental sink of CDDs/CDFs is

believed to be aquatic sediments.

Little specific information exists on the environmental transport and fate of the 11 coplanar PCBs. However, the available information on the physical/chemical properties of coplanar PCBs coupled with the body of information available on the widespread occurrence and persistence of PCBs in the environment indicates that these coplanar PCBs are likely to be associated primarily with soils and sediments, and to be thermally and chemically stable. PCBs volatilize from the surfaces of soils and water bodies and are dispersed via air movement. Subsequently they can be deposited back into soil or water. In water bodies, they can be spread via sediment transport. Though not rapid processes, these mechanisms account for the widespread environmental occurrence of PCBs. Photodegradation to less chlorinated congeners followed by slow anaerobic and/or aerobic biodegradation is believed to be the principal path for destruction of PCBs.

II.2. SOURCES

Ancient human tissue sampling shows much lower CDD/F levels than found today (Ligon et al., 1989). Studies of sediment cores in lakes near industrial centers of the United States have shown that dioxins and furans were quite low until about 1920 (Czuczwa, et al., 1984; Czuczwa and Hites, 1985; Smith, et al., 1992). These studies show increases in CDD/F concentrations beginning in the 1920s and continuing until about 1970. Declining concentrations have been measured since this time. These trends cannot be explained by changes in natural processes and have been shown to correspond to chlorophenol production trends (Czuczwa and Hites, 1984). On this basis, it appears that the presence of dioxin-like compounds in the environment occurs primarily as a result of anthropogenic practices. This section will review the theories of formation and emission of these compounds, and then discuss the possible sources which can release them to the environment.

II.2.1. Theories of Formation During Combustion

The emission of CDDs and CDFs into the environment from combustion processes can be explained by three principal theories, which should not be regarded as being mutually exclusive: (1) contaminated feedstock, (2) formation from precursors, and (3) formation *de novo.* In general, the primary theories can be summarized as follows:

(1) The feed material to the combustor contains CDDs and CDFs and some portion survives the thermal stress imposed by the heat of the incineration or combustion process, and is subsequently emitted from the stack. While this explanation is not thought to be the principal

explanation for dioxin and furan emissions from combustor sources (explanations 2 and 3 below are thought to be the predominant cause of these emissions), in fact it is the single theory best thought to explain the release of the dioxin-like, coplanar PCBs.

(2) CDDs/CDFs are ultimately formed from the thermal breakdown and molecular rearrangement of precursor compounds. Precursor compounds are chlorinated aromatic hydrocarbons having a structural resemblance to the CDD/CDF molecule. Among the precursors that have been identified are polychlorinated biphenyls (PCBs), chlorinated phenols (CPs), and chlorinated benzenes (CBs). The formation of CDDs/CDFs is believed to occur after the precursor has condensed and adsorbed onto the binding sites on the surface of fly ash particles. The active sites of the surface of fly ash particles promote the chemical reactions forming CDDs/CDFs. These reactions have been observed to be catalyzed by the presence of inorganic chlorides sorbed to the particulate. Temperature in a range of 250-450 C has been identified as a necessary condition for these reactions to occur, with either lower or higher temperatures inhibiting the process. Therefore, the precursor theory focuses on the region of the combustor that is downstream and away from the high temperature zone of the furnace or combustion chamber. This is a location where the gases and smoke derived from combustion of the organic materials have cooled during conduction through flue ducts, heat exchanger and boiler tubes, air pollution control equipment or the stack.

(3) CDDs/CDFs are synthesized *de novo* in the same region of the combustion process as described in (2), e.g. the so-called cool zone. In this theory, CDDs/CDFs are formed from moieties bearing little resemblance to the molecular structure of CDDs and CDFs. In broad terms, these are non-precursors and include such diverse substances as petroleum products, chlorinated plastics (PVC), non-chlorinated plastics (polystyrene), cellulose, lignin, coke, coal, particulate carbon, and hydrogen chloride gas. Formation of CDDs/CDFs requires the presence of a chlorine donor (a molecule that provides a chlorine atom to the pre-dioxin molecule) and the formation and chlorination of a chemical intermediate that is a precursor. The primary distinction between theories (2) and (3) is that theory (2) requires the presence of precursor compounds in the feed material whereas theory (3) begins with the combustion of diverse substances that are not defined as precursors, which eventually react to form precursors and eventually, dioxin-like molecules.

II.2.2. Estimates of Annual Releases of Dioxin-Like Compounds

PCBs were produced in relatively large quantities for use in such commercial products as dielectrics, hydraulic fluids, plastics and paints. They are no longer produced, but continue to be

released to the environment through the use and disposal of products manufactured years ago. The chlorinated and brominated dioxins and furans, on the other hand, have never been intentionally produced other than on a laboratory scale basis for use in chemical analyses. They are, however, generated as byproducts from various combustion and chemical processes. Dioxin-like compounds are released to the environment in a variety of ways and in varying quantities depending upon the source. The dioxin like compounds have been found in all media and all parts of the world. This ubiquitous nature of these compounds suggests that multiple sources exist and that long range transport can occur. An unresolved issue is how the relative impacts from local versus distant sources compare at a particular location. Presumably in industrial areas local sources will dominate and in rural areas distant sources will dominate. However, site specific considerations such as stack height, wind patterns, magnitude of local sources, etc. could influence these comparisons.

The major identified sources of environmental release have been grouped into four major types for the purposes of this report:

Industrial/Municipal Processes: Dioxin-like compounds can be formed through the chlorination of naturally occurring phenolic compounds such as those present in wood pulp. The formation of CDDs and CDFs resulting from the use of chlorine bleaching processes in the manufacture of bleached pulp and paper has in the past resulted in the presence of CDDs and CDFs in paper products as well as in liquid and solid wastes from this industry, although more recently this industry has made process changes to minimize CDD/CDF formation. Occasionally, municipal sewage sludge has been found to contain CDDs and CDFs.

Chemical Manufacturing/Processing Sources: Dioxin-like compounds can be formed as by-products from the manufacture of chlorine and such chlorinated compounds as chlorinated phenols, PCBs, phenoxy herbicides, chlorinated benzenes, chlorinated aliphatic compounds, chlorinated catalysts, and halogenated diphenyl ethers. Although the manufacture of many chlorinated phenolic intermediates and products, as well as PCBs, was terminated in the late 1970s in the United States, the continued limited use and disposal of these compounds can result in releases of CDDs, CDFs, and PCBs to the environment.

Combustion and Incineration Sources: Dioxin-like compounds can be generated and released to the environment from various combustion processes when chlorine donor

compounds are present. These processes can include incineration of wastes such as municipal solid waste, sewage sludge, hospital and hazardous wastes; metallurgical processes such as high temperature steel production, smelting operations, and scrap metal recovery furnaces; and the burning of coal, wood, petroleum products, and used tires for power/energy generation.

Reservoir Sources: The persistent and hydrophobic nature of these compounds cause them to accumulate in soils, sediments and organic matter and to persist in waste disposal sites. The dioxin-like compounds in these "reservoirs" can be redistributed by dust or sediment resuspension and transport. Such releases are not original sources in a global sense, but can be on a local scale. For example, releases may occur naturally from sediments via volatilization or via operations which disturb them such as dredging. Aerial deposition and accumulation on leaves may lead to releases during forest fires or leaf composting operations.

As awareness of these possible sources has grown in recent years, a number of changes have occurred which should reduce the release rates (Rappe, 1992). For example, releases of dioxin-like compounds have been reduced due to the switch to unleaded automobile fuels (and associated use of catalytic converters and reduction in halogenated scavenger fuel additives), process changes at pulp and paper mills, new emission standards and upgraded emission controls for incinerators, and reductions in the manufacture of chlorinated phenolic intermediates and products.

Table II-2 presents CDD and CDF air emission estimates for Germany, Austria, the United Kingdom, the Netherlands, Switzerland and the U.S. All the countries except Austria estimate that municipal waste incinerators are an important source (new emission standards in Germany indicate that the emissions from this source are now nearer the lower end of the range listed in Table II-2). Medical waste incinerators, wood burning and metal smelters/refiners also appear to be generally important sources. Rappe (1992) and Lexen et al. (1992) have identified emissions from ferrous and non-ferrous metals smelting and refining facilities as potentially the largest current source in Sweden. Rappe (1992) reported that changes in various industrial practices have lead to reductions in dioxin emissions in Sweden from 400 - 600 g of TEQ/yr in 1985 to 100 - 200 g TEQ/yr in 1991.

Nationwide emission estimates for the United States have not previously been compiled. This task was attempted as part of this project and the air emissions are summarized in Table II-2 and a detailed estimate of emissions to all media are presented in Table II-3. For each source, emissions to air, water, land, and product are estimated where appropriate and where data are

adequate to enable an estimate to be made. The term "product" is defined to include substances or articles (e.g., paper pulp or sewage sludge that is distributed/marketed commercially) that are known to contain dioxin-like compounds and whose subsequent use may result in releases to the environment. In order to make each source emission estimate, information was required concerning both the "emission factor" term for the source (e.g., grams TEQ per kg of material processed) and the "production" term for the source (e.g., kg of material processed annually in the U.S.). Because the quantity and quality of the available information for both terms for each emission source varies considerably, a confidence rating of "high", "medium", or "low" was assigned to both terms. In addition, the uncertainty in these national release estimates is reflected by presenting (where possible) for each source category both a central or "best guess" value and a possible range from a lower to an upper estimate. In general, the emission estimates are quite uncertain since the nationwide approximations were derived by extrapolating only a few facility tests. Insufficient data were available to

Table II-2. CDD and CDF air emission estimates for West Germany, Austria, United Kingdom, Netherlands, Switzerland, and the United States.

Emission Source	West Germany[a] (g TEQ/yr)	Austria[b] (g TEQ/yr)	United Kingdom[c] (g TEQ/yr)	Netherlands[d] (g TEQ/yr)	Switzerland[k] (g/TEQ/yr)	United States[j] (g/TEQ/yr)
Industrial/Municipal Processes Pulp and paper mills		4			1 - 5	2.7
Sewage sludge incineration	0.01 - 1.1	<1		0.3		23
Chemical Manuf./Processing Sources Organic chemical manufacture				0.5		
Combustion and Incineration Sources **Incineration/Energy Recovery** Municipal waste incineration	5.4 - 432	3	1,150	382	90 - 150	3,000
Hazardous waste incineration	0.5 - 72	6	11	16	<1	35
Hospital waste incineration	5.4	4	32	2.1	2 - 3	5,100
Cement kilns						350
Metallurgical Processes Tire combustion						0.3
Ferrous metal smelting/refining	1.3 - 18.9	19[g]		30[g]	6 - 16[g]	
Nonferrous metal smelting/refining	38 - 380					230
Scrap electric wire recovery				1.5		
Drum and barrel reclamation					2 - 14[e]	1.7
Power/Energy Generation Vehicle fuel combustion - leaded	7.2	<1[e]	613[e]	7.0[e]		
- unleaded	0.8					1.3
- diesel	4.6				3 - 22	85

Emission Source	West Germany[a] (g TEQ/yr)	Austria[b] (g TEQ/yr)	United Kingdom[c] (g TEQ/yr)	Netherlands[d] (g TEQ/yr)	Switzerland[k] (g/TEQ/yr)	United States[l] (g/TEQ/yr)
Wood burning		70	16	12		40[m] 320[n]
Coal combustion - residential	1.1	<1[i]	989	3.7[i]		
- industrial			301			
- utility			199			
Oil combustion - residential	1.2		2[h]			
Charcoal briquette combustion (residential)	1.8					
TOTAL	67 - 926	<109	3,870[f]	484[j]	100 - 200	9,200

[a] Source: Fiedler and Hutzinger (1992). Single values represent "minimum" and ranges represent "minimum" to "maximum" emission estimates; Basis Year = 1990.
[b] Source: Riss and Aichinger (1993); Basis Year = 1987/88.
[c] Source: ECETOC (1992); Basis Year = 1989.
[d] Source: Koning et al. (1993); Basis Year = 1991.
[e] Total for all fuel types.
[f] Includes 55g TEQ/yr from combustion of "other organic materials" and 16g TEQ/yr from "accidental fires."
[g] Total for all metal industries including sintering processes.
[h] Total of 2g TEQ/yr from "oil burning".
[i] Total of coal combustion from all sources.
[j] Includes 25g TEQ/yr from combustion of PCP-treated wood, 0.2g TEQ/yr from crematoria, 0.3g TEQ/yr from asphalt mixing plants, and 2.7g TEQ/yr. from various high temperature processes such as soil cleaning, fly ash drying, cement production, production of glass/mineral wool, etc.
[k] Source: Schatowitz et al. (1993); Basis Year = 1990.
[l] Source: Estimates generated in this report; mean values listed when available - all ranges listed in Table II-3.
[m] Estimate for residential wood burning.
[n] Estimate for industrial wood burning.
[o] CDD/CDFs have not been detected in stack gases from U.S. coal-fired utilities; however, CDD/CDFs have been detected in stack gases in Europe. Additional monitoring studies are underway in the United States.
[p] This total includes some sources not shown in this table that have been reported to date only from U.S. sources. See Table II-3 for a complete listing of U.S. sources.

Table II-3. Current CDD and CDF multi-media emission estimates for the United States.

Emission Source	Emissions (g TEQ/yr) to Media															
	Air				Water				Land/Landfill				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Industrial/Municipal Processes Bleached chemical pulp and paper mills	b	b	b	--	74	110	150	H/H	71	100	140	H/H	110	150	210	H/H
Publicly Owned Treatment Works	c	c	c	--					150	210	290	H/H	2.5	3.6	5.0	H/H
Chemical Manuf./Processing/ Use Sources																
Chlorophenols					NEG	NEG	NEG	--	NEG	NEG	NEG	--				
Chlorobenzenes					NEG	NEG	NEG	--	NEG	NEG	NEG	--				
Aliphatic Chlorine Compounds					NEG	NEG	NEG	--								
Dioxazine Dyes/Pigments																
Pesticides																
Combustion and Incineration Sources **Incineration/ Energy Recovery** Municipal waste incineration	1,300	3,000	6,700	H/M	NEG	NEG	NEG	--	810	1,800	4,000	M/M	NA	NA	NA	--
Hazardous waste incineration	11	35	110	M/L	NEG	NEG	NEG	--					NA	NA	NA	--
Medical waste incineration	1,600	5,100	16,000	M/L	NEG	NEG	NEG	--					NA	NA	NA	--
Kraft black liquor boilers	0.9	2.7	4.3	H/M	NEG	NEG	NEG	--					NA	NA	NA	--
Sewage sludge incineration	10	23	52	H/M	NEG	NEG	NEG	--					NA	NA	NA	--
Carbon reactivation furnaces	0.06	0.1	0.3	L/M	NEG	NEG	NEG	--	NA	NA	NA	--	NA	NA	NA	--
Cement kilns	110	350	1,100	H/L					7.6	24	76	H/L				
Metallurgical Processes Ferrous metal smelting/refining													NEG	NEG	NEG	--
Secondary copper smelting/refining	74	230	740	H/L									NEG	NEG	NEG	--
Secondary lead smelting/refining	0.7	1.6	3.5	M/M									NEG	NEG	NEG	--

Table II-3. Current CDD and CDF multi-media emission estimates for the United States.

Emission Source[a]	Emissions (g TEQ/yr) to Media															
	Air				Water				Land/Landfill				Product			
	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]	Lower	Central	Upper	CR[a]
Scrap electric wire recovery	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--	NEG	NEG	NEG	--
Drum and barrel reclamation	0.5	1.7	5.4	L/L									NEG	NEG	NEG	--
Power/Energy Generation Tire combustion	0.1	0.3	1.0	H/L									NA	NA	NA	--
Vehicle fuel combustion - leaded	d	d	d		NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA	--
- unleaded	0.4	1.3	4.1	H/L	NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA	--
- diesel	27	85	270	H/L	NA	NA	NA	--	NA	NA	NA	--	NA	NA	NA	--
Wood burning - residential	13	40	63	H/M	NA	NA	NA	--					NA	NA	NA	--
- industrial	100	320	1,000	H/L									NA	NA	NA	--
Coal combustion - residential					NA	NA	NA	--					NA	NA	NA	--
- industrial													NA	NA	NA	--
- utility													NA	NA	NA	--
Oil combustion - residential					NA	NA	NA	--					NA	NA	NA	--
Charcoal briquette combustion (residential)					NA	NA	NA	--					NA	NA	NA	--
Reservoir Sources Pentachlorophenol treated surfaces																
Forest fires	27	86	270	M/L	NA	NA	NA	--					NA	NA	NA	--
TOTAL[e]	3,300	9,300	26,000		74	110	150		1,000	2,100	4,500		110	150	220	

[a]   CR = Confidence rating. First letter is rating assigned to "production" estimate; second letter is rating assigned to "emission factor" : H = High Confidence,   M = Medium, Confidence,L = Low Confidence.

[b]   See Kraft black liquor boilers below.   [c]   See Sewage sludge incineration below.

[d]   Leaded fuel production in the United States and the manufacture of motor vehicle engines requiring leaded fuel have been prohibited in the United States.

[e]   TOTAL reflects only the total of the estimates made in this report. There are many unknowns as reflected by the number of blank cells.

[f]   It is not known what fraction, if any, of the estimated emissions from forest fires represents a "reservoir" source. The estimated emissions may be solely the result of combustion.

NA = Not applicable   NEG = Expected to be negligible or non-existent.   BLANK = Insufficient data available upon which to base an estimate.

statistically derive estimates of the range of uncertainty surrounding the central emission estimates. Instead, a judgement-based approach was used that assigned a factor of 10 from the low to high end of the range for the low confidence class, a factor of 5 for the medium confidence class and a factor of 2 for the high confidence class. It is emphasized that these ranges should be interpreted as judgements which are symbolic of the relative uncertainty among sources, and not statistical derivations of uncertainty. The emission factors and production values used to generate air emission estimates are illustrated in Figure II-3. Key source categories are discussed below:

Hospital Waste Incinerators: Collectively, this may be the largest source in the United States. This is due to the facts that most of these incinerators do not rely on highly sophisticated control technologies, are high in number (over 6000 facilities) and burn high chlorine content waste. Although the dioxin emissions from these facilities are collectively large, individually they are relatively small. Therefore, local impacts may also be relatively small. However, the area of impact is an uncertain issue in general for combustors. Germany recognized the importance of these facilities several years ago and instituted emission limits which required facilities to upgrade their technology or ship waste to hazardous waste incinerators.

Municipal Waste Incinerators: The current emissions from this category appear relatively high, but upgrading is occurring that should substantially reduce these emissions in the near future. Dioxin is also present in the ash generated from these facilities. The amount estimated to be in municipal incinerator waste ash nationally is the largest among the few source categories where estimates could be made concerning solid residues.

Cement Kilns: EPA is currently evaluating dioxin levels in the clinker dust and stack emissions from these facilities. The preliminary information suggests that collectively these facilities could be a moderate to large source. About 16% of the facilities burn hazardous waste as an auxiliary fuel; limited data suggests that the CDD/F levels in clinker dust and stack emissions of these kilns may be significantly higher than the kilns which do not burn hazardous waste.

Figure II-3. Estimated TEQ emissions to air from combustion sources in the United States.
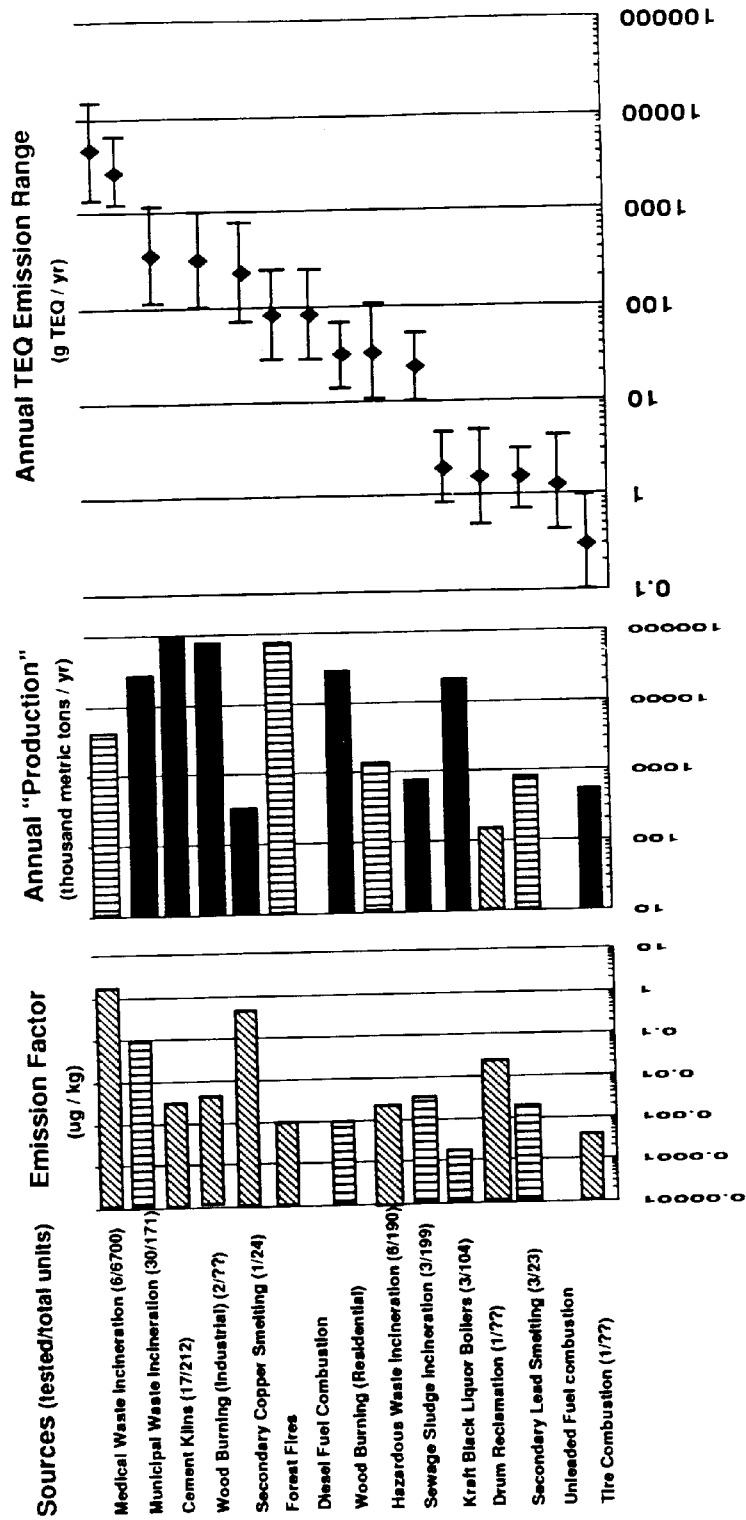
Derivation of emission factors and annual "production" (e.g., kg of waste incinerated) are presented in Chapter 3, Volume II. The emission factor for diesel fuel and unleaded fuel combustion are based on μg of TEQ per km driven. The difference in bar shading indicates the degree of confidence in the estimate. The set of numbers following the source categories indicates the number of facilities for which stack test data are available versus the number of facilities in the category.

Wood Burning: A large quantity of wood is burned at industrial operations, but the practice has not been well characterized. The emission estimates presented here are based on stack tests at two facilities. A number of studies have found dioxins in the emissions and ash/soot from wood fires in nonindustrial situations. The emission estimates for residential wood burners were made on the basis of two recent European studies. CDD/Fs may also be emitted during forest fires, but very little direct emission data are available for evaluating this issue. The estimates shown here were derived from tests on wood stoves under conditions of uncontrolled draft. Considering the many differences between combustion in wood stoves and forest fires, these estimates must be considered highly uncertain. Only one test has been conducted that directly measured CDD/F in smoke of forest fires (Clement and Tashiro, 1991). Low levels were detected, but the authors caution that some portion of these emissions could represent resuspended material from aerial deposits rather than originally formed material. The theory that much of today's body burden could be due to natural sources (such as forest fires) has been largely discounted by testing of ancient tissues which show levels much lower than those found today (Ligon et al. 1989).

Metals Industry: Secondary smelters which recover metal from waste products such as scrap automobiles have the potential for dioxin formation due to chlorine in the plastic in the feed material. Processes in the primary metals industry, such as sintering of iron ore, have also been identified as potential sources. Germany (see Table II-2) has identified the metals industry as potentially one of the most important. Table II-3 estimates moderate emissions for secondary copper smelting (based on testing at only one facility) and relatively low emissions for secondary lead smelting (based on testing at three facilities). No data are available to estimate emissions from other secondary smelters or primary smelters. Accordingly, these facilities are a high priority for future emissions testing.

Diesel Vehicles: The literature on dioxin emissions from diesel vehicles is quite limited and somewhat contradictory. The tunnel study by Oehme et al. (1991) suggests a relatively high level of emissions. This study is based on Norwegian fuels which may differ in composition from U.S. fuels and, although aggregate samples were collected representing hundreds of vehicles, the indirect method of analysis introduces uncertainty. Much lower emissions were measured by Marklund et al. (1990) on the basis of direct tailpipe tests involving diesel fuel in a heavy-duty Swedish vehicle (Marklund et al., 1990). This study reported no emissions at a detection limit of 100 pg/l or approximately 0.05 ng/km. This is a factor of 100 lower than the emission rate

reported by Oehme et al. (1991). Because this study's results are based on only one vehicle using Swedish fuel, this emission factor is also quite uncertain. These two studies yield a very wide range of emission estimates and clearly suggests that further testing is needed.

Coal-Fired Utilities: The importance of these facilities remains unknown. Only one U.S. facility has been tested and no detectable levels of dioxin were found. If dioxin were present at the detection limit, an emission factor can be calculated which suggests that, due to their number, these plants could collectively represent a moderately sized source. The potential importance of this source is enhanced by several factors. In addition to being numerous, they are large in size and their high stacks indicate that they could impact very large areas. Testing is currently underway to better characterize these emissions.

Pulp and Paper Mills: These facilities can have dioxin releases to water, land and paper products. The paper industry has recently made process changes which they estimate have reduced dioxin emissions by 90% from 1988 to 1992 (NCASI, 1993). Extensive surveys encompassing virtually all mills have been conducted, making this industry one of the best characterized in terms of dioxin emissions.

The other combustors evaluated in this report appear to be relatively minor sources on a national scale (although their local impacts could be important to evaluate). These include sewage sludge incinerators, hazardous waste incinerators, Kraft liquor boilers, drum and barrel reclaimers, tire combustors, carbon reactivation furnaces and scrap electric wire recovery facilities. The releases associated with chemical manufacturing could not be quantified due to the lack of test data. Potentially such releases could occur via the product itself or as emissions to the air, land or water. Such releases have lead to the termination of production of PCBs and some phenoxy herbicides. Recently, some claims have been made that significant dioxin emissions may occur during the production of vinyl chloride monomer and associated products. These claims have been strongly disputed by the industry. Insufficient emission data are currently available to make an independent evaluation.

Several investigators have attempted to conduct "mass balance" checks on the estimates of national dioxin releases to the environment. Basically, this procedure involves comparing estimates of the emissions to estimates of aerial deposition. Such studies in Sweden (Rappe, 1991) and Great Britain (Harrad and Jones, 1992) have suggested that the estimated deposition exceeds the estimated emissions by about 10 fold. These studies are acknowledged to be quite

speculative due to the strong potential for inaccuracies in emission and deposition estimates. In addition, the apparent discrepancies could be explained by long range transport from outside the country, resuspension and deposition of reservoir sources, atmospheric transformations or unidentified sources. Bearing these limitations in mind, this procedure has been used here to compare the estimated emissions and deposition in the United States.

Deposition measurements have been made at a number of locations in Europe (see Volume II) and two places in the United States (Koester and Hites, 1992). These limited data suggest that a deposition rate of 1 ng TEQ/m^2-yr is typical of remote areas and that 2-6 ng TEQ/m^2-yr is more typical of populated areas. Applying the values of 1 ng TEQ/m^2-yr to Alaska and 2-6 ng TEQ/m^2-yr to the continental United States, the total U.S. deposition can be estimated as 20,000 to 50,000 g TEQ/yr. This range can be compared to the range of emissions for the United States, 3,300 to 26,000 g TEQ/yr, as presented in Table II-3. It is not clear whether this type of mass balance can ever be refined to the point where definitive conclusions can be drawn. However, it remains one of the few methods of evaluating the existence of unknown sources.

II.3. OCCURRENCE AND BACKGROUND EXPOSURES

Polychlorinated dibenzo-*p*-dioxins (CDDs), polychlorinated dibenzofurans (CDFs), and polychlorinated biphenyls (PCBs) have been found throughout the world in practically all media including air, soil, water, sediment, fish and shellfish, and other food products such as meat and dairy products. The highest levels of these compounds are found in soils, sediments, and biota; very low levels are found in water and air. The widespread occurrence observed is not unexpected considering the numerous sources that emit these compounds into the atmosphere, and the overall resistance of these compounds to biotic and abiotic transformation.

II.3.1. United States Food Data

All available data on background levels in United States food are summarized in Table II-4. "Background" concentrations are defined here as those for which no source of dioxin-like compound contamination was identified to have impacted the concentrations reported. The background TEQ estimates are presented first assuming that nondetects equal half the detection limits and second assuming that nondetects equal zero. For food groups such as eggs, a wide range of TEQ estimates are seen indicating a high percent of nondetects among individual congeners. The higher of the two TEQ estimates, that calculated using half the detection limit for nondetects, are generally comparable to the TEQ estimates derived from studies conducted in Germany (Fürst et al. 1991) and Canada (Gilman and Newhook, 1991). The German and

Canadian studies did not, however, report how nondetects were treated in deriving their TEQs, but did report many nondetects in some food groups. In summary, the limited number of United States food samples and the high incidence of nondetects make an uncertain basis for estimating national background levels, although they are reasonably consistent with food level estimates reported for Canada and Germany. It is clear that more data are needed to adequately characterize the levels of dioxin-like compounds in the United States food supply. Although a large scale survey could confirm residue levels of CDD/F, some attention also needs to be paid to sampling/analytical methodology. Since many of the detected values are only a few multiples above reported detection limits, significant uncertainty results in reported mean values when there are many nondetects in a food category.

II.3.2. Summary of Media Levels

The estimated levels of CDD/CDFs in environmental media and food are summarized in Table II-5 and shown graphically in Figure II-4. Except for the TEQ levels in European food which are based on data reported for German food by Fürst et al. (1990), all other TEQ levels presented in Figure II-4 are based on the data analyzed in this study. The background TEQ levels of CDD/CDFs in water and air were found to be lower than in any of the other environmental media evaluated and were not included in Figure II-4. For most

Table II-4. Summary of CDD/F levels in United States food (pg/g fresh weight)

	Mean TEQ ND=0.5 DL	Mean TEQ ND=zero	Number of Samples	Reference
Beef/Veal	0.48	0.29	14	Stanley & Bauer (1989), LaFleur et al. (1990), Schecter et al. (1993)
Pork	0.26	0.10	12	Stanley & Bauer (1989), LaFleur et al. (1990), Schecter et al. (1993)
Chicken	0.19	0.07	9	Stanley & Bauer (1989), Schecter et al. (1993)
Eggs	0.13	0.0004	8	Stanley & Bauer (1989),
Dairy Products	0.36	0.35	5	Schecter et al. (1993)
Milk	0.07	0	2	EPA, 1991b
Fish	1.2	0.59	60	EPA, 1992

ND = Nondetect; DL - Detection Limit

Table II-5. Summary of CDD/F levels in environmental media and food (whole weight basis).

Media		North America[a]	Europe[a,e]
Soil, ppt:	TEQ	7.96 ± 5.70 (n=95)	8.69 (n=133)
Sediment, ppt:	TEQ	3.91[b] (n=7)	34.89[b] (n=20)
Fish, ppt:	TEQ	1.16 ± 1.21 (n=60)	0.93[f] (n=18)
Air, pg/m^3:	TEQ	0.0949 ± 0.24 (n=84)	0.108[g] (n=454)
Water, ppq:	TEQ	0.0056 ± 0.0079 (n=214)	NDA
Milk, ppt:	TEQ	0.07[c,d] (n=2)	0.05[h] (n=168)
Dairy, ppt:	TEQ	0.36 ± 0.29 (n=5)	0.08[i] (n=10)
Eggs, ppt:	TEQ	0.135 ± 0.119 (n=8)	0.152[d] (n=1)
Beef ppt:	TEQ	0.48 ± 0.99 (n=14)	0.32[j]; 0.61[k] (n=7)
Pork, ppt:	TEQ	0.26 ± 0.13 (n=12)	<0.06[l] (n=3)
Chicken, ppt:	TEQ	0.19 ± 0.29 (n=9)	0.21[l] (n=2)

Footnotes:

NDA = No data available.

[a] Values are the arithmetic mean TEQs and standard deviations.

[b] Standard deviations could not be calculated because detection limits for most samples were not reported.

[c] Value was calculated from the raw data used in EPA (1991b) using half the detection limits for nondetects.

[d] Standard deviation could not be calculated because data were limited for the congener that contributed the most to the total TEQ.

[e] Soil, sediment, and air values based on data from a variety of European countries (see Tables B-17 to B-30); egg data based on Beck et al. (1989); and other food levels based on data from Germany (Fürst et al., 1990).

[f] TEQ calculated from Fürst et al. (1990) for fresh water fish by assuming 7% fat content (EPA, 1993).

[g] TEQ assumed to be the mean of the midpoints of the ranges reported in four European studies (Clayton et al., 1993; König et al., 1993a; Liebl et al., 1993; Wevers et al., 1993).

[h] TEQ calculated from Fürst et al. (1990) by assuming 4% fat content.

[i] TEQ calculated for cheese from Fürst et al. (1990) by assuming 8% fat content.

[j] TEQ for beef calculated from Fürst et al. (1990) by assuming 19% fat content.

[k] TEQ for veal calculated from Fürst et al. (1990) by assuming 19% fat content.

[l] TEQ calculated from Fürst et al. (1990) by assuming 15% fat content.new Table II-5
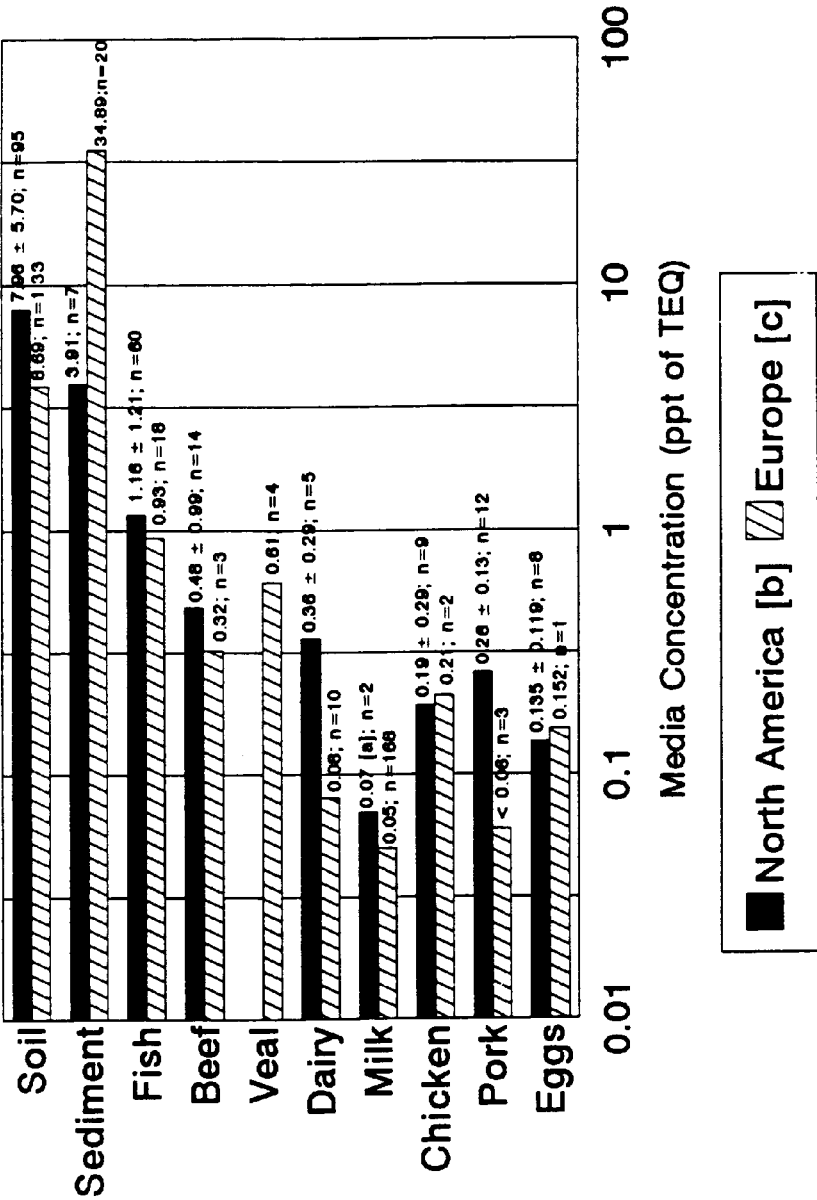
Figure II-4. Background environmental levels in TEQ.

■ North America [b] ▨ Europe [c]

Media Concentration (ppt of TEQ)

Soil: 7.96 ± 5.70; n=95 / 8.89; n=133
Sediment: 3.91; n=7 / 34.89; n=20
Fish: 1.16 ± 1.21; n=60 / 0.93; n=18
Beef: 0.48 ± 0.99; n=14 / 0.32; n=3
Veal: 0.61; n=4
Dairy: 0.36 ± 0.29; n=5 / 0.06; n=10
Milk: 0.07 [a]; n=2 / 0.05; n=166
Chicken: 0.19 ± 0.29; n=9 / 0.21; n=2
Pork: 0.26 ± 0.13; n=12 / < 0.06; n=3
Eggs: 0.155 ± 0.119; n=8 / 0.152; n=1

[a] based on an examination of raw data reported by EPA (1991b); [b] based on N. American studies;
[c] environmental media levels based on various European studies, food levels based on Fürst, et al. (1990), egg levels
based on Beck, et al. (1989)

media, the average levels appear to be similar between North America and Europe. However, differences were noted in three areas:

Sediment: The background levels in Europe were estimated to be higher than North America. It should be noted, however, that only the 2,3,7,8-TCDD/F and OCDD/F congeners were analyzed for background sediment sites in the United States and Europe. The sediment data are quite variable and can be very high in impacted areas (i.e., 2,3,7,8-TCDD levels over 1000 ppt have been measured in industrial areas). Also, it was difficult to interpret whether some of the European data truly represent unimpacted areas. Thus, these differences may be due more to the weakness of the data base and interpretation difficulties, rather than real differences.

Dairy Products: The data on dairy products suggest that North America levels are higher than European. Dairy products include a wide variety of food items with varying amounts of fat. Thus, the CDD/F levels would vary correspondingly. Differences in the mix of dairy products used for the North America and European estimates could explain these differences.

Pork: The pork data suggests that North America levels are higher than European levels. The low number of samples collected in both Europe and North America may mean this estimate is not representative.

In general, the differences noted above probably reflect the sparseness or inequalities in the data rather than real differences. The small number of samples available for analysis, particularly for food, should be considered when evaluating data from the United States and elsewhere. The human tissue data (see discussion below) suggest similar body burden levels in the North America, Europe and other industrial countries. Thus, it seems likely the media levels would also be similar. Large scale "market basket" type food surveys would be needed to confirm these levels.

II.3.3. Conclusions for Mechanisms of Impact to Food Chain

CDD/F can enter aquatic systems by either direct effluent discharges or atmospheric deposition. CDD/Fs in the atmosphere can deposit directly onto water bodies or onto watersheds and run off into the water system. The mechanism of impact which dominates in aquatic systems will depend on site specific conditions.

This assessment proposes the hypothesis that the primary mechanism by which dioxin-like compounds enter the terrestrial food chain is via atmospheric deposition. Deposition can occur directly onto plant surfaces or onto soil. Soil deposits can enter the food chain via direct ingestion (i.e. earth worms, fur preening by burrowing animals, incidental ingestion by grazing animals, etc). CDD/F in soil can become available to plants by volatilization and vapor absorption or particle resuspension and adherence to plant surfaces. In addition, CDD/F in soil can adsorb directly to underground portions of plants, but uptake from soil via the roots into above ground portions of plants is thought to be insignificant (McCrady, et al. 1990).

Support for this air-to-food hypothesis is provided by Hites (1991) who concluded that "background environmental levels of PCD/F are caused by PCD/F entering the environment through the atmospheric pathway." His

conclusion was based on demonstrations that the congener profiles in lake sediments could be linked to congener profiles of combustion sources. Further argument supporting this hypothesis is offered below:

  Numerous studies have shown that CDD/Fs are emitted into the air from a wide variety of sources (see Chapter 3 of Volume II).

  Studies have shown that CDD/Fs can be measured in wet and dry deposition in most locations including remote areas (Koester and Hites, 1993; Rappe, 1991).

  Numerous studies have shown that CDD/Fs are commonly found in soils throughout the world (see Chapter 4 of Volume II). Atmospheric transport and deposition is the only plausible mechanism that could lead to this widespread distribution.

  Models of the air-to-plant-to-animal food chain have been constructed. Exercises with these models show that measured deposition rates and air concentrations can be used to predict measured food levels (Travis and Hattemer-Frey, 1991; also see Chapter 7 of Volume III).

Alternative mechanisms to the air-to-food hypothesis seem less likely:

> - Uptake from water into food crops and livestock is minimal due to the hydrophobic nature of
> these compounds. Travis and Hattemer-Frey (1987, 1991) estimate water intake accounts for less
> than 0.01% of the total daily intake of 2,3,7,8-TCDD in cattle. Experiments by McCrady, et al.
> (1990) show very little uptake in plants from aqueous solutions.

> - Relatively little uptake is expected in food from soil residues that originate from sources
> other than atmospheric dispersion, i.e. pesticides, sewage sludge, and waste disposal
> operations. Pesticides are discussed below. Sewage sludge application onto agricultural fields
> is not a widespread practice and the amount of CDD/F in this material is quite low compared to the
> amount emitted to the atmosphere (See Chapter 3 of Volume II). Waste disposal operations can be
> the dominant source of CDD/F in soils at isolated locations such as Times Beach, but are not
> sufficiently widespread to explain the ubiquitous nature of these compounds.

> - The contribution of CDD/Fs to the environment via pesticides has been reduced in recent years
> but remains somewhat uncertain. In the past, CDD/Fs have been associated with certain phenoxy
> herbicides. Many of these compounds are no longer produced and EPA has sponsored data call-ins
> requiring certain pesticide manufacturers to test their products for dioxin content. The
> responses, so far, indicate that levels in these products are below or near the limit of
> quantitation (see Chapter 3 of Volume II).

- Uptake into food from paper products also appears to be minimal. In the early 1980s, testing showed that CDD/Fs could migrate from paper containers into food. Current levels in paper products are now much lower, and food testing in products such as milk and beef have shown detectable levels prior to packaging, suggesting packaging is not the major source (see Chapter 4 of Volume II).

A related issue is whether the CDD/F in food results more from current or past emissions. Sediment core sampling indicates that CDD/F levels in the environment began increasing around the beginning of the twentieth century and have been declining since about 1980 (Smith et al, 1992). Thus, CDD/Fs have been accumulating for many years and may have created a reservoir that continues to impact the food chain. As discussed in Chapter 3 of Volume II, researchers in several countries have attempted to compare known emissions with deposition rates. These studies may suggest that annual deposits exceed annual emissions. One explanation may be that the reservoir sources cause deposition through volatilization/atmospheric scavenging or particle resuspension. These mass balance studies are highly uncertain and it remains unknown how much of the food chain impact is due to current versus past emissions.

II.4. TEMPORAL TRENDS

Small amounts of dioxin-like compounds may be formed during natural fires suggesting that these compounds may have always been present in the environment. However, it is generally believed that much more of these compounds have been produced and released into the environment in association with man's industrial and combustion practices, and as a result, environmental levels are likely to be higher in modern times than they were in prior times. However, the trend may now be reversing (i.e., releases and environmental levels may be gradually decreasing) due to changes in industrial practices (Rappe, 1992). As discussed earlier, the potential for environmental releases of dioxin-like compounds have been reduced due to the switch to unleaded automobile fuels (and associated use of catalytic converters and reduction in halogenated scavenger fuel additives), process changes at pulp and paper mills, improved emission controls for incinerators, and reductions in the manufacture and use of chlorinated phenolic intermediates and products.

Studies that may be used to assess temporal trends in human exposure to dioxins and furans are extremely limited. Analysis of sediment core layers has shown increases in CDD/CDF concentrations beginning in the 1920's and continuing until the late 1970's (Smith et al, 1992). Another useful study for evaluating changes in human exposure over time is EPA's National Human Adipose Tissue Survey or NHATS. The purpose of NHATS is to monitor the human body burden of selected chemicals in the general U.S. population (EPA, 1991a). The results of this study indicate that exposure to certain dioxins and furan congeners may have decreased over this 5-year time period. However, further studies are needed to verify that these changes are not a result of protocol changes, but actual reductions in exposures. A recent study by Patterson et al. (1994) found decreases in PCB body burdens from 1982 to 1988/89 based on human tissue and blood testing.

II.5. BACKGROUND EXPOSURE LEVELS

Table II-6 illustrates the derivation of a background exposure level to CDD/F for the United States on the basis of diet. This estimate was derived using the upper-range background concentrations (i.e., those calculated using one-half the detection limit for the non-detects) and central estimates of ingestion rates. This approach yields a total background exposure estimate for CDD/Fs of 119 pg TEQ/d. The exposures by pathway are diagrammed in Figure II-5.

The background exposure estimates are intended to be representative of the general population. They do not account for individuals with higher consumption rates of a specific food group (e.g., subsistence fishermen, nursing infants, and subsistence farmers--these are discussed Section II-6).   The fish concentration used to estimate background exposures, represents the average value found in fish from fresh and estuarine waters (see Section 4.5 of Volume II). Correspondingly, the ingestion rate used here reflects the per capita average ingestion rate of fresh/estuarine fish (EPA, 1989). Many individuals are likely to have higher ingestion rates of marine fish. However, the limited data on marine species indicates that the dioxin levels may be one to two orders of magnitude lower than fresh/estuarine water fish (also see Section 4.5 of V. II).

The contact rates for ingestion of fish, soil, and water, and inhalation were derived from the Exposure Factors Handbook (EPA, 1989). For food products such as milk, dairy, eggs, beef, pork, and poultry, a different approach was taken because there is evidence that consumption rates have changed since the data for the Exposure Factors Handbook were collected. Contact rates for these food groups were derived from commodity disappearance data from the United States Department of Agricultures's (USDA) report on

Table II-6. Estimated TEQ background exposures in the United States.

Media	North America				
	Conc. TEQ[a]	Contact rate[b]	Daily intake[c] mg/day	Daily intake pg/day	% of total
Soil ingestion	8.0 ppt	100 mg/day	8.0×10^{-10}	0.8	0.7
Fish ingestion	1.2 ppt	6.5 g/day	7.8×10^{-9}	7.8	6.6
Inhalation	0.095 pg/m^3	23 m^3/day	2.2×10^{-9}	2.2	1.8
Water ingestion	0.0056 ppq	1.4 L/day	7.8×10^{-12}	0.008	0.01
Milk ingestion	0.07[d] ppt	251 g/day	1.8×10^{-8}	17.6	14.8
Dairy ingestion	0.36 ppt	67 g/day	2.4×10^{-8}	24.1	20.3
Eggs ingestion	0.14 ppt	29 g/day	4.1×10^{-9}	4.1	3.4
Beef and veal ingestion	0.48 ppt	77 g/day	3.7×10^{-8}	37.0	31.2
Pork ingestion	0.26 ppt	47 g/day	1.2×10^{-8}	12.2	10.3
Chicken ingestion	0.19 ppt	68 g/day	1.3×10^{-8}	12.9	10.9
Total			1.08×10^{-7}	119	100

Footnotes: NA = Not applicable, NDA = No Data Available.
[a] Values from Table 4-10, Chapter 4, Volume II of this assessment.
[b] Values from Exposure Factors Handbook (EPA, 1989), and EPA (1984)
[c] Daily intake = Contact rate x Conc. TEQ x Unit Conversion (soil unit conversion = 10^{-12}, all other media unit conversion = 10^{-9}).
[d] Value was calculated from data in EPA (1991b).

Food Consumption, Prices, and Expenditures between 1970 and 1992 (USDA, 1993), and intake data from USDA's Nationwide Food Consumption Survey (NFCS) (USDA, 1992). USDA (1993) estimated per capita consumption rates using disappearance data (i.e., the quantity of marketable food commodities utilized in the United States over a specified time period) divided by the total population. The average of USDA disappearance and NFCS intake rates were used in this study to represent the most current estimates of typical ingestion rates in the United States.

These background exposure estimates for the United States are comparable to analogous estimates for European countries, as displayed in Figure II-6. These include estimates for Germany, which range from 79 pg TEQ/day based on Fürst, et al. (1990) to 158 pg TEQ/day based on Fürst, et al. (1991), 118-126 pg TEQ/day exposure via numerous routes in the Netherlands (Theelen, 1991), and 140-290 pg TEQ/day for the typical Canadian exposed mainly through food ingestion (Gilman and Newhook, 1991). It is generally concluded by these researchers that dietary intake is the primary pathway of human exposure to CDDs and CDFs. Over 90 percent of human exposure is estimated to occur through the diet, with foods from animal origins being the predominant sources.

Background exposures can also be estimated on the basis of body burdens through the use of pharmacokinetic models. Pharmacokinetic compartmental models are presented in Chapter 6 of Volume II which can be used to estimate daily dose intake of 2,3,7,8-TCDD from adipose tissue or blood lipid concentrations. Using this approach, exposure levels to 2,3,7,8-TCDD are estimated to be about 10 to 30 pg/day which is consistent with the estimates derived using diet-based approaches. The model can also be applied to other dioxin congeners with knowledge of their biophysical properties.

The most extensive United States study of CDD/F body burdens is the National Human Adipose Tissue Survey (NHATS) (EPA, 1991a). This survey analyzed for CDD/Fs in 48 human tissue samples which were composited from 865 samples. These samples were collected during 1987 from autopsied cadavers and surgical patients. The sample compositing prevents use of this data to examine the distribution of CDD/F levels in tissue among individuals. However, it did allow conclusions in the following areas:

- **National Averages:** The national averages for all TEQ congeners were estimated and totaled to 28 pg of TEQ/g.

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Total Exposure = 119 pg/day

Beef Ingestion — 37.0
Dairy Ingestion — 24.1
Milk Ingestion — 17.6
Chicken Ingestion — 12.9
Pork Ingestion — 12.2
Fish Ingestion — 7.8
Egg Ingestion — 4.1
Inhalation — 2.2
Soil Ingestion — 0.8
Water Ingestion — Negligible

North America Daily Intake (pg/day) of TEQ

0.0   10.0   20.0   30.0   40.0
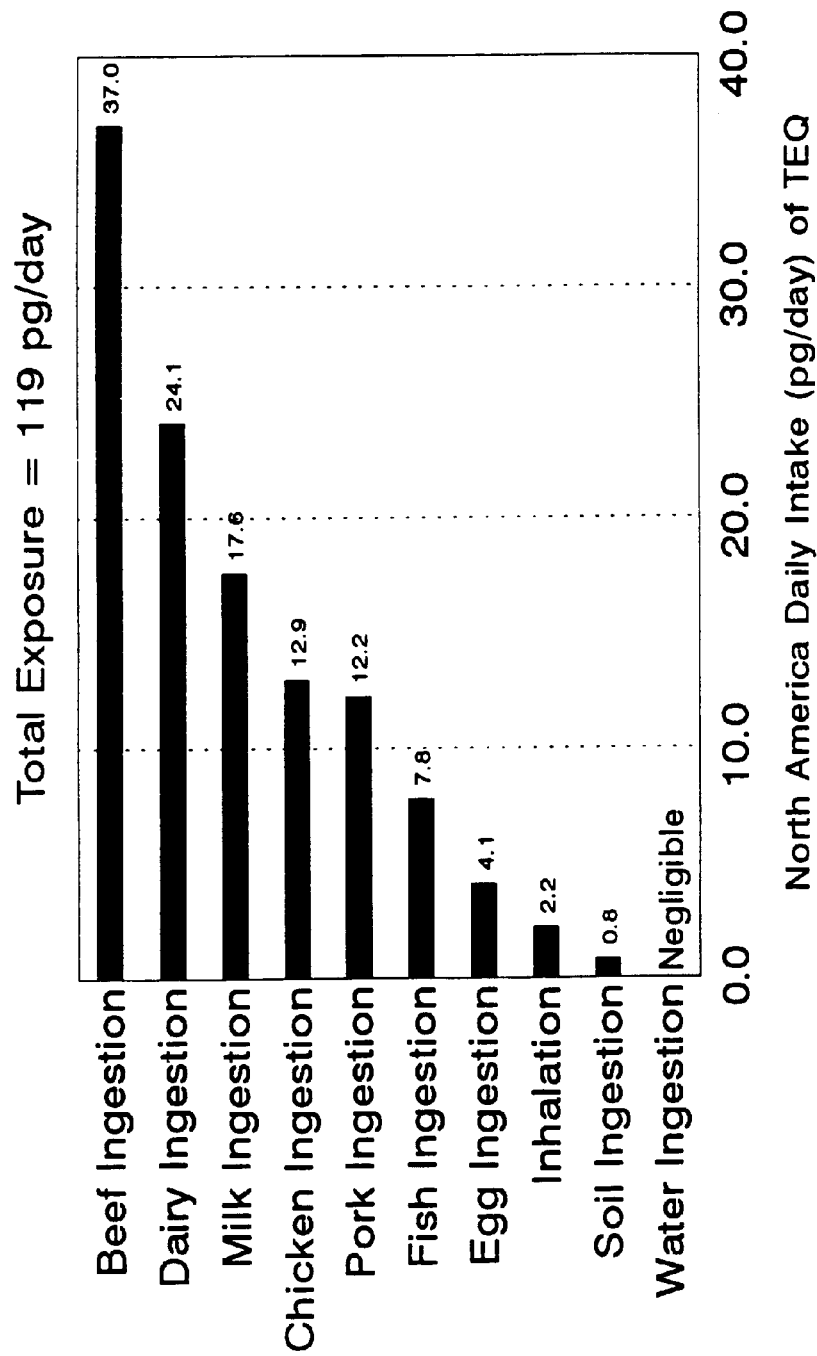
Figure II-5. Background TEQ exposures for North America by pathway.

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Figure II-6. Comparison of background TEQ exposures for North America, Germany, and the Netherlands.

NORTH AMERICA [a]
119 pg/day

GERMANY [b]
79 pg/day

NETHERLANDS [c]
117 pg/day

[a] based on current assessment
[b] based on Fürst, et al. (1990, 1991)
[c] based on Theelen (1991)

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- **Age Effects:** Tissue concentrations of CDD/Fs were found to increase with age.
- **Geographic Effects:** In general, the average CDD/F tissue concentrations appeared fairly uniform geographically.
- **Race Effects:** No significant difference in CDD/F tissue concentrations were found on the basis of race.
- **Sex Effects:** No significant difference in CDD/F tissue concentrations were found between males and females.
- **Temporal Trends:** The 1987 survey showed decreases in tissue concentrations relative to the 1982 survey for all congeners. However, it is not known whether these declines were due to improvements in the analytical methods or actual reductions in body burden levels. The percent reductions among individual congeners varied from 9 percent to 96 percent.

New information on levels of dioxin-like compounds in human tissue/blood has recently been published (Patterson et al., 1994). The adipose tissue samples (collected from 28 individuals) were analyzed for PCBs 77, 81, 126 and 169. The TEQ levels for these coplanar PCBs summed to 17 ppt (using the toxic equivalency factors proposed by Safe, 1990). The PCB levels generally exceeded the mean 2,3,7,8-TCDD level (10.4 ppt) and PCB-126 exceeded the 2,3,7,8-TCDD level by over an order of magnitude. The authors found that the PCBs contributed 24% of the total TEQs. Patterson et al. (1994) also studied serum collected by the CDC blood bank in Atlanta during 1982, 1988 and 1989. These samples were pooled from over 200 donors. The serum data appears to indicate a decrease in exposure to PCBs from 1982 to 1988/1989. In general, the Patterson et al. (1994) data suggests that the coplanar PCBs can contribute significantly to body burdens of dioxin-like compounds. The data suggest that the coplanar PCBs can increase the total background body burden to over 40 ppt of TEQ. This conclusion is uncertain because the people studied by Patterson et al. (1994) may not be representative of the overall U.S. population, and the toxic equivalency factors proposed by Safe (1990) have been acknowledged to be conservative.

Levels of these compounds found in human tissue/blood appear similar in Europe and North America. Schecter (1991) compared levels of dioxin-like compounds found in blood among people from U.S. (100 subjects) and Germany (85 subjects). Although mean levels of individual congeners differed by as much as a factor of two between the two populations, the total TEQ averaged 42 ppt in the German subjects and was 41 ppt in the pooled U.S. samples.

II.6. HIGHLY EXPOSED POPULATIONS

Certain groups of people may have higher exposures to the dioxin-like compounds than the general population. This section discusses such exposures which result from dietary habits. Other population segments can be highly exposed due to occupational conditions or industrial accidents and are discussed in the Epidemiology Chapter if the Dioxin Health Reassessment Document (EPA, 1994) and should be consulted if further details are desired.

Although the subpopulations discussed below have the potential for high exposure to dioxin-like compounds, a careful evaluation is needed to confirm this possibility. It would generally be inappropriate to compute the total background exposure for a certain group by simply adding the dioxin intake from the highly consumed food to the background exposure levels. The background exposure estimate assumes a typical pattern of food ingestion, whereas persons in a subpopulation who have a high consumption rate of one particular food type are likely to eat less of other food types. Ideally, the assessor should base this evaluation on the entire diet of the subpopulation and use case-specific values for food ingestion rates and concentrations of dioxin-like compounds.

One group of potentially highly exposed individuals is nursing infants. Schecter et al. (1992) reports that a study of 42 U.S. women found an average of 16 ppt of TEQ (3.3 ppt of 2,3,7,8-TCDD) in the lipid portion of breast milk. A much larger study in Germany (n = 526) found an average of 29 ppt of TEQ in lipid portion of breast milk. The level in human breast milk can be predicted on the basis of the estimated dioxin intake by the mother. Such procedures have been developed by Smith (1987) and Sullivan et al. (1991) and are presented in Chapters 5 and 6 of Volume II.

Using these procedures and assuming that an infant breast feeds for one year, has an average weight during this period of 10 kg, ingests 0.8 kg/d of breast milk and that the dioxin concentration in milk fat is 20 ppt of TEQ, the average daily dose to the infant over this period is predicted to be about 60 pg of TEQ/kg-d. This value is much higher than the estimated range for background exposure to adults (i.e., 1-3 pg of TEQ/kg-d). However, if a 70 yr averaging time is used, then the lifetime average daily dose is estimated to be 0.8 pg of TEQ/kg-d which is near the lower end of the adult background exposure range. On a mass basis, the cumulative dose to the infant under this scenario is about 210 ng compared to a lifetime background dose of about 1700 to 5100 ng (suggesting that 4 to 12 percent of the lifetime dose may occur as a result of breast feeding). Traditionally, EPA has used the lifetime average daily dose as the basis for evaluating cancer risk and the average daily dose (i.e., the daily exposure per unit body weight occurring during an exposure event) as the more appropriate indicator of risk for noncancer

endpoints. This issue is discussed further in the companion document on dioxin health effects.

The possibility of high exposure to dioxin as a result of fish consumption is most likely to occur in situations where individuals consume a large quantity of fish from one location where the dioxin level in the fish are elevated above background levels. Most people eat fish from multiple sources and even if large quantities are consumed are not likely to have unusually high exposures. However, individuals who fish regularly for purposes of basic subsistence are likely to obtain their fish from one source and have the potential for elevated exposures. Such individuals may consume quite large quantities of fish. EPA (1989) presents studies that indicate that recreational anglers near large water bodies consume 30 g/d (as a mean) and 140 g/d (as an upper estimate). Wolfe and Walker (1987) found subsistence fish ingestion rates up to 300 g/d in a study conducted in Alaska.

Several studies have identified potentially highly exposed populations as a result of fish consumption:

Svensson et al. (1991) found elevated blood levels of CDDs and CDFs in high fish consumers living near the Baltic Sea in Sweden.

Dewailly et al. (1994) observed elevated levels of coplanar PCBs in the blood of fishermen on the north shore of the Gulf of the St. Lawrence River who consume large amounts of seafood. Coplanar PCB levels were 20 times higher among the 10 highly exposed fishermen than among the controls. Dewailly et al. (1994) also observed elevated levels of coplanar PCBs in the breast milk of Inuit women of Arctic Quebec. The principal source of protein for the Inuit people is fish and sea mammal consumption.

Studies are underway to evaluate whether native Americans living on the Columbia River in Washington have high dioxin exposures as a result of fish consumption. These tribes consume large quantities of salmon from the river. A recent study (Columbia River Intertribal Fish Commission, 1993) suggests that these individuals have an average fish consumption rate of 30 g/day. Currently studies are underway to measure dioxin levels in fish from this region.

The possibility of high exposure to dioxin as a result of consuming meat and dairy products is most likely to occur in situations where individuals consume a large quantity of these foods from one location where the dioxin level is elevated above background levels. Most people eat meat and diary products from multiple sources and even if large quantities are consumed are not likely to have unusually high exposures. Individuals who raise their own livestock for purposes of basic subsistence, however, have the potential for elevated exposures. No

epidemiological studies were found in the literature evaluating this issue. Volume III of this document, however, presents methods for evaluating this type of exposure on a site-specific basis.

REFERENCES FOR VOLUME II

Bidleman, T.F. (1988)   Atmospheric processes. Wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Techol., 22:4, pp 361-367.

Beck, H.; Eckart, K.; Mathar, W.; Wittkowski, R. (1989) PCDD and PCDF body burden from food intake in the Federal Republic of Germany. Chemosphere 18 (1-6):   417-424.

Clayton, P.; Davis, B.; Duarte-Davidson, R.; Halsall, C.; Jones, K.C.; Jones, P. (1993) PCDDs and PCDFs in ambient UK urban air. Presented at: Dioxin '93, 13th Symposium on Dioxins and Related Compounds; Vienna, Austria; September 1993.

Clement, R.E.; Tashiro, C. (1991) Forest fires as a source of PCDD and PCDF. Presented at: Dioxin '91, 11th International Symposium on Chlorinated Dioxins and Related Compounds; RTP, NC. September 23 - 27, 1991.

Columbia River Intertribal Fish Commission (1993) A fish consumption survey of the Umtilla, Nez Perce, Yakima, and Warm Springs tribes of the Columbia River basin. Peer Review Draft Report.

Czuczwa, J.M.; Hites, R.A. (1984) Environmental fate of combustion-generated polychlorinated dioxins and furans. Environ. Sci. Techol., 18:6, pp 444-450.
.
Czuczwa, J.M.; Hites, R.A. (1985) Historical record of polychlorinated dioxins and furans in Lake Huron sediments. In: Keith, L.H.; Rappe, C.; Choudhary, G., eds. Chlorinated Dioxins and Dibenzofurans in the Total Environment. Butterworth Publishers, Boston, MA. pp. 59-63.

Czuczwa, J.M.; McVeety, B.D.; Hites, R.A. (1984) Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments from Siskiwit Lake, Isle Royale. Science 226.

Dewailly, E.; Ryan, J.J.; Laliberte, C.; Bruneau, S.; Weber, J.P.; Gingras, S.; Carrier, G. (1994) Exposure of remote maritime populations to coplanar PCBs. Environmental Health Perspectives. Vol. 102, Suppl. 1:205-209.

ECETOC (1992) European Centre for Ecotoxicology and Toxicology of Chemicals. Exposure of man to dioxins: a perspective on industrial waste incineration. Technical Report No. 49. Brussels, Belgium.

Fiedler, H.; Hutzinger, O. (1992) Sources and sinks of dioxins: Germany. Chemosphere, 25:1487-1491.

Fürst, P.; Fürst, C.; Groebel, W. (1990) Levels of PCDDs and PCDFs in food-stuffs from the Federal Republic of Germany. Chemosphere 20 (7-9): 787-792.

Fürst, P.; Fürst, L.; Widmers, K. (1991) Body burden with PCDD and PCDF from food. In: Biological Basis for Risk Assessment of Dioxins and Related Compounds. Banbury Report #35. Edited by M. Gallo, R. Scheuplein and K. Van der Heijden. Cold Springs Harbor Laboratory Press. Plainview, NY.

Gilman, A; Newhook, R. (1991)   An updated assessment of the exposure of Canadians to dioxins and furans. Chemosphere 23:1661-1667.

Harrad, S.J.; Jones, K.C. (1992) A source inventory and budget for chlorinated dioxins and furans in the United Kingdom environment. The Science of the Total Environment 126:89-107.

Hites, R.A. (1991) Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans. Prepared for the U.S. Environmental Protection Agency, Methods Research Branch, Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC. EPA/600/3-91/002.

Koester, C.J.; Hites, R.A. (1992) Wet and dry deposition of chlorinated dioxins and furans. Environ. Sci. Technol. 26:1375-1382.

König, J.; Balfanz, E.; Günther, W.J.; Liebl, K.H.; Büchen, M. (1993b) Ambient air levels of polychlorinated biphenyls at different sites in Hessen, Germany. Presented at: Dioxin '93, 13th International Symposium on Chlorinated Dioxins and Related Compounds; Vienna, Austria; September 1993.

Koning, J.; Sein, A.A.; Troost, L.M.; Bremmer, H.J. (1993) Sources of dioxin emissions in the Netherlands. Presented at: Dioxin '93, 13th International Symposium on Chlorinated Dioxins and Related Compounds; Vienna, Austria; September 1993.

LaFleur, L.; Bousquet, T.; Ranage, K.; Brunck, B.; Davis, T.; Luksemburg, W.; Peterson, B. (1990) Analysis of TCDD and TCDF on the ppq-level in milk and food sources. Chemosphere 20(10-12):1657-1662.

Lexen, K.; De Wit, C; Jansson, B.; Kjeller, L.O.; Kulp, S.E.; Ljung, K.; Soderstrom, G.; Rappe, C. (1992) Polychlorinated dibenzo-p-dioxin and dibenzofuran levels and patterns in samples from different Swedish industries analyzed within the Swedish dioxin survey. Presented at: Dioxin '92, 12th International Symposium on Dioxins and Related Compounds; Tampere, Finland; August 1992.

Liebl, K.; Büchen, M.; Ott, W.; Fricke, W. (1993) Polychlorinated dibenzo(p)dioxins and dibenzofurans in ambient air; concentration and deposition measurements in Hessen, Germany. Presented at Dioxin '93, 13th International Symposium on Chlorinated Dioxins and Related Compounds; Vienna, Austria; September 1993.

Ligon, W.V.; Dorn, S.B.; May, R.J.; Allison, M.J. (1989) Chlorodibenzofuran and chlorodibenzo-p-dioxin levels in Chilean mummies dated to about 2800 years before the present. Environ. Sci. Technol. 23:1286-1290.

Marklund, S.; Andersson, R.; Tysklind, M.; Rappe, C.; Egeback, K.E.; Bjorkman, E.; Grigoriadis, V. (1990) Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20(5):553-561

McCrady, J.K.; McFarlane, C.; Gander, L.K. (1990) The transport and fate of 2,3,7,8-TCDD in soybean and corn. Chemosphere 21:359-376.

NCASI (1993) National Council of the Paper Industry for Air and Stream Improvement.

Summary of data reflective of pulp and paper industry progress in reducing the TCDD/TCDF content of effluents, pulps and wastewater treatment sludges. New York, NY. NCASI, June, 1993.

Oehme, M.; Larssen,S.; Brevik, E.M. (1991) Emission factors of PCDD/F for road vehicles obtained by a tunnel experiment. Chemosphere, 23:1699-1708.

Patterson, D.G.; Todd, G.D.; Turner, W.E.; Maggio, V.; Alexander, L.R.; Needham, L.L. (1994) Levels of nonortho-substituted polychlorinated biphenyls, dibenzo-p-dioxins, and dibenzofurans in human serum and adipose tissue. Environmental Health Perspectives. Vol. 101, Suppl. 1:195-204.

Rappe, C. (1991) Sources of human exposure to PCDDs and PCDFs. In: Gallo, M.; Scheuplein, R.; Van der Heijden, K., eds. Biological basis for risk assessment of dioxins and related compounds. Banbury Report #35. Plainview, NY: Cold Spring Harbor Laboratory Press.

Rappe, C. (1992) Sources of PCDDs and PCDFs. Introduction. Reactions, levels, patterns, profiles and trends. Chemosphere 25(1-2):41-44.

Riss, A.; Aichinger, H. (1993) Reduction of dioxin emissions and regulatory measures in Austria. Presented at: Dioxin '93, 13th International Symposium on Chlorinated Dioxins and Related Compounds; Vienna, Austria; September 1993.

Safe, S. (1990) Polychlorinated biphenyl, dibenzo-p-dioxins, dibenzofurans, and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors. CRC Crit. Rev. Toxicol. 21:51-88.

Schatowitz, B.; Brandt, G.; Gafner, F.; Schlumpf, E.; Biihler, R.; Hasler, P.; Nussbaumer, T. (1993) Dioxin emissions from wood combustion. Presented at: Dioxin '93, 13th International Symposium on Chlorinated Dioxins and Related Compounds; Vienna, Austria; September 1993.

Schecter, A. (1991) Dioxins and related compounds in humans and in the environment. In: Biological Basis for Risk Assessment of Dioxins and Related Compounds. Banbury Report #35. Edited by M. Gallo, R. Scheuplein and K. Van der Heijden. Cold Spring Harbor Laboratory Press. Plainview, NY.

Schecter, A.; Papke, O.; Ball, M.; Startin, J.R.; Wright, C.; Kelly, M. (1993) Dioxin levels in food from the U.S. with estimated daily intake. Submitted to Dioxin '93.

Schecter, A.; Papke, O.; Ball, M.; Startin, J.R.; Wright, C.; Kelly, M. (1992) Dioxin and dibenzofuran levels in food from the United States as compared to levels in food from other industrial countries. 12th International Symposium on Dioxins and Related Compounds. Tampere, Finland August 1992. Finnish Institute of Occupational Health, Helsinki, Finland. pp. 243-246.

Smith, A.H. (1987) Infant exposure assessment for breast milk dioxins and furans derived from waste incineration emissions. Risk Analysis 7(3): 347-353.

Smith, R.M.; O'Keefe, P.W.; Aldous, K.M.; Briggs, R.; Hilker, D.R.; Connor, S. (1992) Measurement of PCDFs and PCDDs in air samples and lake sediments at several

locations in upstate New York. Chemosphere 25(1-2): 95-98.

Stanley, J.S.; Bauer, K.M. (1989) Chlorinated dibenzo-p-dioxin and dibenzofuran residue levels in food. Sacramento, CA: State of California Air Resources Board. ARB Contract No. A6-197-32.

Sullivan, M.J.; Custance, S.R.; Miller, C.J. (1991) Infant exposure to dioxin in mother's milk resulting from maternal ingestion of contaminated fish. Chemosphere 23(8-10):1387-1396.

Svensson, B.G.; Nelsson, A.; Hansson, M.; Rappe, C.; Akesson, B.; Skerfving, S. (1991) Exposure to dioxins and dibenzofurans through the consumption of fish. New England Journal of Medicine. 324(1):8-12.

Theelan, RMC. (1991)   Modeling of human exposure to TCDD and I-TEQ in the Netherlands: background and occupational. In: Gallo M, Scheuplein r;, Van der Heijden, K, eds. Biological Basis for Risk Assessment of Dioxins and Related Compounds. Banbury Report #35. Plainview, NY.

Travis, C.C.; Hattemer-Frey, H.A. (1987) Human exposure to 2,3,7,8-TCDD. Chemosphere 16,:2331-2342.

Travis, C.C.; Hattemer-Frey, H.A. (1991) Human exposure to dioxin. Sci. Total Environ. 104: 97-127.

U.S. Department of Agriculture (1992) Food and nutrient intakes by individuals in the United States, 1 day, 1987-88: Nationwide Food Consumption Survey 1987-88. Washington, DC: USDA Human Nutrition Information Service. NFCS Rpt. No. 87-I-1 in preparation.

U.S. Department of Agriculture (1993) Food consumption, prices, and expenditures, 1970-1992. Washington, DC: USDA Economic Research Service. Statistical Bulletin 867.

U.S. Environmental Protection Agency. (1984) An estimation of the daily food intake based on data from the 1977-1978 USDA Nationwide Food Consumption Survey. Washington, DC., Office of Radiation Programs, EPA 520/1-84-015.

U.S. Environmental Protection Agency. (1989) Exposure Factors Handbook. Exposure Assessment Group, Office of Health and Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency. EPA/600/8-89/043. July, 1989.

U.S. Environmental Protection Agency. (1991a) Chlorinated dioxins and furans in the general U.S. population: NHATS FY87 results. Washington, D.C. Office of Toxic Substances, EPA-560/5-91-003.

U.S. Environmental Protection Agency. (1991b) Feasibility of environmental monitoring and exposure assessment for a municipal waste combustor: Rutland Vermont Pilot Study. Washington, DC: Office of Research and Development, EPA-600/8-91/007.

U.S. Environmental Protection Agency. (1992) National study of chemical residues in fish. Washington, DC: Office of Science and Technology. EPA/823-R-02-008.

U.S. Environmental Protection Agency. (1994) Health Assessment for 2,3,7,8-TCDD and Related Compounds. External Review Draft. EPA/600/BP-92/001a-c.

Wevers, M.; De Fré, R; Rymen, T. (1992) Dioxins and dibenzofurans in tunnel air. Vol 9 (Sources of Exposure) of Extended Abstracts. Presented at: Dioxin '92, 12th International Symposium on Chlorinated Dioxins and Related Compounds; Tampere, Finland; August 1992.

Wevers, M.; De Fré, R.; Van Cleuvenbergen, R.; Rymen, T. (1993) Concentrations of PCDDs and PCDFs in ambient air at selected locations in Flanders. Presented at Dioxin '93, 13th International Symposium on Chlorinated Dioxins and Related Compounds; Vienna, Austria; September 1993.

Wolfe, R.J.; Walker, R.J. (1987) Subsistence Economics in Alaska: Productivity, Geography and Developmental Impacts. Arctic Anthropology 24(2):56-81.

VOLUME III. SITE-SPECIFIC ASSESSMENT PROCEDURES

III.1.   EXPOSURE EQUATION

Volume III describes procedures for conducting site specific exposure assessments to estimate potential dose. A potential dose is defined as a daily amount of contaminant inhaled, ingested, or otherwise coming in contact with outer surfaces of the body, averaged over an individual's body weight and lifetime. The general equation used to estimate potential dose normalized over body weight and lifetime is as follows:

$$\text{Lifetime Average Daily Dose (LADD)} = \frac{(\text{exposure media concentration} \times \text{contact rate} \times \text{contact fraction} \times \text{exposure duration})}{(\text{body weight} \times \text{lifetime})}$$

This procedure is used to estimate dose in the form needed to assess cancer risks. Each of the terms in this exposure equation is discussed briefly below:

● **Exposure media concentrations:**   These include the average concentrations in the media to which individuals are exposed. Media considered in this assessment include soil, air, water, vegetables/fruits, fish, beef, and milk.

● **Contact rate:**   These include the ingestion rates, inhalation rates, and soil contact rates for the exposure pathways.

● **Contact fraction:**   This term describes the distribution of total contact between contaminated and uncontaminated media. For example, a contact fraction of 0.8 for inhalation means that 80% of the air inhaled over the exposure period contains dioxin-like compounds in vapor form or sorbed to air-borne particulates.

● **Exposure duration:**   This is the overall time period of exposure, mostly pertinent to adult exposures. Another exposure duration considered in this methodology is one associated with a childhood pattern of soil ingestion. The exposure duration in this case is 5 years.

● **Body weight:**   For all the pathways, the human adult body weight of 70 kg is assumed. This value represents the United States population average. The body weight for child soil ingestion is 17 kg (EPA, 1989).

● **Lifetime:**   Following convention, and because cancer risk slope factors are derived

based on a 70-year human lifetime, the average adult lifetime assumed throughout this document is 70 years.

III.2. PROCEDURE FOR ESTIMATING EXPOSURE

Before making exposure estimates, the assessor needs to gain a more complete understanding of the exposure setting and the contamination source. The approach used for this assessment is termed the exposure scenario approach. A "road map" of that procedure including identification of chapters in Volumes II and III where key information can be found, is shown in Figure III-1. Brief descriptions of 7 steps in this approach are:

Step 1. Identify Source: Three principal sources are addressed in this document: contaminated soils, stack emissions, and effluent discharges.

Step 2. Estimate Release Rates: Estimating the release of contaminants from the initial source is the first step towards estimating the concentration in the exposure media. Releases from soil contamination include volatilization, and wind and soil erosion.   Stack emissions and effluent discharges are point source releases into the environment.

Step 3. Estimate Exposure Point Concentrations: Contaminants released from soils, emitted from stacks, or discharged into surface waters move through the environment to points where human exposure may occur, and/or to impact environmental media to which humans are exposed. Various fate, transport, and transfer models are used to predict exposure media concentrations given source releases.

Step 4. Characterize Exposed Individuals and Exposure Patterns: Exposed individuals in the scenarios of this assessment are individuals who are exposed in their home environments. They are residents who breathe air at their residence, fish recreationally, have a home garden, farm, and are children ages 2-6 for the soil ingestion pathway. Exposures which are occur at the workplace or other locations are not discussed in this assessment, although the procedures could be adapted for other exposure sites. Each of these pathways are evaluated separately. Since it is unlikely that single individuals would experience all of these pathways, the exposures across pathways are not added. Each pathway has a set of exposure parameters including contact rates, contact fractions, body weights, exposure durations, and a lifetime.

STEPS	DOCUMENT CHAPTERS
Step 1. Identify Sources	
A. Soil, on and off-site	Chapter 4, Volume II
B. Stack emissions	Chapter 3, Volume III
	Chapter 3, Volume II
C. Effluent Discharges	Chapter 3, Volume II
Step 2. Estimate Release Rates	
A. Volatilization, erosion, etc.	Chapter 4, Volume III
B. Stack emissions	Chapter 3, Volume III
	Chapter 3, Volume II
C. Effluent discharges	Chapter 4, Volume III
	Chapter 3, Volume II
Step 3. Estimate Exposure Point Concentrations	
A. Transport, bioaccumulation, etc.	Chapter 4, Volume III
B. Atmospheric dispersion, deposition, etc.	Chapter 3, Volume III
Step 4. Characterize Exposed Individuals and Exposure Patterns	
A. Contact rates, exposure durations	This Chapter
Step 5. Put It Together in Terms of Exposure Scenarios	
A. Scenario concept expanded	This Chapter
B. Demonstration with scenarios	Chapter 5, Volume III
Step 6. Estimate Exposure and Risk	
A. Equations and background	This Chapter
B. Results for example scenarios	Chapter 5, Volume III
Step 7. Assess Uncertainty	
A. Parameter uncertainty/variability, validity of media concentrations, other models	Chapter 7, Volume III
B. Sensitivity analysis, parameter discussions	Chapter 6, Volume III

Figure III-1. Road map for assessing exposure and risk to dioxin-like compounds.

Step 5. Put It Together in Terms of Exposure Scenarios: A common framework for assessing exposure is with the use of "settings" and "scenarios." Settings are the physical aspects of an exposure area and the scenario characterizes the behavior of the population in the setting and determines the severity of the exposure. A wide range of exposures are possible depending on behavior pattern assumptions. An exposure scenario framework offers the opportunity to vary any number of assumptions and parameters to demonstrate the impact of changes to exposure and risk estimates.

Step 6. Estimate Exposure: The end result of having followed the above 5 steps are estimates of individual exposures to a characterized source of contamination.

Step 7. Assess Uncertainty: Uncertainties should be considered when applying procedures in this document to a particular site. Pertinent issues explored in this assessment include: 1) model predictions of exposure media concentrations compared to field measurements, 2) similarities and differences for alternate models for estimating exposure media concentrations, 3) sensitivity of model results to a range of values for methodology parameters, 4) mass balance checks, and 5) qualitative and quantitative discussions on the uncertainties with the model parameters and exposure estimates generated for the demonstration scenarios.

III.3. ESTIMATING EXPOSURE MEDIA CONCENTRATIONS

Literally hundreds of fate and transport models have been published which differ widely in their technical sophistication, level of spatial or temporal resolution, need for site specific parameterization, and so on. This makes selection of the most appropriate one for any particular situation very difficult. For this assessment, relatively simple, screening level models are used to model fate, transport, and transfer of dioxin-like compounds from the source to the exposure media. Simple assumptions are often made in order to arrive at the desired result, which is long-term average exposure media concentrations. Perhaps the most critical of the assumptions made is that the source strength remains constant throughout the period of exposure.

It is important to understand that EPA is not endorsing the algorithms of this assessment as the best ones for use in all dioxin assessments. They are suggested as reasonable starting points for site-specific or general assessments. All assumptions for the

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models and selection of parameter values are carefully described. If these assumptions do not apply to a particular situation, or where assessors require more spatial or temporal resolution, more complex models should be selected. Finally, it cannot be overemphasized that measured concentrations are generally more reliable than modeled ones. Assessors should use measured concentrations if available and if such measurements can be considered spatially and temporally representative for the exposed populations.

III.3.1.   Overview of Fate, Transport, and Transfer Algorithms of the Methodology

Figures III.2 through III.5 provide an overview of algorithms used to evaluate the fate, transport, and transfer of dioxin-like compounds from contaminated soil, stack emissions, and effluent discharge (called "source categories" in this document). Algorithms are presented which link each of these sources to estimated concentrations in a number of media which may be contaminated as a result, and are therefore potential "exposure media": 1) surface soils, 2) surface-water associated media: suspended and bottom sediment and dissolved phase concentrations, 3) air including the vapor phase and in particulate form, and 4) biota including beef, milk, fruit and vegetables, and fish. The remainder of this section describes how each potential exposure medium can be affected by each source, and the algorithms used to make this link.

● **Surface soils:** Exposure to contaminated soil may be a result of direct contact with soil on the site of the "source" contamination, or indirectly after the contaminated soil has been transported off-site. These cases are known as the "on-site" scenario and the "off-site" scenario, respectively. In either case, soil concentrations are specified for the contaminated source. For the on-site scenario, the soil at the residence or farm (where exposures occur) is contaminated. In the off-site scenario, soil contamination is assumed to be adjacent to an accessible area known as the "exposure site". Examples here would include a landfill or a Superfund site. Residues which reach the exposure site mix with soil already there; the mixing is assumed to take place to either a "tilled" depth or a "non-tilled depth". The tilled depth is assumed to be 20 cm (approximately 8 inches), typical of soil mixing for growing below-ground vegetables. The concentrations derived from using a 20 cm mixing depth are also used to estimate concentrations for dermal contact for individuals in farming families (i.e., dermal contact is assumed to occur as a result of

Figure III-2. Diagram of the fate, transport, and transfer relationships for the on-site source category.
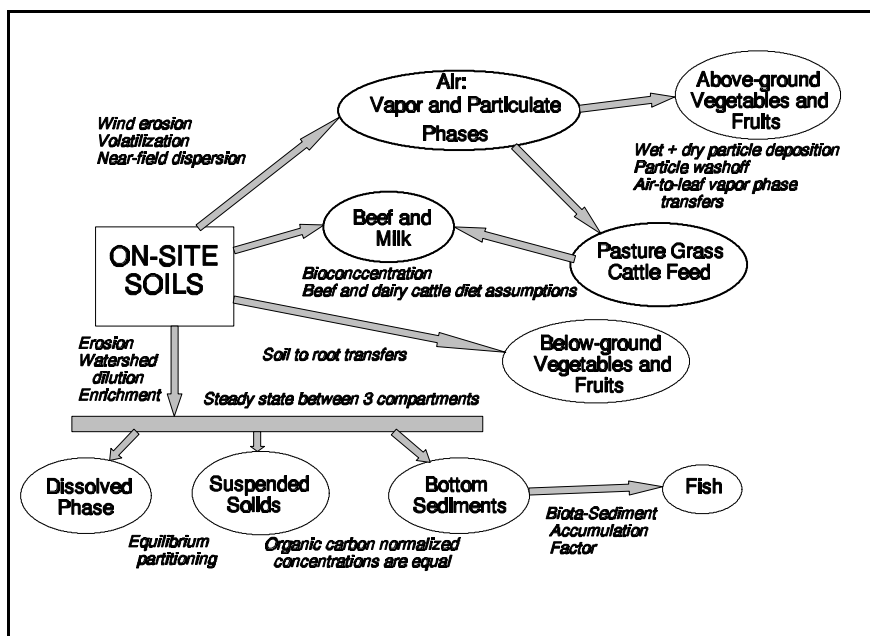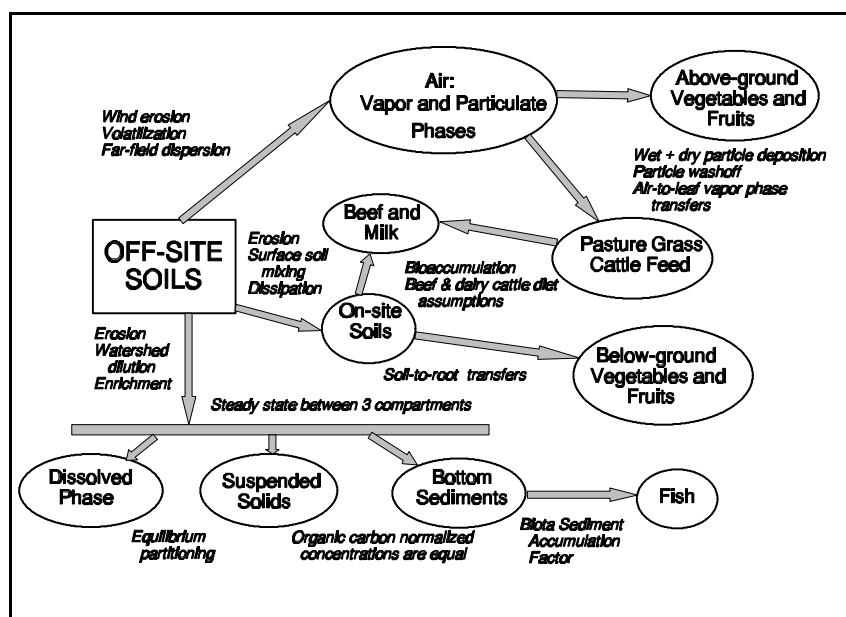

Figure III-3. Diagram of the fate, transport, and transfer relationships for the off-site source category.
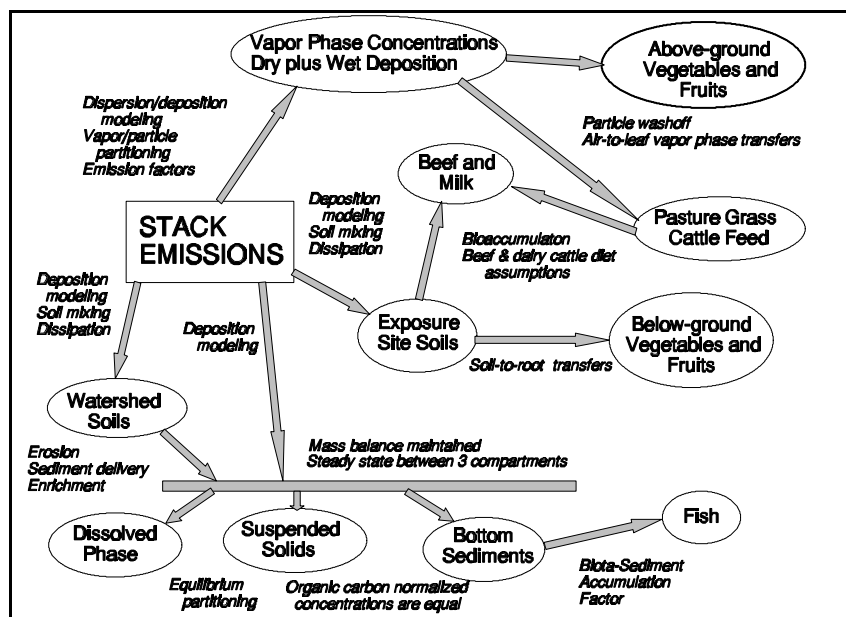
Figure III-4. Diagram of the fate, transport, and transfer relationships for the stack emission source category.
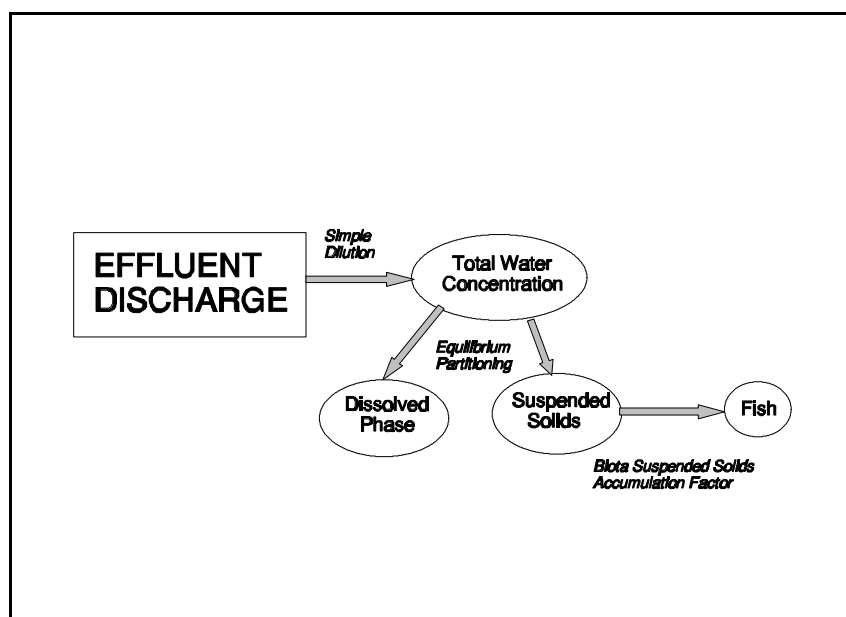

Figure III-5. Diagram of the fate, transport, and transfer relationships for the effluent discharge source category.

farming activities). The non-tilled mixing depth is assumed to be 5 cm (approximately 2 inches) when erosion transports residues to a site of exposure where deep tilling or plowing does not routinely occur. The concentrations derived using this mixing depth are used for dermal contact exposures in residential settings, for childhood soil ingestion in residential and farm settings, and for cattle soil ingestion (used in estimation of beef and milk concentrations).

Exposure site soils can also be impacted from stack emissions due to air transport of either vapor or particulate residues from the stack to the exposure site. Deposition modeling for particles allows for estimation of tilled and non-tilled soil concentrations. When stack emissions are the source, however, the nontilled depth of mixing is assumed to 1 cm (about 0.4 inch) instead of 5 cm, on the assumption that particle deposition is a less turbulent process than soil erosion. A key assumption for evaluating the exposure site as a result of both off-site erosion and stack emissions is that contaminants impact a thin layer of soil and do, in fact, dissipate. For the on-site soil scenario, on the other hand, the contamination is assumed to extend into the soil and surface concentrations are not dissipated over time. Dissipation processes could include volatilization, photolysis, or other processes. A soil dissipation half-life of ten years is assumed for all dioxin-like compounds.

● **Surface Water:**   The principal assumption driving the solutions for the soil and stack emission source categories is that the suspended and bottom sediments of water bodies originate as watershed soils, which are subsequently eroded. For the stack emission source category, a portion of the sediments also originates from directly-depositing particulates. The process of erosion transports soils within the watershed to the water body. Unit rates of erosion along with watershed size determine the total potential amount of soil which could be delivered to the water body. Sediment delivery ratios reduce that potential amount. A mass balance assures that soil eroding on an annual basis becomes either suspended or bottom sediment within an annualized volume of surface water. "Enrichment" of eroded soil is assumed, which means that eroded soil from a contaminated source is assumed to be higher in concentration of dioxin-like compounds than *in situ*, off-site soils. Once in the water body, a standard partitioning model based on the organic carbon partition coefficient, Koc, determines the concentration of contaminant in the water in truly dissolved form and the concentration on suspended sediments. The organic carbon normalized concentrations of suspended and

bottom sediment are assumed to be equal. Watershed soil concentrations are model input parameters for determining the effect on surface water from contaminated soils. For stack emissions, a total (dry + wet) deposition rate of contaminant which represents average depositions onto the watershed is specified as an input parameter, as well as a mixing depth representing the watershed. In this way, average watershed soil concentrations are calculated for the stack emission source category.

For effluent discharges as sources, watershed soils are not considered. An amount of contaminant is discharged into an annual flow volume to obtain a simple dilution concentration. This total concentration is partitioned into a truly dissolved phase and a phase sorbed to suspended sediments using the organic carbon partition coefficient, the Koc. Bottom sediments are not considered for effluent discharges.

● **Soil to Air:**   From contaminated soils, residues become airborne via the processes of volatilization and wind erosion. For on-site soil contamination, these vapor and particle phase fluxes are translated to ambient air concentrations using a near-field dispersion model. For the off-site scenario, the same approach is used to estimate ambient air exposure site concentrations, except that a far-field dispersion model is used. These airborne reservoirs are the basis for inhalation exposures, and are also used to estimate plant concentrations for vegetable ingestion and in grass and feed for estimating beef and milk concentrations.

● **Stack Emissions, Atmospheric Transport Modeling:**   Air dispersion/deposition models consider the basic physical processes of advection, turbulent diffusion, and removal via wet and dry deposition to estimate the atmospheric transport, resulting ambient air concentration, and settling of particles. Volume III uses the COMPDEP model for air dispersion and deposition modeling. Besides discussions in Volume III, further discussions on the COMPDEP model can be found in EPA (1990d).

COMPDEP contains modifications of the Industrial Source Complex model (Short-Term version), and COMPLEX I to incorporate algorithms to estimate dispersion, and resulting ambient air concentrations, and wet and dry deposition flux. COMPLEX I is a second level screening model applicable to stationary combustion sources located in complex and rolling topography (EPA, 1986). The model was developed specifically to evaluate the effects of complex terrain that exceeds the stack height of the source as developed by Turner (1986). To account for pollutant deposition, the concentration algorithms in COMPLEX 1 were

replaced with those from the Multiple Point Source Algorithm with Terrain Adjustments Including Deposition and Sedimentation (MPTER-DS) model (Rao and Sutterfield, 1982). The MPTER-DS algorithms incorporate the gradient transfer theory described by Rao (1981), and are extensions of the traditional Gaussian plume algorithms. The dispersion algorithms contained in the Industrial Source Complex, Short-term version (ISCST), have been incorporated in COMPDEP to analyze ground-level receptors located below the height of the emission plume. COMPDEP uses the generalized Briggs (1975, 1979) equation to estimate plume-rise and downwind dispersion as a function of wind speed and atmospheric stability. A wind-profile exponent law is used to adjust the observed mean wind speed from the measurement height to the emission height for the plume rise and pollutant concentration calculations. The Pasquill-Gifford curves are used to calculate lateral and vertical plume spread (EPA, 1986). These curves are based on Pasquill's definitions of atmospheric stability classes, e.g., extremely unstable, moderately unstable, slightly unstable, neutral, slightly stable, and moderately stable, that correspond to various intensities of solar radiation and wind speeds (Seinfeld, 1986). The incorporation of these two basic models into COMPDEP permits analysis of a source located in all types of terrain. Further details on the use of the COMPDEP model are:

1. Emission factors: The first step in the use of the COMPDEP model is to determine "emission factors" for dioxin-like congeners. These factors are defined as the µg (or other mass unit) congener emitted per kg (or other mass unit) feed material combusted. Once assuming a rate of feed material combusted in appropriate units, kg/day, these emission factors can be translated to the units appropriate for atmospheric transport modeling, µg/sec. This assessment promotes the generation of specific congener emission factors, rather than TEQ or homologue group emission factors. A TEQ concentration can be generated for exposure media concentrations once congener-specific concentrations are estimated using the Toxicity Equivalency Factor (TEF) scheme. This recommendation is made because fate, transport, and transfer parameters, and TEFs, are different for specific congeners, leading to a TEQ exposure media concentration which would be different but more accurate than, say, assuming only a TEQ emission factor and one set of parameters for further modeling. Emission factors for the demonstration were generated from actual test

data from an incinerator burning organic wastes (source otherwise unspecified). Emission estimates for this example incinerator are similar to emissions that are known to be emitted from combustors employing sophisticated air pollution control devices (e.g., scrubbers combined with fabric filters). In order to place the demonstration scenario in context, the emissions from the hypothetical incinerator were ranked with other types of waste incinerators that are well controlled with some combination of a scrubber device and/or a fabric filter, as follows:

        1. Medical waste incineration: 25 - 200 ng TEQ/kg waste combusted.

        2. Hazardous waste incineration: 0.18 - 119 ng TEQ/kg waste combusted.

        3. Hypothetical waste incinerator: 4.5 ng TEQ/kg waste combusted.

        4. Municipal solid waste incineration: 0.05 - 3 ng TEQ/kg waste combusted.

        5. Sewage sludge incineration: 0.002 - 0.03 ng TEQ/kg sludge combusted. *2. Vapor/Particle Partitioning:* The second step in atmospheric transport modeling is to determine the percent of totally emitted dioxin-like congener which is in a vapor phase, and the percent which is in the particle phase. The partitioning of stack emissions into these two phases was examined by reviewing stack testing data, ambient air sampling data, and a theoretical approach developed in Bidleman (1988). A summary of the vapor/particle (V/P) partitioning surmised from these three sources is given in Table III-1. From this review, it is generally concluded that:

    a. Stack gas sampling: The stack gas sampling methods in use today to monitor and measure the concentration of CDDs/CDFs emitted to the air from combustion sources do not provide a credible basis for assuming the vapor phase and particle bound partitioning at the point of release. There is no consistent pattern to the interpretation of V/P based on where the CDD/CDF segregates in the instrument, e.g., the glass fiber filter or the XAD resin. Factors that may contribute to this are: the relatively long residence time spent traversing the stack interior; the probe to the instrument is inserted into a relatively hostile environment of the hot combustion gas; the static temperature of the particulate filter caused by heating the particulate filter housing; the fact that located between the particulate trap and the vapor trap is a condensing section consisting of glass

Table III-1. Percent distribution of CDDs and CDFs between vapor-phase (V) and particulate-phase (P) as interpreted by various stack sampling methods, ambient air monitoring, and ambient air theoretical partitioning.

		4CDD	5CDD	6CDD	7CDD	8CDD	4CDF	5CDF	6CDF	7CDF	8CDF
Stack	V	76	70	71	73	63	76	66	64	62	73
Testing[1]	P	24	30	29	27	37	24	34	36	38	27
Ambient air	V	87	69	30	10	4	83	65	35	11	2
Monitoring[2]	P	13	31	70	90	96	17	35	65	89	98
Theoretical[3]	V	55	26	4	2	1	71	36	7	3	1
	P	45	74	96	98	99	29	64	93	97	99

[1] Average of 18 data points from 9 separate references; "not reported" and "not detected" from these references not included in averages.

[2] Average of 15 data points from 6 references; "not reported" and "not detected" from these references not included in averages.

[3] calculated from procedures in Bidleman (1988); congener group listing above are rather the V/P for specific congeners with non-zero toxicity for single congeners within congener group (e.g., result for 4CDD is that of 2,3,7,8-TCDD), or average when more than one congener is within congener group (e.g., result for 5CDF is average of P of 0.58 for 12378-PCDF and 0.70 for 23478-PCDF).

tubing surrounded by an ice bath.

    b. Ambient air sampling: On the other hand, the ambient air sampling methods do give an approximate indication of the V/P ratio that seems to be responsive to changes in temperature, and degree of chlorination of the CDDs/CDFs. This is in accordance with what would be expected from their individual vapor pressures. There is no artificial heating or cooling of any component of the sampler. The sampler is exposed to actual temperature, pressure, and humidity of the ambient air. This reduces the possibility that the vapor phase-particle bound partitioning operationally defined as the compound segregating to the particulate trap and vapor trap is actually an artifact induced by artificial heating and cooling within the system. Therefore, the methods present a realistic picture of partitioning under variable ambient conditions. However, the method has certain limitations that currently prevent deriving a true measurement of V/P partitioning in the ambient air:

    🕐   The glass fiber filter is designed to capture and retain particulate matter greater

than or equal to 0.1 μm diameter. Particles less than this diameter may pass through the filter and be retained in the polyurethane foam vapor trap downstream. If this is the case, the amount of CDDs/CDFs observed to be particle bound would be underestimated, and the amount observed to be in vapor phase would be overestimated.

☼   The relatively high sampled volume of air passed through the system (200 to 400 m^3 of air per 24 hours) may redistribute the more volatile congeners from the filter to the adsorbent trap by a process known as 'blow-off'.

c. Theoretical partitioning: Until sampling methods are improved and modified such that they give results that indicate the true V/P ratio of CDDs/CDFs in ambient air, the theoretical construct described by Bidleman (1988) is used to calculate the V/P ratio for purposes of air dispersion and deposition modeling of emissions from the hypothetical case demonstrated in Chapter 5 of Volume III. Key advantages to the theoretical approach are that the theoretical construct relies on current adsorption theory, considers the molecular weight and the degree of halogenation of the congeners, uses the boiling points and vapor pressures of the congeners, and uses the availability of surface area for adsorption of atmospheric particles that correspond to a variety of ambient air shed classifications having variable particulate matter densities. Four air shed classifications are described in Bidleman (1988): "clean continental", "background", "background plus local sources", and "urban". The classification used for the example scenarios in Chapter 5 of Volume III, and shown in Table III-1, is "background plus local sources".

3. Two runs of the COMPDEP model: In order to provide estimates of vapor and particle phase concentrations of dioxin-like compounds, as well as estimates of wet/dry particle deposition flux, it is necessary that to run the COMPDEP model twice. Both model runs should assume a "unit emissions release rate", e.g., 1 g/s. Results from these unit runs can easily be transformed to final outputs given assumptions on emissions in vapor and particle forms. A vapor phase run involves turning wet/dry deposition switches to the "off" position. This inactivates a plume depletion equation that subtracts out losses in ambient air concentration due to particle deposition. What is left are the Gaussian dispersion algorithms. The vapor phase concentrations are used for inhalation exposures and also for vapor transfers onto vegetation for food chain modeling. A second run of COMPDEP with wet/dry

deposition switches turned to the "on" position is considered a simulation of particle-bound contaminant. Outputs from this run include wet and dry deposition rates, and air concentrations of contaminants in the particulate phase. The depositions are used in soil and food chain modeling, and the concentrations are added to the vapor phase concentrations from the first COMPDEP run to arrive at the total air-borne reservoir for inhalation exposures.

   4. Assumed particle size distributions of emitted particles: In order to estimate deposition flux, certain inferences must be made concerning the distribution of particulates according to particle diameter (μm). The distribution of particulate matter by particle diameter will differ from one combustion process to another, and is greatly dependent on the type of feed material, conditions of combustion, and the efficiency of various air pollution control devices. For purposes of demonstration, three particle size categories were generalized from available data on particle fractionation: Category 1: < 2 μm, Category 2:   2 to 10 μm, Category 3: > 10 μm. By using data on the proportion of total particles emitted per size category, and conducting a surface area to volume calculation, it was estimated that 87.5% of the emission rate of particle-bound dioxin-like congener is associated with particles less than 2 μm in diameter, 9.5% is associated with the particle size of 2 to 10 μm, and only 3% is associated with particles greater than 10 μm. Finally, the particle size distribution is further simplified by assuming a median particle diameter to represent each broad particle size category, as follows:

- Particulate category 1 = 1 μm particle diameter
- Particulate category 2 = 6.78 μm particle diameter
- Particulate category 3 = 20 μm particle diameter

   5. Dry deposition: The COMPDEP estimates dry deposition flux based on the model developed by Dumbauld, et al. (1976). This model assumes that a fraction of the particulate comes into contact with the ground surface by the combined processes of gravitational settling, atmospheric turbulence, and Brownian diffusion. The COMPDEP model contains enhancements to calculate dry deposition flux using a computerized routine developed by the State of California Air Resources Board (CARB, 1986). The routine is based on a summary of dry deposition velocity curves developed by Sehmel (1980) for a broad range of particle diameters. For the example application of the COMPDEP model in Chapter 5 of Volume III, particles less than 2 μm, represented by a 1 μm size, were assumed to deposit at a velocity

of 0.00711 cm/sec. Particles between 2 and 10 μm, represented by a 6.78 μm size, were assumed to deposit at 0.287 cm/sec. Finally, particles greater than 10 μm, represented by a 20 μm size, were assumed to deposit at a velocity of 2.47 cm/sec.

6. Wet deposition: Wet deposition flux depends primarily on the fraction of the time precipitation occurs and the fraction of material removed by precipitation per unit of time by particle size. Based on these relationships, scavenging coefficients were developed by Cramer (EPA, 1986) for varying types and intensities of precipitation relative to different particle diameters by incorporating the observations of Radke, et al. (1980) in a study of scavenging of aerosol particles by precipitation. The principal assumptions made in computing wet deposition flux are: (1) The intensity of precipitation is constant over the entire path between the source and the receptor; (2) The precipitation originates at a level above the top of the emission plume so that the precipitation passes vertically through the entire plume; (3) The flux is computed on the bases of fraction of the hour precipitation occurs as determined by hourly precipitation measurements compiled by the National Weather Service. The remaining fraction (1-f) is subject only to dry deposition processes. Thus no dry deposition occurs during hours of steady precipitation, and dry deposition occurs between the periods of precipitation.

● **Biota:** Simple bioconcentration/biotransfer approaches are used to estimate biota concentrations in this assessment. Specifics for each biota considered are:

1. Fish - The soil contamination and stack emission source categories estimate the concentration of contaminant on bottom sediments of water bodies. A fish lipid concentration is estimated based the organic carbon normalized bottom sediment concentration and a BSAF, or Biota Sediment Accumulation Factor. Whole fish concentrations for exposure estimation then equal this lipid concentrations times a whole fish lipid content (or a fillet lipid content). For the effluent discharge source category, fish lipid concentrations are estimated as a function of organic carbon normalized concentrations and the closely related BSSAF, or Biota Suspended Solids Accumulation Factor. This recently introduced bioaccumulation factor (EPA, 1993) is analogous to the BSAF, and it is suggested in EPA (1993) that, as a first estimate, it take on the same chemical-specific numerical value as the BSAF.

2. Vegetation - Concentrations in three types of vegetation are considered in this assessment: below ground vegetables (carrots, potatoes, e.g.), above ground vegetables/fruits

(tomatoes, apples), and above ground grass and cattle feed which are required for estimation of beef and milk concentrations. Assumptions critical to all three include: above ground vegetation is impacted by vapor phase transfers and particle deposition - there is no root to shoot translocation, outer portions of the vegetation are only impacted with minimal within plant translocation, a steady state is reached between vapor phase contaminants in air and vegetation, particle bound contaminants deposit onto and mix in a vegetative reservoir and are subject to a fourteen-day dissipation half-life which represents particle washoff, and vegetables/fruits which have an outer protective layer (peas, citrus e.g.) are unimpacted by dioxin-like compounds. Below ground vegetable concentrations are estimated from soil water concentrations and a Root Concentration Factor, or RCF. Above ground concentrations due to vapor phase transfers are a function of the vapor phase air-borne reservoir, an air-to-leaf transfer factor, B_{vpa}, and a surface area to volume reduction factor, VG, which is equal to 1.00 for grasses and other leafy vegetation and less than 1.00 for bulky vegetation.

3. Beef and Milk - Weighted average concentrations of dioxin-like compounds in the diets of cattle raised for beef or lactating cattle are multiplied by a congener-specific bioconcentration factor, BCF, which yields the concentrations in the fat of beef or milk. The same congener-specific BCF is used for beef and milk. This presumes that dioxin-like compounds bioaccumulate equally in body fat and milk fat of beef and dairy cattle. While there is expected to be some difference in bioaccumulation tendencies, the literature was not clear on this issue. Fries and Paustenbach (1990) discuss the importance of the dietary habits of cattle raised for beef versus those raised for dairy products; beef cattle tend to be grazed substantially more, while dairy cattle tend to be barn-fed for a greater proportion of their dietary intake. Like this assessment, Fries and Paustenbach (1990) model beef and milk concentrations using a single BCF for 2,3,7,8-TCDD. They used a BCF of 5.0 for 2,3,7,8-TCDD. A set of BCFs for all dioxin-like congeners for this assessment were based on a set of data on a lactating cow (i.e., dietary intakes of dioxin congeners, concentrations in milk, and other pertinent quantities; McLachlan, et al., 1990). The BCF for 2,3,7,8-TCDD from this data set was 4.32. Beef and dairy cattle diets are described in terms of proportions in pasture grass, cattle feed (silage, grains), and soil. Models described above estimate concentrations in these cattle intakes.

III.4. DEMONSTRATION OF METHODOLOGY

EPA (1992a) states, "In exposure scenario evaluation, the assessor attempts to determine the concentrations of chemicals in a medium or location and link this information with the time that individuals or populations contact the chemical. The set of assumptions about how this contact takes place is an exposure scenario." These assumptions can be made many different ways producing a wide variety of scenarios and associated exposure levels. The number of people exposed at different levels form a distribution of exposures. Ideally assessors would develop this entire distribution to fully describe the exposed population. Since the necessary information for developing a population distribution is rarely available, EPA (1992a) recommends developing a central and high end scenario to provide some idea of the possible range of exposure levels.

The basic setting for which the methodologies are demonstrated is a rural setting which contains both farms and non-farm residences. The three principal sources of contamination, the soil (both on-site and off-site), stack emission, and effluent discharge, categories, are assumed to exist in such a setting. "Central" scenarios are based on typical behavior at a residence and "high end" scenarios are comprised of a farm family that raises a portion of its own food. Key distinguishing features between the high end and central scenarios include: 1) individuals in high end scenarios are assumed to be at their home a greater proportion of the day than the central scenarios (which impacts assignment of contact fraction), 2) individuals in high end scenarios are exposed to impacted beef and milk which they raise on their farm while these exposures are not considered for the central scenarios, 3) the exposure duration for individuals in the high end scenario is 20 years compared to 9 years for the central scenario, and 4) certain exposure parameters, such as water ingestion rate which is 1.4 L/day for the central scenarios and 2 L/day for the high end scenario, are different.

The example scenarios were carefully crafted to be plausible and meaningful, considering key factors such as source strength, fate and transport parameterization, exposure parameters, and selection of exposure pathways.   However, it should be clearly understood that the purpose of the demonstration scenarios is to provide users of this methodologies with a comprehensive example of their application. The demonstration exposure scenarios were:

Exposure Scenarios 1 and 2: On-site Soil Contamination, Residence and Farm

Surface soils on a 4,000 m^2 (1-acre roughly) rural residence (Scenario 1) and on a 40,000 m^2 (10-acres) small rural farm (Scenario 2) contained residues of the three example contaminants. The concentrations of the contaminants are uniformly set at 1 part per trillion, which was evaluated as reasonable background levels.

Exposure Scenario 3: Off-site Soil Contamination, Farm

A 40,000 m^2 rural farm is located 150 m (500 ft) from a 40,000 m^2 area of bare soil contamination; an area that might be typical of contaminated industrial property. The surface soil at this property is contaminated with the three example compounds to the same concentration of 1 part per billion. This is evaluated as reasonable for industrial sites of contamination of dioxin-like compounds, and three orders of magnitude higher than concentrations for Scenarios 1 and 2.

Exposure Scenarios 4 and 5: Stack Emissions, Residence and Farm

A 4,000 m^2 rural residence (Scenario 4) is located 5000 meters downwind from a stack emission source, and a 40,000 m^2 rural farm (Scenario 5) is located 500 meters from the same stack emission source. The emissions of dioxin-like compounds were evaluated as within the range observed for various stack emission sources which have sophisticated air pollution control devices (e.g., scrubbers combined with fabric filters).

Exposure Scenario 6: Effluent discharge into a river

As has been discussed, this source category is different from others in that the air, soil, and vegetation at a site are not impacted. Rather, only surface water impacts, and exposures to ingestion of drinking water and fish, are considered. The source strength was developed from data on pulp and paper mill discharges of 2,3,7,8-TCDD. Discharge rates were based on data from EPA's 104-mill study (EPA, 1990c), and then reduced considering recent improvements in the bleaching process which have reduced discharges.

Three compounds were demonstrated for the two soil source categories, on- and off-site soil contamination, and for the effluent discharge source category. For purposes of illustration, one compound was arbitrarily selected from each of the major classes of dioxin-like compounds. They are: 2,3,7,8-tetrachlorodibenzo-p-dioxin (abbreviated 2,3,7,8-TCDD), 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PCDF), and 2,3,3',4,4',5,5'-heptachloro-PCB (HPCB).

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For the stack emission demonstration, Scenarios 4 and 5, a different approach was taken. Exposures to 2,3,7,8-TCDD alone are determined, as in the other demonstrations. Emission rates for all dioxins and furans with non-zero toxicity equivalency factors (abbreviated TEFs) were available for the demonstration of the stack emission source category. Use of the full suite of emissions allowed for the opportunity to demonstrate an appropriate methodology for estimating TEQ exposures. The framework takes the individual deposition rates and concentrations for the individual congeners and models the exposure media concentrations individually with unique fate and bioaccumulation parameters, and then determines a final TEQ exposure media concentration using TEFs.

III.4.1.   Results from the Demonstration of the Stack Emission Source Category

For brevity, only the results from the stack emission source category will be summarized. Table III-2 gives the exposure media concentrations estimating for 2,3,7,8-TCDD and for TEQs for Example Scenario #5, the high end scenario for the stack emission source category. Table III-3 gives the estimated Lifetime Average Daily Doses, LADDs, for the exposure pathways modeled in this assessment.

Much of the differences between exposure pathways and scenarios is due to differences in exposure media estimation. Therefore, the discussion below on trends for LADD follows directly from how the methodologies estimate exposure media concentrations. It is important to understand that exposure estimates generated for the demonstration scenarios are specific to the site conditions assumed for the examples and are not generalizable to other sites. Following are some key observations:

1)   The highest exposures were associated with the off-site soil contamination scenario, Scenario #3. This scenario had the highest exposure media concentrations for all exposure media. The source of contamination was a 40,000 m^2 land area with soil concentrations initialized at 1 ppb for the three example compounds. The lowest LADDs

Table III-2. Exposure media concentrations estimated for the demonstration of the stack emission source category[1].

Exposure media concentration	2378-TCDD	TEQ
1. Concentration of contaminants in soil for soil ingestion and dermal contact pathways, ng/kg	$1*10^{-3}$	$2*10^{-2}$
2. Concentration of contaminants in air for inhalation pathway, pg/m^3	$1*10^{-5}$	$2*10^{-4}$
3. Concentration of contaminants in water for water ingestion pathway, pg/L	$4*10^{-6}$	$5*10^{-5}$
4. Concentration of contaminants in fish for fish ingestion pathway, ng/kg	$6*10^{-5}$	$1*10^{-3}$
5. Concentration of contaminants in below ground vegetables, ng/kg fresh weight	$8*10^{-8}$	$1*10^{-6}$
6. Concentration of contaminants in above ground fruit and vegetables, ng/kg fresh weight	$3*10^{-6}$	$1*10^{-4}$
7. Concentration of contaminants in beef for beef ingestion pathway, ng/kg whole beef (22% fat)	$5*10^{-4}$	$1*10^{-2}$
8. Concentration of contaminants in milk for milk ingestion pathway, ng/kg whole milk (3.5% fat)	$6*10^{-5}$	$1*10^{-3}$

[1] The exposure site was located 500 meters from the stack; emission rates of 2,3,7,8-TCDD and TEQs were $9.2*10^{-11}$ g/sec and $1.6*10^{-9}$ g/sec, respectively.

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Table III-3. Lifetime Average Daily Doses, LADD, for the high end stack emission demonstrations scenario (LADD in units of ng/kg-day).

Exposure Pathway	2378-TCDD	TEQ
Soil ingestion	$4*10^{-9}$	$8*10^{-8}$
Soil dermal contact	$5*10^{-11}$	$1*10^{-9}$
Inhalation	$1*10^{-9}$	$2*10^{-8}$
Water ingestion	$3*10^{-11}$	$4*10^{-10}$
Fish ingestion	$1*10^{-9}$	$2*10^{-8}$
Fruit ingestion	$3*10^{-10}$	$2*10^{-8}$
Vegetable ingestion	$4*10^{-10}$	$2*10^{-8}$
Beef ingestion	$9*10^{-8}$	$2*10^{-6}$
Milk ingestion	$3*10^{-8}$	$6*10^{-7}$

were estimated for the demonstration of the stack emission source category. Although the intensity of the source strength between a stack emission source and a soil source cannot be directly related, it is noted that the releases of 2,3,7,8-TCDD and TEQs used to demonstrate the stack emission source were comparable to other stack emission sources with sophisticated air pollution control devices. Exposures to 2,3,7,8-TCDD were about 5% of exposures to TEQs. This mirrors the comparison of the 2,3,7,8-TCDD release rate and total TEQ release rate from the stack. Only a fish and a water ingestion pathway were considered for the effluent discharge source category. The exposures estimated for these two pathways were similar in magnitude to the fish and water ingestion exposures estimated for demonstration of the on-site soil source category, demonstrations #1 and #2. For those demonstrations, watershed soils were initialized at 1 ppt, a concentration that researchers have found for 2,3,7,8-TCDD in background settings.

2) Differences between analogous "central" and "high end" exposures for the on-site soil source demonstration scenarios were near or less than an order of magnitude. "Analogous" exposures are those estimated for both scenarios. They include inhalation, soil ingestion and dermal contact, water, vegetable/fruit, and fish ingestion exposures. Only beef

and milk are not analogous since they were only estimated for the high end scenario. Analogous exposures were within an order of magnitude of each other because the exposure parameters used to distinguish typical and high end exposures, the contact rates, contact fractions, and exposure durations, themselves did not differ significantly, and these were the only distinguishing features for the central and high end demonstrations of the on-site soil source category. In the stack emission scenario, placing exposed individuals either 500 or 5000 meters away from the incinerator did significantly impact the results. In this case, the difference was closer to 2 orders of magnitude for all analogous exposures except water and fish exposures, which were not a function of distance from the stack. The order of magnitude difference in distance added about an order of magnitude difference in exposure media concentrations and hence LADD estimates.

3) It is inappropriate to compare and rank exposure pathways across all scenarios because the source terms are different. However, relationships between different pathways within each scenario can be discussed. Table III-4 was constructed by summing the LADDs for all pathways, and then determining the percent contribution by each pathway. Before the summation, LADDs were corrected to account for absorption - all ingestion LADDs assumed 50% absorption and inhalation LADDs assumed 75% (data on bioavailability from animal feeding studies, suggests that the absorption of 2,3,7,8-TCDD is around 50%; 75% for inhalation reflects a general assumption of greater absorption for this pathways; both simple assumptions made only for the purpose of this comparative exercise). The dermal contact LADD was the only one where absorption was already considered in its estimation: absorbed dose was estimated as 3% of dose contacting the body. Also, this exercise assumes all pathways occur simultaneously. Table III-4 was generated only for the 2,3,7,8-TCDD example compound, and the rows are listed generally from the highest to lowest percentage contribution. The following observations are made:

⏱ In high end scenarios which assumed exposure to home grown beef, milk, and fish, Scenarios 2, 3, and 5, exposures to these three foods dominated the results. In Scenarios where beef and milk were not considered, but fish was considered, Scenarios 1, 4, and 6, fish exposures dominated. The general dominance of beef, fish, and milk exposures underscores the importance of food chain exposures.

⏱ Milk exposures were lower than beef exposures because of less milk fat

Table III-4.   Percent contribution of the different exposure pathways within each exposure scenario.*

Exposure Pathway	Scenario #					
	1	2	3	4	5	6
Meat Ingestion	NA	26	50	NA	72	NA
Fish Ingestion	56	44	2	27	1	95
Soil Ingestion	36	15	32	23	3	NA
Milk Ingestion	NA	6	11	NA	23	NA
Soil Dermal	4	8	4	0	0	NA
Vegetable Ingestion	1	0	0	5	0	NA
Fruit Ingestion	0	0	0	5	0	NA
Water Ingestion	3	1	0	1	0	5
Vapor Inhalation	0	0	0	39	1	NA
Particle Inhalation	0	0	0	NA	NA	NA

* Assumes exposed individual experiences all relevant pathways and exposures are additive.

ingestion (10.5 g/day milk fat versus 22 g/day beef fat) and lower concentrations in milk as compared to beef.

⏱ Fish was the principal impacted media for the effluent discharge source category, with fish ingestion 19 times higher than water ingestion, the only two pathways considered for the effluent discharge category. However, fish is much less important than beef or milk for the high end stack emission scenario which had a beef and a milk pathway, and when a small site of contamination is near a farm raising a portion of the farming families beef and milk ingestion.

⏱ Soil ingestion exposures were also noteworthy, particularly in scenarios that did not consider beef and milk, the central on-site scenario, #1, and the central stack emission scenario, #4. Soil ingestion was also the second highest pathway in the scenario evaluating the impact of nearby soil contamination, #3, ranking higher than milk or fish ingestion. Dermal exposures were non-trivial, but ranked behind the four ingestion pathways previously discussed: beef, milk, fish, and soil.

⏱ Inhalation was the highest impact for the stack emission scenario when farm

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animal products were not considered, in Scenario #4. Fruit and vegetable exposures were noteworthy only in this same scenario. These trends imply that, where farm animal products are not being produced near a stack emission source, fish and vegetative food products still may dominate the overall exposure, but inhalation exposure can become critical.

     �; Water ingestion exposures were very low in comparison to the other exposures in these scenarios.

These demonstration scenarios represent only one approach to scenario development; other approaches might consider the quality of exposure media not associated with the home environment. For example, if the bulk of an individual's ingestion of produce comes from local farms, and local farms may be impacted by an stack emission source, then perhaps 90-100% of an individual's fruit and vegetable ingestion, rather than the 20-40% assumed in this assessment, should be considered impacted.

III.5. USER CONSIDERATIONS

This section discusses three issues pertinent to use of the methodologies. The first subsection below discusses the use of the parameter values selected for the demonstration scenarios for other applications. The next subsection is a sensitivity analysis exercise on the parameters required for algorithms estimating exposure media concentrations. The last subsection addresses the issue of mass balance with regard to the source strength terms of the four source categories.

III.5.1. Categorization of Methodology Parameters.

Table 6.1 in Chapter 6 of Volume III lists all the parameters, including names, definitions, and units, that are required for the methodologies of this assessment except the exposure parameters. Exposure parameters are given in Table 2.1 in Chapter 2 of Volume III. Table 6.1 also gives four additional pieces of information for each parameter listed. Three are numerical values which were used in the sensitivity analysis exercises that are described below. One of those parameters is labeled "selected", which were the ones used in the demonstration exposure scenarios. High and low values of parameters selected for sensitivity analysis were carefully developed and might be considered a reasonable range of values for other uses of the methodology (with obvious exceptions such as areas of contamination,

distances from contaminated to exposure site, and so on). The chemical specific parameters are those only for 2,3,7,8-TCDD. The fourth piece of information is a qualitative judgement on the part of the authors of this document as to the appropriateness of using the "selected" parameter values for other assessments. This judgement is categorized in three ways:

1) **First Order Defaults:** As defaults, these parameters are independent of site specific characteristics. As first order defaults, it is felt that the values selected for the demonstration scenarios carry a sufficient weight of evidence from current literature such that these values are recommended for other assessments. Several of the chemical specific parameters, such as the Henry's Constant, H, and the organic carbon partition coefficient, Koc, fall into this category. The qualifier above, "current literature", indicates that new information could lead to changes in these values.

2) **Second Order Defaults:**   Like the above category, these parameters are judged to be independent of site specific characteristics. However, unlike the above category, the current scientific weight of evidence is judged insufficient to describe values selected for demonstration purposes as first order defaults. Parameters of principal note in this category are the bioconcentration parameters specific to the chemicals, such as the Biota Sediment Accumulation Factor, or BSAF. This parameter translates a bottom sediment concentration to a fish tissue concentration. Users should carefully review the justification for the SOD values selected for the demonstration scenarios before using the same values. 3) **Site Specific:** These parameters should or can be assigned values based on site-specific information. The information provided on their assignment for the demonstration scenarios, and for selection of high and low values for sensitivity analysis testing, is useful for determining alternate values for a specific site. A key class of SS parameters which are the source strength terms - the soil concentrations, effluent discharge rates, and stack emission rates. If users are unable to obtain site-specific information, or their use of the methodologies is for general purposes, they should review the justification for selection of values for methodology demonstration, as well as information provided giving ranges of likely values for model parameters.

The exposure parameters can be categorized as have the contaminant fate and transport/transfer parameters. Assignment of these values are critical as LADD estimates are linearly related to parameter assignments - doubling exposure duration assumptions double LADDs, and so on. Some of the exposure parameters are appropriately described as first

order defaults. These include: lifetime, body weights, water ingestion rates, inhalation rates, and an exposure duration for a childhood pattern of soil ingestion. All of the other exposure parameters are better described as either second order defaults or site-specific. All exposure parameters were developed based on information and recommendations in EPA's *Exposure Factors Handbook* (EPA, 1989) and *Dermal Exposure Assessment: Principals and Applications* (EPA, 1992c). Attaining site-specific information is recommended for exposure parameters.

III.5.2.   Sensitivity Analysis

Sensitivity analysis was undertaken in order to evaluate the impact to exposure media concentration estimations with changes in fate and transport/transfer model parameters. Figure III-5 shows an example of sensitivity analysis conducted. This figure describes the impact of key factors for the stack emission source category for determining biota impacts. The x-axis contains the names of the parameters evaluated. The key below the figure gives the definition of the parameters and the values selected for the demonstration scenarios. The y-axis shows the numerical change to the key model result, in this case, vegetable and beef concentrations, to the changes made in the parameter. These changes are noted above and below the bars.   For example, vegetable concentration is about 3 times higher at 200 ft from the stack emission source than it is at 500 meters from the source, the distance used in the demonstration scenario.   Some of the observations made for this test, typical for the type of observations which were made for sensitivity testing, include:

1) Mixing depth, described by the parameter d_{not}, has very little impact on final beef concentrations.

2) Nearer to and further from the stack had different impacts for above and below vegetable concentrations as compared to beef concentrations. The farm was assumed to
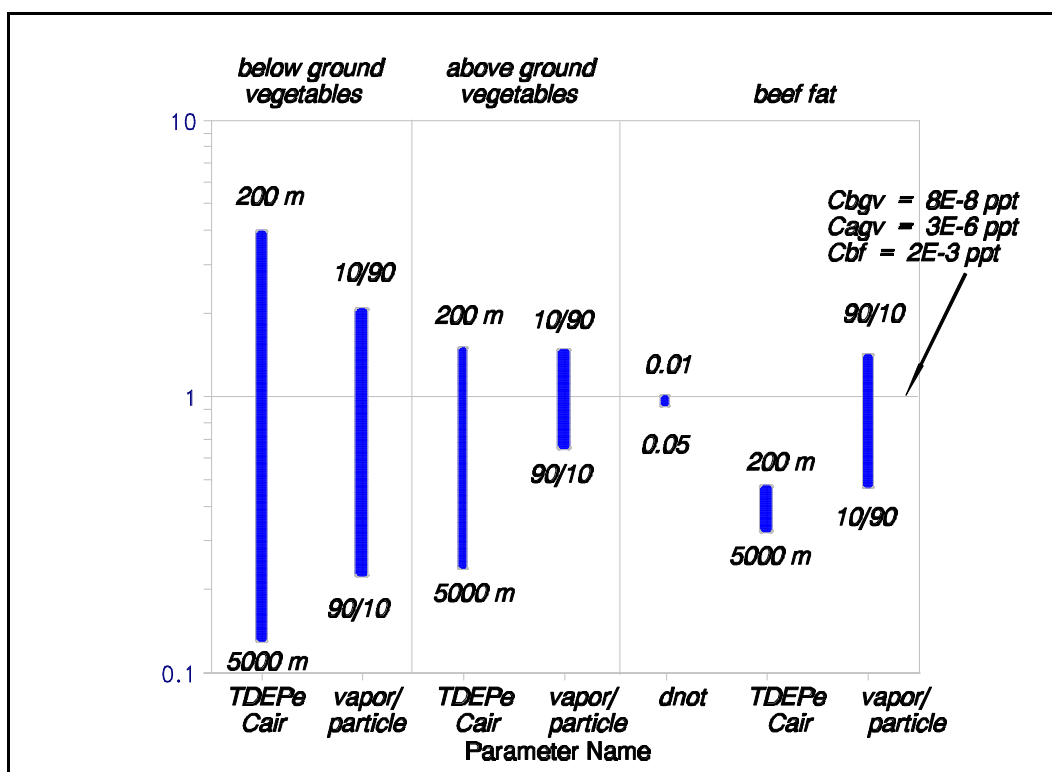
below ground
vegetables

above ground
vegetables

beef fat

10

200 m

10/90

Cbgv = 8E-8 ppt
Cagv = 3E-6 ppt
Cbf = 2E-3 ppt

200 m 10/90

90/10

0.01

1

0.05

90/10

200 m

10/90

90/10

5000 m

5000 m

0.1

5000 m

| TDEPe Cair | vapor/ particle | TDEPe Cair | vapor/ particle | dnot | TDEPe Cair | vapor/ particle |

Parameter Name

Figure III-6. Results of sensitivity analysis of algorithms estimating above and below ground vegetation, and beef fat concentrations resulting from stack emissions.

Parameter Name	Definition	Selected
C_{bgv}	below grd. veg. conc., fresh wt, ng/kg (ppt)	$8*10^{-8}$
C_{bgv}	above grd. veg. conc., fresh wt, ng/kg (ppt)	$3*10^{-6}$
C_{bf}	beef fat concentration, ng/kg (ppt)	0.002
$TDEP_e$	total dep, dry + wet, on exp. site, µg/m²-yr	$1.2*10^{-6}$
C_{air}	vapor phase concentration at exp. site, µg/m³ (note: 200 and 5000 m refers to use of $TDEP_e$ and C_{air} at these distances in sensitivity testing)	$7.6*10^{-12}$
vapor/particle	percent of contaminant arriving at exposure site assumed to be in vapor and particle phases	55%/45%
d_{not}	no-till depth at exposure site, m	0.01

be 500 meters from the stack. Nearer to the stack at 200 meters, ambient air concentrations and dry deposition amounts were lower, but wet deposition was at its maximum. One effect

of this was that vegetable concentrations increased. Below ground vegetables increased by about a factor of 4, due to the same increase in soil concentration as a result of much higher wet deposition. Above ground vegetation increased by about 50%. Particle depositions dominated above ground vegetable/fruit concentrations. Therefore, an increase in overall particle depositions due to an increase in wet depositions led to increased above ground vegetable/fruit concentrations. However, the trend was not the same for beef and milk fat. The reason for this was that grass and other cattle feeds were dominated by vapor contributions, not particle depositions, as were above ground vegetables. For bulky above ground vegetables, vapor phase impacts were empirically reduced considering the difference in bulk for these vegetables compared to the leafy grass and azalea leaf for which the air-to-leaf vapor transfer factor was developed. Therefore, a drop in ambient air vapor phase concentrations at 200 meters as compared to 500 meters dominated the result, and the net impact was to reduce beef fat concentrations. Further from the stack at 5000 meters, all biota concentrations were lower. Vapor phase air concentrations were roughly halved, and dry and wet deposition were lower by 60 and 80% respectively. This led to substantial reductions in vegetable concentrations. Interestingly, beef concentrations were lower at 5000 meters than at 200 meters, but not by much. This is because vapor phase concentrations at 5000 meters were, in fact, greater than they were at 200 m. The net results, according to the modeled depositions and air concentrations, is that beef and milk fat impacts are ironically fairly similar at 200 and 5000 meters.

3) Changing the vapor/particle partitioning assumption also had inverse effects for above and below ground vegetables as compared to beef. The baseline vapor/particle partitioning for 2,3,7,8-TCDD was 55% vapor/45% particle. When decreasing the vapor to 10% and increasing the particle to 90%, both vegetations increased. Below ground vegetables increased because below ground vegetables were not a function of vapor phase concentrations, only of soil concentrations, which were a function of particle depositions. Above ground vegetable concentrations increased as well, as they are dominated by particle depositions. As noted above, however, cattle vegetations are driven by vapor transfers. Therefore, increasing the vapor portion tended to increase these vegetations and hence beef concentrations.

Following are key overall observations from the sensitivity analysis:

1) **Source terms are the most critical for exposure media impacts.** Source terms include soil concentrations, stack emission rates, and effluent discharge rates. In all cases, the impact to exposure media is linear with changes to source terms. Proximity to the source term can be important as well, as demonstrated with differences in distance from the stack emission source.

2) **Chemical-specific parameters, particularly the bioconcentration/biotransfer parameters, are the second most critical model inputs.** Some of these have lesser impacts within the range tested, such as the organic carbon partition coefficient, Koc, for surface water impacts. Generally, at least an order of magnitude in range in possible media concentrations is noted with the range of chemical-specific parameter ranges tested. The impact of changes to bioconcentration/biotransfer parameters is mostly linear. This is because these transfer factors estimate media concentrations as a linear transfer from one media to another. For example, fish lipid concentrations are a linear function of the organic carbon normalized concentration of contaminants in sediments. These transfer parameters are also identified as uncertain parameters. Tested ranges sometimes spanned over an order of magnitude for 2,3,7,8-TCDD.

3) **All other parameters had less of an impact as compared to source strength and chemical specific parameters; nearly all impacts were within an order of magnitude for the range of tested values.** Part of the reason for this trend is that there is a reasonably narrow range for many of the non-chemical specific or source term parameters - soil properties, wind speeds, vegetation yields, and others.

4) **The sensitivity analysis exercises unearthed a dichotomy in model performance between the soil source category and the stack emission source category.** The on-site soil source category was demonstrated with a 1 ppt soil concentration of 2,3,7,8-TCDD, a concentration similar to measured concentrations of 2,3,7,8-TCDD in rural settings. Air concentrations are esimtated to be $4*10^{-5}$ pg/m^3 (vapor+particle phases summed). Atmospheric transport modeling in the demonstation of the stack emission source category resulted in an exposure site air concentration (vapor+particle phases summed also) at 500 meters from the stack to be $1*10^{-5}$ pg/m^3. With similar air concentrations predicted to occur at the exposure site for the demonstration of the soil and stack emission categories, one might hypothesize that all subsequent impacts would be similar. That was not the case. The stack

emission source algorithms deposited particulates onto soil to estimate a soil concentration that was in the 10^{-3} ppt range for the 1-cm untilled depth and the 10^{-5} range for the 20-cm tilled depth. This compares to the 1 ppt concentration for the on-site soil source category demonstration. With similar air concentrations but a 3+ order of magnitude difference in soil concentrations in the demonstration of the soil and the stack emission sources, the following trends were noted:

    ⊕ Below ground vegetables had much higher concentrations for the soil source demonstration scenario.

    ⊕ Soil-related exposures (dermal contact and soil ingestion) were much higher for the soil source demonstration scenario.

    ⊕ Soil was significantly more critical in predicting beef and milk fat concentrations in the soil source category. The following shows the relative impact of soil versus vegetations (grass and cattle feed) for the on-site soil demonstration and the stack emission demonstration:

Description	Percent impact due to ingestion of:		
	Soil	Grass	Feed
Soil contamination, beef	90	7	3
Soil contamination, milk	87	2	11
Stack emission, beef	5	59	32
Stack emission, milk	3	15	82

Subsequently, beef and milk concentrations were almost two orders of magnitude higher for the soil source category as compared to the stack emission source category.

    ⊕ Because above ground vegetations are driven by air concentrations, above ground vegetables/fruit and grass/cattle feed concentrations were similar for both demonstrations.

Further examination of the results and other model testing did suggest that the air-to-soil algorithm may be underestimating soil concentrations, and the soil-to-air algorithms may be underestimating air concentrations. If both these observations are correct, and model or parameter adjustments corrected these underestimations, then model performance would be more similar for the two source categories.

The evidence for the air-to-soil underestimation came in an air-to-beef food chain model exercise (see Table III-5 below on model testing for a summary of this test). An air-borne reservoir of dioxin-like compounds was crafted to be typical of rural environments. Depositing this reservoir onto soil resulted in a predicted concentration about an order of magnitude lower than observed concentrations in rural settings. Speculated causes include: 1) the 10-year half-life for dioxin-like compounds may not be long enough, 2) vapor-phase transfers to soils were not modeled, and 3) detritus input to soils was not considered. Empirical evidence for the possible underestimation of air concentrations over soils came in two forms. One, plant:soil ratios modeled in the soil source demonstration scenario appeared lower than experimentally determined plant:soil ratios by about an order of magnitude. This could be due to an underestimation of air concentrations. Two, air concentrations of 2,3,7,8-TCDD predicted to occur over a 1 ppt soil concentration was lower than by an order of magnitude for concentrations found in a "remote" area of Sweden, and about two orders of magnitude lower than crafted to be typical of rural setting in the United States.

While the soil-to-air algorithm may be underestimating air concentrations, it is also possible that they are not underestimating these concentrations. The expectation that releases of dioxins from soils in background settings should result in air concentrations typical of background settings may not be a realistic expectation. The argument was developed in Section II.3.3. Conclusions for Mechanisms of Impact to Food Chain earlier in this Executive Summary that the food chain is impacted via atmospheric depositions, and that industrial emissions followed by long range transport ultimately explain media concentrations in background settings. What is not known is, what portion of air concentrations in rural settings can be attributed to long range transport and what portion attributed to suspension of reservoir sources (soil and other reservoir sources). What is really needed to test the soil to air algorithm are measured concentrations over soils not known to be otherwise impacted by dioxin like compounds. Such information could not be found in the literature.

III.5.3. Mass Balance Considerations for Soil Contamination

The purpose of this exercise is to evaluate whether a principal of mass balance will be violated with the models and parameters used for the demonstration of the off-site soil source category - that principal being that dioxin releases from a site cannot exceed the original

amount at the site (assuming no replenishment). A simplifying assumption for the off-site soil source category was that the soil concentration remained constant over the period of exposure - there was not a systematic depletion of the reservoir over time due to modeled dissipation processes.

First, an estimate of the "reservoir" of 2,3,7,8-TCDD that is implied with the demonstration parameters was made. Then, an estimate of the rate at which this reservoir dissipated using the solution algorithms for dissipation: volatilization and wind erosion flux from soils, and soil erosion, was made. Other routes of dissipation that were examined are the soil ingestion by cattle and children, losses in runoff and leaching, the loss via dermal contact, and the removal via harvest of below ground vegetation. These were shown to be minuscule in comparison to air and soil erosion. The premise examined was that, if it takes substantially more time than the exposure period to dissipate the reservoir, then it may be fair to conclude that the assumption of a constant soil concentration may be suitable for purposes of exposure assessments. On the other hand, complete dissipation within a time period less than or even near to the period of exposure would mean that exposures and risks are being overestimated. This analysis led to a conclusion that the reservoir modeled in the exercise above would take more than 90 years to dissipate.

This was not a definitive exercise, by any means, but it does lend some confidence that a principal of mass balance may not have been violated for the soil source categories, and for the assumption of 20 years exposure duration.

III.6.   UNCERTAINTY

Some discussion of the issues commonly lumped into the term "uncertainty" is needed at the outset. The following questions capture the range of issues typically involved in uncertainty evaluations:

(1) How certain are site specific exposure predictions that can be made with the methods?

(2) How variable are the levels of exposure among different members of an exposed local population?

(3) How variable are exposures associated with different sources of contamination?

The emphasis in Volume III is in providing the technical tools needed to perform site-

specific exposure assessments. For the assessor focusing on a particular site, question (1) will be of preeminent importance. Therefore the emphasis of the uncertainty evaluation is to elucidate those uncertainties inherent to the exposure assessment tools presented. This chapter examines the capabilities and uncertainties associated with estimating exposure media concentrations of the dioxin-like compounds using the fate, transport, and transfer algorithms, and also identifies and discusses uncertain parameters associated with with human exposure patterns (contact rates and fractions, exposure durations, etc.).

A site specific assessment will also need to address the variability of risks among different members of the exposed population, the second key question above. The level of detail with which this can be done depends on the assessors knowledge about the actual or likely activities of the exposed population. In this document, one approach to evaluating this variability is demonstrated. Separate "central" and "high end" scenario calculations are presented to reflect different patterns of human activities within a hypothetical rural population.

A key issue with regard to intra-population variability is that it is best (if not only) addressed within the context of a specifically identified population. If such information is available, a powerful tool that can be used to evaluate the variability within a population is Monte Carlo Analysis. Three recent Monte Carlo studies which have been done for exposure to 2,3,7,8-TCDD were reviewed. Assumptions on distributions of exposure patterns and fate and transport parameter distributions are described, as are the results of their analyses. Monte Carlo procedures require distributions for the input parameters used in the assessment. Such distributions have not been established by the Agency. Decisions on the use and definition of such distributions affect assessments of all chemicals and cut across all Agency programs. Thus, it is not appropriate to establish such polices in this document.

The Agency does have efforts underway to evaluate these generic issues. For example, the Office of Health and Environmental Assessment (OHEA) is in the process of revising the Exposure Factors Handbook and held public review meetings in 1993. In addition, OHEA is developing a guidance document on generating exposure scenarios. Several offices have projects specific to Monte Carlo:

⏱ Office of Health and Environmental Assessment - A Workshop on approaches to evaluating uncertainty (including the use of Monte Carlo) was held in 1992.

☝ Office of Policy, Planning and Evaluation - A workshop on using Monte Carlo methods was held in 1993.

☝ Office of Pollution Prevention and Toxics - A handbook on the use of Monte Carlo is being developed for publication at a later date.

With regard to question (3), this document does not present a detailed evaluation of how exposure levels will vary between different sources of release of dioxin-like compounds into the environment. While Volume III does demonstrate the methodologies developed for sources of release of dioxin-like compounds into the environment with source strengths and environments crafted to be plausible and meaningful, there is still a great deal of variability on both the source strengths and on the environments into which the releases occur. For example, the frequency with which farms and rural residences are near stack emissions of dioxin-like compounds is not addressed. Comprehensive comparisons and rankings of different sources and exposure patterns are generally not available, although pieces of the puzzle are beginning to come together. Volume II of this assessment does estimate national releases of dioxin-like compounds from several sources. References to EPA and other assessments on dioxin-like compounds have been made throughout Volumes II and III of this assessment, such as those related to soil exposures (Paustenbach, et al., 1992), exposures to contaminated fish (EPA, 1991), and exposures resulting from land disposal of sludges from pulp and paper mills (EPA, 1990b).

There was a concerted effort to evaluate the capabilities of the fate, transport, and transfer algorithms by comparing key outputs from these models - predictions of concentrations and ratios of media to media concentrations - with literature reports. A summary of key comparative tests is given in Table III-5.

Table III-5. Summary of key tests of the fate, transport, and transfer models.

Description of Test	Summary of Results
Predicted vs. observed air concentrations	Air concentrations resulting from 1 ppt background 2,3,7,8-TCDD concentration were about three orders of magnitude lower than observed urban air concentrations of these contaminants, two orders of magnitude lower than a concentration speculated to be more typical of rural settings in the United States, and one order of magnitude lower than a measured air concentration in a "remote" setting in Sweden. This suggests that the volatilization/dispersion algorithms for soil contamination may be underestimating air concentrations. Air concentrations resulting from a 1 ppb soil concentration, more typical of Superfund sites, were comparable to urban air concentrations.
Plant concentration to soil concentration ratio	A comparison of ratios for the soil contamination source category showed the modeled ratios tended to be lower for all vegetation (above and below ground fruit and vegetation, grass and cattle feed) by about one order of magnitude. This could partly be due to underestimations or air concentrations, as described above. A complication in understanding the measured data, however, was that as soil concentrations increased, plant:soil ratios decreased - that is, proportionally less transfer from soil to plant was occurring as soil concentration increased. No explanation was available for this phenomena, and the models cannot duplicate it. The observation made above that modeled ratios tended to be lower was true for lower experimental soil concentrations, in the low ppb to ppt range.
Background soil concentration to bottom sediment concentration ratio	The Connecticut Department of Environmental Protection (CDEP, 1992) monitored ambient air, soils, surface water bottom sediments, and fish in the vicinity of seven resource recovery facilities and one background site. Six of the eight sites were characterized as "rural"; sites in Hartford and Bridgeport might be more appropriately characterized as suburban or urban. The average concentration in all soil samples (n = 77; assuming non-detects were half detection limits with a detection limit at 0.1 ppt; soil samples were all within 3 miles of sampled water bodies) was 0.77 ppt, which also supported the hypothesis that soils in the area of these RRFs were near background levels. The average concentration in sediment samples (n = 346; same detection limits and procedures for average concentration estimation) was 2.16 ppt. The sediment to surface soil concentration ratio was 2.8 (2.16 ppt/0.77 ppt). The sediment to surface soil concentration ratio for 2,3,7,8-TCDD was also 2.8 for the demonstration of the on-site source category, where basin-wide soil concentrations were set at 1.0 ppt and bottom sediment concentrations were modeled as 2.8 ppt using the soil to sediment algorithms of the soil contamination source categories. This exercise lends some credibility to an enrichment ratio - soils eroding into water bodies are enriched in comparison to in-situ soils - and an assignment of 3.0 to the enrichment ratio in this assessment.

Table III-5. (cont'd)

Description of Test	Summary of Results

Predicted vs. observed fish tissue concentrations

With background soil concentrations of 2,3,7,8-TCDD of 1 ppt, estimated fish concentrations were 0.6 ppt. With a bounded site of 1 ppb soil concentrations, fish concentrations were 3.0 ppt. These were compared with analagous results from the National Study of Chemical Residues in Fish (NSCRF; EPA, 1992b). For NSCRF sites that were evaluated as comparable to background settings, fish concentrations ranged from 0.56 ppt to 1.02 ppt. Average fish tissue concentrations from National Priority List (NPL) and similar industrial contaminated sites ranged from 1.4 to 30.0 ppt, with the 30 ppt average from National Priority List (NPL) sites and all other site averages under 4.4 ppt. The comparison indicates that the magnitude of concentrations appears to have been captured, and the magnitude of difference between background and higher source strength categories of the NSCRF also appears to have been duplicated.

Predicted vs. observed fish concentrations for the 104-mill pulp paper mill study

The "sources" of 2,3,7,8-TCDD loadings into surface water were pulp and paper mills of the 104-mill study (EPA, 1990c). A complete set of "observed" data (fish concentrations from the NCSRF described above, 2,3,7,8-TCDD discharges other than non-detects, water body characteristics, etc.) were available for only 47 mills and 95 fish samples (in some cases, more than one fish was identified downstream of a mill). A dichotomy in model performance was observed for 9 mills (and 21 associated fish samples), which differed from the other 38 in that the receiving water body flow volumes were significantly larger. The average for these 9 mills was $3*10^{10}$ L/hr, while the average for the other 38 was $5*10^8$ L/hr. The average predicted whole fish tissue concentration of 2,3,7,8-TCDD for the 38 mills was 7 ppt, and the average observed concentration in 74 fish was 15 ppt. For the 8 mills and 21 fish, the average predicted fish concentration was 0.7 ppt compared to an observed 5.3 ppt. The correlation over all mills and samples was low, at $r^2 = 0.41$. However, the merit of generating this descriptor should be considered: it assumes that the single observed discharge of 2,3,7,8-TCDD represents long term discharges for a given mill, that the single or the few fish samples represent observed impacts from the mill, and so on. One pertinent result was that the maximium "observed" fish tissue concentration of 143 ppt was matched by the maximum predicted concentration of 89 ppt. The key assumption was that the pulp and paper mills were the only sources impacting fish tissue concentrations; it is suggested that other sources impacting the large water bodies explain why observed fish concentrations were about an order of magnitude higher than model predictions for these water bodies.

(cont'd on next page)

Table III-5. (cont'd)

Description of Test	Summary of Results
Predicted vs. observed water concentrations	Data in the literature suggests concentrations of dioxin-like compounds mostly below 1 pg/L. Models predicted concentrations of 10^{-2} pg/L and lower in demonstration of all source categories.
Predicted vs. observed beef concentrations	A profile of "observed" air concentrations of dioxin-like compounds was crafted from available air concentration data. An urban air profile of TEQs developed in Volume II was 0.095 pg/m^3, and based on evidence that rural air concentrations (which are the ones most appropriate for beef concentrations) are 4-6 times lower than urban air concentrations, a rural air profile was crafted, totalling 0.019 pg TEQ/m^3. These concentrations were routed through the food chain model to arrive at beef TEQ concentrations which were compared with a TEQ beef concentration profile generated from measurements in Volume II. A predicted TEQ concentration of 0.36 ng/kg whole beef concentration (19% fat) was compared to the observed 0.48 ng TEQ/kg in whole beef. Also evaluated were the capabilities of the model to evaluate air to leafy vegetation transfers (vapor and particle) by looking at model predictions and comparing them a single set of observations taken in a rural location in Minnesota (Reed, et al., 1990). Model predictions and observations also compared favorably, except for octa congeners, where predictions were much lower than observations. However, the model for vapor/particle partitioning indicated that the octa congeners would reside fully on particles, i.e., ϕ (particle fraction) = 1.00. In fact, ϕ the for both octa congeners equalled 0.998. Allowing calibration for ϕ , values equalled 0.9998 for OCDD and 0.998 for OCDF, and leafy vegetation predictions, as well as octa beef measurements, now closely matched observations. An air-to-soil evaluation was also done, comparing model predictions of dioxin congener soil concentrations with measurements taken in the United States in rural settings. It was found that the model generally underpredicted soil concentrations by about an order of magnitude, although a more close match would not have greatly affected the predictions in beef since soil is only a small part of the cattle diet. Speculations for why the model was underpredicting soil concentrations included: 1) vapor transfers to soils were not considered, 2) detritus contributions to soil concentrations were not considered, and 3) the assumed half-life of 10 years for this exercise might not be long enough.
Predicted vs. observed beef fat:soil and milk fat:soil concentration ratios	Fries (1985) had developed fat:soil ratios for a farm known to be contaminated with PBBs, compounds similar in fate and persistence, and bioaccumulation tendencies, as the dioxin-like compounds. Field data showed ratios of 0.10-0.39 for beef and dairy cow body fat:soil, and 0.02-0.06 for milk fat:soil. Modeled ratios in the both soil contamination (on and off-site) example scenarios for 2,3,7,8-TCDD were 0.12 for beef fat:soil and 0.06 for milk fat:soil.

A summary of key discussions from the uncertainty evaluation is now presented. First is a summary of three exposure parameters common to all pathways:

1. Lifetime, Body Weights, and Exposure Durations: Of these three parameters, the exposure duration is the most uncertain. The estimates of 9 and 20 years were made in this assessment for non-farming residents in rural settings, and farming residents in rural settings. These values were based on assumptions of time living at one residence. A critical assumption of a constant soil concentration for contaminated soil sites should be carefully considered for site-specific assessments. Data on degradation indicates very slow rates of degradation, and only photolysis as a possible degradation mechanism, which would not impact residues below the surface. A mass balance exercise on the demonstration of the off-site source category (where a 40,000 m^2 area had soil concentrations averaging 1 ppb 2,3,7,8-TCDD) indicates that it would take 90 years to dissipate a reservoir of 2,3,7,8-TCDD extending 6 inches into the soil. An adult body weight of 70 kilograms and a lifetime of 70 years are standard assumptions for exposure and risk and, although variability is recognized for these parameters, these variations are not expected to add significant uncertainty in exposure estimates. The same is true for the 17 kg child body weight in the childhood exposure pattern of soil ingestion.

2. Soil Ingestion and Soil Dermal Contact: Soil ingestion for older children and adults were not considered, which may have underestimated lifetime soil ingestion exposures. Pica soil ingestion patterns were not evaluated in this assessment. The ingestion rates (200 mg/day for central scenarios and 800 mg/day for high end scenarios, during ages 2-6) considering this appear reasonable. For the soil dermal contact pathway, key uncertain parameters include the soil adherence (0.2 mg/cm^2-event for the central residential scenario and 1.0 mg/cm^2-event for the high end farming scenario) and the absorption fraction (0.03 for dioxin-like compounds).

A major area of uncertainty for both pathways is the estimation of soil concentrations where the source of contamination is located distant from the site of exposure. For this assessment, this includes the off-site soil source category and the stack emission source category. Results from sensitivity analysis exercises for the erosion algorithm suggests that

the 0.28 ppb soil concentration (within a 5-cm layer) used for soil ingestion and dermal contact, and which resulted from the 1 ppb nearby (150 m) soil contaminated site, may be high. Specifically, when all parameters for the erosion algorithm remained constant except the dissipation half-life, which initially was 0.0693

yr^{-1} (half-life of 10 years) and then was reduced by a factor of ten to 0.00693 yr^{-1} (half-life of 100 years), the soil concentration 150 meters away at the site of exposure increased to slightly above 1.00 ppb. While dissipation of surface residues which have arrived at an exposure site from a distant source is an appropriate assumption, the outcome of a higher soil concentration 150 meters from a site of soil contamination when no dissipation is assumed (albiet assuming infinite time such that a steady state is reached) is questionable. Key uncertain parameters identified include the dissipation rate (0.0693 yr^{-1}), the mixing depth (5 cm), and the use of an enrichment ratio (equal to 3.0) which increases the concentration of dioxin-like compound on eroded soil relative to in-situ soil. This latter parameter was speculated to the one most likely to be inaccurate for evaluation of off-site soil impacts. Its assignment was not based on data specific to dioxin-like compounds, but rather to general literature data on enrichment ratios for soil nutrients and pesticides showing a range of between 1 and 5. On the other hand, support for an enrichment ratio of 3.00 came in a data set including background soil and concurrent bottom sediment data in receiving water bodies in Connecticut (see Table III.5 for a summary of this data set). There, the ratio of sediment concentrations of 2,3,7,8-TCDD to soil concentrations was 2.8, suggesting that bottom sediments are enriched in comparison to surface soils. The model for bottom sediment impact from watershed soils includes the enrichment ratio, which was set at 3.00, and the demonstration scenarios did show a sediment:soil ratio of 2.8, like the observed data.

An uncertain outcome was also identified for the particle deposition algorithm used for the stack emission source category. An analysis suggests that the soil concentration in a 1-cm layer resulting from depositing particles may be underestimated by about an order of magnitude. The pertinent analysis for this observation came from the air-to-beef food chain model validation exercise conducted for dioxin-like compounds (further details of this exercise are found in Table III-5). There, a rural air profile of dioxin-like compounds were deposited onto soils, and the resulting concentrations of dioxin-like compounds were compared against observations from four United States reports on soil concentrations in rural areas. Generally,

the model underpredicted soil concentrations by about an order of magnitude. Suggested causes for this underprediction include: 1) the model does not consider vapor phase transfers to soils, 2) the model does not consider detritus contributions to soil, and 3) the half-life of 10 years may not be long enough for dioxin-like compounds.

In summary, principally identified uncertain parameters for the algorithms transporting eroding soil and depositing particles include: the mixing zone depth for untilled situation of 1 and 5 cm, the dissipation half-life of 10 years, the lack of consideration of vapor phase depositions and detritus additions to soils, and the use of an enrichment ratio for eroded soil of 3.0.

3. Ingestion of Water: A comparison of alternate modeling approaches for estimating water concentrations showed similar results to the models adopted for this assessment. There also does not appear to be a wide range of possible values for water ingestion rate (1.4 L/day for central scenarios and 2.0 L/day for high end scenarios) and contact fraction (0.75 for central scenarios and 0.90 for high end scenarios), and these are not expected to introduce significant uncertainty into water ingestion exposure estimates.

4. Inhalation: The inhalation rate assumed for both central and high end scenarios was 20 m^3/day. The distinction in the scenarios was in the contact fractions: central scenarios assumed a contact fraction of 0.75 and high end scenarios had a 0.90 contact fraction. These fractions correspond to time at the home environment. These fractions and the inhalation rate are not expected to add significant uncertainty in inhalation exposure estimates.

Sensitivity analysis showed air concentrations resulting from soil emissions to be sensitive to Koc and H, and also to key source strength and delivery terms such as areas of contamination and wind speed. Assuming these non-chemical specific parameters can be known with reasonable certainty for site-specific applications, the most uncertainty lies with chemical specific data.

Alternate approaches for volatilization and air dispersion tested included the volatilization approach developed by Jury, et al. (1983) and the box model for dispersion calculations. The Jury model predicted about 1/3 as much volatilization flux (given the

selection of parameters, made equal to or most analogous to the models of this assessment) as the Hwang, et al. (1986) model of this assessment. The box model predicted about 6 times higher air concentrations than the near-field dispersion approach of this assessment. This reasonable comparison lends some credibility to the models selected.

Approaches to estimate particulate phase concentrations are empirical and based on field data. They are based on highly erodible soils but are specific to inhalable size particles, those less than 10 µm. As such, they may overestimate inhalation exposures, but may underestimate the total reservoir of particulates, which becomes critical for the particle deposition to vegetation algorithms. Another area of uncertainty is the assumption that volatilized contaminants do not become sorbed to airbone particles - this is also critical because vapor phase transfers dominate plant concentration estimation. A final key area of uncertainty is that transported contaminants from a contaminated to an exposure site via erosion are assumed not to volatilize or resuspend at the exposure site or from soils between the contaminated and the exposure site - air borne exposure site concentrations may be underestimated as a result.

5. Fruit and Vegetable Ingestion: All ingestion parameters assumed are evaluated as reasonable for general exposure to broad categories of fruits and vegetables. However, great variability is expected if using these procedures on a specific site where home gardening practices can be more precisely ascertained. Concepts of below and above ground vegetations were developed to accomodate soil to root algorithms and soil to air to vegetation algorithms. Protected vegetations - those with outer inedible protections such as citrus or corn - were assumed not to be impacted by dioxin-like compounds.

A key assumption in the vegetation algorithm, that dioxin-like compounds do not translocate from root to shoot, was verified by two experiments. Vapor-phase contributions to vegetation dominated the contaminated soil and stack emission source categories, with one exception. Particle depositions were more important for above ground fruit/vegetable concentrations for the stack emission source.

A critical empirical parameter was the above and below ground correction factors, VG_{ag} and VG_{bg}, both set at 0.01 for fruits and vegetables. These factors were justified for dioxins based on the fact that the experiments for derivation of the below ground empirical transfer

factor and the above ground empirical transfer factor were conducted with thin barley roots and azalea leafs, respectively. Whole plant concentrations for these vegetations are likely to be much higher than whole plant concentrations of bulky fruits and vegetables; hence the introduction of the VG parameters. VG for grass was set at 1.00, which assumes that grass leaves and azalea leaves are analagous with regard to vegetative bulk. VG for cattle feed was set at 0.50, which assumes that some cattle feed is leafy (hay), while some is bulky (corn silage). A different assumption for VG of fruits and vegetables, such as 0.10, would increase estimated concentrations and perhaps make plant:soil concentration ratios more in line with literature values (see Table III-5).

Experimental evidence that a VG_{ag} for vapor transfers of dioxin-like compounds is justified came in a recent study by McCrady (1994). McCrady experimentally determined uptake rate constants, termed k_1, for vapor phase 2,3,7,8-TCDD uptake into several vegetations including kale, grass, pepper, spruce needles, apple, tomato, and azalea leaves. The uptake rate for an apple divided by the uptake rate for the grass leaf was 0.02 (where uptake rates were from air to whole vegetation on a dry weight basis). For the tomato and pepper, the same ratios were 0.03 and 0.08. The VG_{ag} was 0.01 for fruits and vegetables in this assessment. McCrady (1994) then went on to normalize his uptake rates on a surface area basis instead of a mass basis; i.e., air to vegetative surface area instead of air to vegetative mass. Then, the uptake rates were substantially more similar, with the ratio of the apple uptake rate to the grass being 1.6 instead of 0.02; i.e., the apple uptake rate was 1.6 times higher than that of grass, instead of 1/50 as much when estimated on an air to dry weight mass basis. The ratios for tomato and pepper were 1.2 and 2.2, respectively. In his article, McCrady (1994) concludes, "The results of our experiments have demonstrated that the exposed surface area of plant tissue is an important consideration when estimating the uptake of 2,3,7,8-TCDD from airborne sources of vapor-phase 2,3,7,8-TCDD. The surface area to volume ratio (or surface area to fresh weight ratio) of different plant species can be used to normalize uptake rate constants for different plant species." McCrady does caution, however, that uptake rates are only part of the bioconcentration factor estimation, and is unsure of the impact of surface area and volume differences on the elimination phase constant, k_2 (personnal communication, J. McCrady, US EPA, ERL-Corvallis, Corvallis, OR 97333). Still, his recent experiments do appear to justify the use of a VG parameter since the

air-to-leaf transfer parameter was developed on an air-to-whole-plant-mass basis, and his results are consistent with the assignment of 0.01 for fruits and vegetables.

An uncertain experimentally derived empirical factor described the transfer of compounds from soil to below ground vegetables, the Root Concentration Factor, RCF. An analagous uncertain parameter describes the transfer of vapor-phase dioxin-like compounds from air to above ground vegetations, the air-to-leaf transfer factor, B_{vpa}. Both of these parameters are estimated as functions of the contaminant properties; both used contaminant octanol water partition coefficient, Kow, and the B_{vpa} also used contaminant-specific Henry's Constant, H. The B_{vpa} was developed in a series of experiments by Bacci, et al. (1990, 1992) using 14 different organic contaminants and azalea leaves. Adjustments to the B_{vpa} as formulated by Bacci were suggested by the experiments on the transfer of 2,3,7,8-TCDD to grass leaves by McCrady and Maggard (1993). The adjustments dealt with the impact of photodegradation, which was not considered in the experimental design of Bacci, and in the different plant species used by McCrady and Maggard. Those adjustments were made for the dioxin-like compounds in this assessment. The range of log Kow for 2,3,7,8-TCDD found in the literature was 6.15 to 8.5. An alternate value of log Kow for 2,3,7,8-TCDD would more likely be higher than lower, given the selected value of 6.64. Increasing log Kow tends to decrease below ground vegetation, by as much as an order of magnitude, while increasing above ground vegetation by as much as an order of magnitude.

5. Ingestion of Fish: The key exposure parameter for this pathway was the fish ingestion rate. The rates assumed in the demonstration scenarios were low in comparison to estimates given for subsistence fisherman or others who live near large water bodies where fish are commercially caught. The justification for the lower ingestion rate for demonstration purposes was that the setting demonstrated was described as rural, containing farms and non-farm residences, where the emphasis is on agriculture. A relatively small watershed with a small impacted water body was assumed. Daily ingestion rates of 1.2 (central) and 4.1 (high end) g/day were assumed, based on an assumption of 3 fish meals per year (150 g/fish meal) obtained from the water body for the central scenario and 10 fish meals per year for the high end scenario. Other fish ingestion rates that can be considered for exposure assessments include: 6.5 g/day characterized as a national average ingestion rate for

freshwater and estuarine fish and shellfish (EPA, 1984), and 30 and 140 g/day, which are described as 50th and 90th percentile rates for recreational fisherman in areas where large water bodies are present (EPA, 1989).

Other models for estimating fish concentration based on water column concentrations, rather than suspended sediment concentrations, were described in EPA (1993) and demonstrated in this assessment. Results indicated that the water column approaches would predict similar whole fish concentrations compared with the sediment concentration approaches of this assessment. However, the various models would respond differently to changes in model parameters. For example, a bioaccumulation parameter based on whole water concentration (total contaminant, the sum of sorbed and dissolved amounts, divided by water volume) will be mostly insensitive to changes in organic carbon content of sediments. In contrast, this is a critical parameter for bioaccumulation parameters which are based on sediment concentrations (as in this assessment) or dissolved-phase water column concentrations.

A key uncertain parameter for estimating fish tissue concentrations is the Biota Sediment Accumulation Factor, or BSAF, and the Biota Suspended Sediment Accumulation Factor, or BSSAF. A range of 0.03 to 0.30 for 2,3,7,8-TCDD is hypothesized for column feeding fish, while the Connecticut data (CDEP, 1992) and some other data on bottom feeding fish indicate higher BSAFs ranging up to 0.86 for 2,3,7,8-TCDD. A value of 0.09 for 2,3,7,8-TCDD for BSAF and BSSAF is used in this assessments. Data is scarce for BSAF and BSSAF for other dioxin-like compounds, although available data does suggest that these parameter values decrease as the degree of chlorination increases. A key parameter is the fish lipid content, which can vary from below 0.05 to above 0.20. The model estimates a fish lipid concentration. Multiplying fish lipid concentration by fish lipid content arrives at a whole fish concentration or an edible fish concentration, depending on the user's assignment and characterization of the fish lipid content variable. For this assignment, the fish lipid content was assigned a value of 0.07 for the demonstration scenarios, based on lipid content of fish in EPA's Lake Ontario study (EPA, 1990a).

7. Beef and Milk Ingestion: The rates of beef and milk fat ingestion are 22 and 10.5 g/day, respectively. The median whole beef and whole milk ingestion rates are given as

100 and 300 g/day, respectively (EPA, 1989), and these were assumed for the demonstration scenarios. Beef fat and milk fat contents are assumed to be 22% and 3.5%, respectively. Only the high end demonstration scenarios included beef and milk ingestion pathways. These scenarios were farm settings, and the assumption was that farming families would obtain a portion of their ingestion of these foods would come from home produced beef and milk. The assumptions for contact fractions for beef and milk (fractions of their total consumption that comes from home supplies) was 0.44 and 0.40, respectively. These were average consumption fractions for farming families, whether or not the farm families home consumed, and were developed from a USDA (1966) survey of farming families. Since exposure estimates from these pathways are linearly related to ingestion rate and contact fraction, these are critical exposure parameters for site specific applications.

Comparison with earlier modeling approaches showed that the current approach to estimating beef and milk concentrations is the same as earlier approaches, although mathematically formulated differently. Earlier approaches also estimated cattle dose of 2,3,7,8-TCDD from contaminated air (directly) and contaminated ground water - these earlier estimations showed these contributions to be minimal, and they were not considered in this assessment. Early efforts in the literature did not consider vapor transfers to vegetations; one later assessment did include vapor transfers, and a key result in that assessment, as well as this one, is that vapor transfers are critical for beef impacts. Finally, earlier assessments considered the practice of fattening beef cattle prior to slaughter by feeding them residue-free grains. These efforts estimated over a 50% reduction in beef concentration due to residue degradation or elimination and/or dilution with increases in body fat. The demonstrations scenarios in this assessment did not consider this practice. However, this practice was considered in the air-to-beef food chain validation exercise. There, a 50% reduction in beef concentrations due to feedlot fattening was assumed.

Key uncertain and variable parameters for beef/milk concentrations include: 1) the assumptions concerning vapor/particle partitioning for the stack emission source category, 2) the air-to-leaf transfer parameter, B_{vpa}, for vapor phase contaminants, 3) beef cattle exposure assumptions, 4) the weathering factor for particles depositing on vegetations which cattle consume, and 5) uncertainties as discussed above for air to soil algorithms and soil to air algorithms.

REFERENCES FOR VOLUME III

Bacci, E.; Calamari, D.; Gaggi, C.; Vighi, M. (1990) Bioconcentration of Organic Chemical Vapors in Plant Leaves: Experimental Measurements and Correlation. Environ. Sci. Technol. 24: 885-889.

Bacci, E.; M.J. Cerejeira; C. Gaggi; G. Chemello; D. Calamari; M. Vighi (1992) Chlorinated Dioxins: Volatilization from Soils and Bioconcentration in Plant Leaves. Bull. of Env. Cont. and Tox. 48(3):401-408.

Bidleman, T.F. (1988) Atmospheric processes. Wet and dry depostion of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Techol., 22:4, pp 361-367.

Briggs, G.A. (1975). Plume rise predictions. In: Lectures on air pollution and environmental impact analyses, American Meteorology Society.

Briggs, G.A. (1979). Plume rise. USAEC Critical Review Series. NTIS publication no. TID-25075.

CARB (1986) Subroutines for calculating dry depostion velocities using Sehmel's curves. Prepared by Bart Croes, California Air Resources Board.

CDEP (1992) Data on the Connecticut Department of Environmental Protection (CDEP) program to monitor soil, sediment, and fish in the vicinity of Resource Recovery Facilities. Data supplied by C. Fredette, CDEP, 165 Capitol Ave, Hartford, CT, 06106.

Dumbauld, R.K.; Rafferty, J.E.; Cramer, H.E. (1976) Dispersion deposition from aerial spray releases. Preprint volume for the Third Symposium on Atmospheric Diffusion and Air Quality. American Meteorological Society.

Fries, G.F. 1985. Bioavailability of soil-borne polybrominated biphenyls ingested by farm animals. Journal of Toxicology and Environmental Health 16: 565-579.

Fries, G.F.; Paustenbach, D.J. (1990) Evaluation of Potential Transmission of 2,3,7,8-Tetrachlorodibenzo-p-dioxin-Contaminated Incinerator Emissions to Humans Via Foods. J. Toxicol. Environ. Health 29: 1-43.

Hwang, S.T.; Falco, J.W.; Nauman, C.H. (1986) Development of Advisory Levels for Polychlorinated Biphenyls (PCBs) Cleanup. Exposure Assessment Group, Office of Research and Development, U.S. Environmental Protection Agency. EPA/600/6-86/002.

Jury, W.A.; Spencer, W.F.; Farmer, W.J. (1983) Behavior assessment model for trace

organics in soil I. Model description. Journal of Environmental Quality 4:558-564.

McCrady, J.K.; Maggard, S.P. (1993) Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Env. Sci. Technol. 27:343-350.

McCrady, J.K. (1994) Vapor-phase 2,3,7,8-TCDD sorption to plant foliage - a species comparison. Chemosphere 28(1):207-216.

McLachlan, M.S.; Thoma, H.; Reissinger, M.; Hutzinger, O. (1990) PCDD/F in an agricultural food chain. Part I: PCDD/F mass balance of a lactating cow. Chemosphere 20:1013-1020.

Paustenbach, D.; Wenning, R.; Lau, V.; Harrington, N.; Rennix, D.; Parsons, A. (1992) Recent developments on hazards posed by 2378-TCDD in soil: Implications for setting risk-based cleanup goals at residential and industrial sites. J. Tox. Env. Health, 36:103-149.

Radke, L.F.; Hobbs, P.V.; Eltgroth, M.W. (1980) Scavenging of aerosol particles by precipitation. Journal of Applied Meteorology 19:715-722.

Rao, K.S. (1981) Analytical solutions of a gradient-trasnfer model for plume deposition and sedimentation. NOAA Technical memorandum. ERL ARL-109.

Rao, K.S.; Sutterfield, L. (1982) MPTER-DS. The MPTER model including deposition and sedimentation. U.S. EPA, Research Triangle Part, NC. EPA 600/8-82/024.

Reed, L.W.; Hunt, G.T.; Maisel, B.E.; Hoyt, M.; Keefe, D.; Hackney, P. (1990) Baseine assessment of PCDDs/PCDFs in the vicinity of the Elk River, Minnesota generating station. Chemosphere 21:159-171.

Sehmel, G.A. (1980)   Particle and gas dry depostion: A review. Atmospheric Environ. 14, pp 983-1011.

Seinfeld, J.H. (1986)   Atmospheric chemistry and physics of air pollution. New York, NY., John Wiley and Sons.

Turner, D.B. (1986) Fortran computer code/user's guide for COMPLEX I Version 86064: An air quality dispersion model in section 4. Additional models for regulatory use. Source file 31 contained in UNAMAP (VERSION 6). National Techical Information Service, Sprinfield, VA. NTIS PB86-222361/AS.

U.S. Department of Agriculture. (1966) Household food consumption survey 1965-1966. Report 12. Food Consumption of households in the U.S., Seasons and years 1965-1966. United States Department of Agriculture, Washington, D.C. U.S. Government Printing Office.

4/94

U.S. Environmental Protection Agency. (1984) Ambient water quality criteria document for 2,3,7,8-tetrachlorodibenzo-p-dioxin. Office of Water Regulations and Standards, Washington, D.C. EPA-440/5-84-007.

U.S. Environmental Protection Agency. (1986). Industrial source complex (ISC) dispersion model user's guide-second edition. Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA-450/4-86-005a.

U.S. Environmental Protection Agency. (1989) Exposure Factors Handbook. Office of Health and Environmental Assessment. EPA/600/8-89/043. July, 1989.

U.S. Environmental Protection Agency. (1990a) Lake Ontario TCDD Bioaccumulation Study Final Report. Cooperative study including US EPA, New York State Department of Environmental Conservation, New York State Department of Health, and Occidental Chemical Corporation. May, 1990.

U.S. Environmental Protection Agency. (1990b) Assessment of Risks from Exposure of Humans, Terrestrial and Avian Wildlife, and Aquatic Life to Dioxins and Furans from Disposal and Use of Sludge from Bleached Kraft and Sulfite Pulp and Paper Mills. Office of Toxic Substances and Office of Solid Waste, EPA 560/5-90-013. July, 1990.

U.S. Environmental Protection Agency. (1990c) *USEPA/Paper Industry Cooperative Dioxin Study "The 104 Mill Study" Summary Report* and *USEPA/Paper Industry Cooperative Dioxin Study "The 104 Mill Study" Statistical Findings and Analyses* Office of Water Regulations and Standards, July 13, 1990.

U.S. Environmental Protection Agency. (1990d) Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions. Interim Final Office of Health and Environmental Assessment. EPA/600/6-90/003. January, 1990.

U.S. Environmental Protection Agency. (1991) A Methodology for Estimating Population Exposures from the Consumption of Chemically Contaminated Fish. Prepared by Tetra Tech, Inc., Fairfax VA. for Office of Policy, Planning, and Evaluation and Office of Research and Development, US EPA. EPA/600/9-91/017.

U.S. Environmental Protection Agency. (1992a) Guidelines for exposure assessment. Office of Health and Environmental Assessment, Washington, DC. EPA/600-Z-92/001. published in Federal Register, May 29, 1992, p. 22888-22938.

U.S. Environmental Protection Agency. (1992b) National Study of Chemical Residues in Fish. Volumes I and II. Office of Science and Technology EPA 823-R-92-008a & 008b. September, 1992.

U.S. Environmental Protection Agency. (1992c) Dermal Exposure Assessment: Principals

and Applications. Office of Health and Environmental Assessment. EPA/600/8-91/011B.

U.S. Environmental Protection Agency. (1993) Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Risks to Aquatic Life and Associated Wildlife. Office of Research and Development, Environmental Research Laboratory at Duluth, MN. EPA/600/R-93/055. March, 1993.

IV. RECOMMENDATIONS FOR FUTURE RESEARCH

Although the dioxin-like compounds have probably been studied more than any other set of organic compounds in the environmental field, numerous data gaps remain. Basic questions such as what sources contribute most to human body burdens are still unanswered. This section summarizes the research needs for exposure to dioxin-like compounds.

IV.1. SOURCES, FORMATION, CONTROLS AND MONITORING

Research on how CDD/F is formed provides a seminal basis for understanding CDD/F sources. Three basic theories on the formation and emission of CDD/Fs during the combustion of chlorine-bearing wastes and fuels have been advanced by research in the international scientific community and are summarized in Volume II, Chapter 3, Section 3.5. Scientific knowledge on the mechanisms of formation of CDD/F within combustion processes can help to provide answers in a number of important areas, including:

- identification of unknown combustion sources that have yet to be tested for emissions.
- identification of process changes and operating practices that will prevent the formation of CDD/Fs in various combustion sources.
- help with development of engineering controls to reduce CDD/F emissions at known combustion sources.

Further research recommendations relating to sources are outlined below.

● **Combustion Source Testing:**   For purposes of setting priorities on research to better characterize combustion sources, consideration must be given to the estimated size of the source on an individual and collective basis and level of confidence in current estimates. This analysis, given in Table IV-1, suggests that the following source categories are high priority for further testing: 1) medical waste incinerators, 2) cement kilns, 3) industrial

Table IV-1. Analysis of air emission sources.

Facility Type	Magnitude of Release (collectively and per unit)	Uncertainty in Emission Estimate	Overall Priority For Further Testing
Medical Waste Incinerators	Collectively high, individually small	High, 6 of 6,700 facilities tested	High
Municipal Waste Combustors	Collectively high, individually variable	Medium, 30 of 171 facilities tested	Medium, many facilities tested and new tests already planned
Cement Kilns	Collectively high, individually high for facilities burning hazardous waste	High, 17 of 212 kilns tested	High
Industrial Wood Burners	Collectively high, individually variable	High, 2 facilities tested of an unknown total	High
Secondary Metal Industry	Lead and Copper appear low to moderate, Aluminum, Magnesium, ferrous unknown	Medium, 1 of 24 copper smelters tested, 3 of 23 lead smelters tested	Medium for Pb and Cu, high for ferrous, Al, and Mg
Primary Metals Industry	Unknown, some European testing indicates could be high	High, no U.S. tests	High for Al, Mg, Cu, Fe
Forest Fires	Moderate	High, no direct tests	Medium
Diesel Vehicles	Moderate to High	High, 2 widely divergent studies, no U.S. tests	High
Residential Wood Burners	Collectively moderate, individually small	Medium, 2 recent studies	Medium
Hazardous Waste Incinerators	Collectively moderate, individually small	High, 6 of 190 facilities tested, variable feed	Medium
Sewage Sludge Incinerators	Collectively moderate, individually small	Medium, 3 of 199 facilities tested	Low
Coal Fired Power Plants	Unknown	High, no recent tests completed	Depends on results of tests now underway

wood burners, 4) primary metals industry (aluminum, magnesium, iron, copper) and secondary metals industry (aluminum, magnesium, steel) and 5) diesel engine exhaust. For each of these source categories, a field survey is needed involving emissions testing at selected facilities. In planning such a survey, consideration must be given to statistical issues, cost issues, sample collection/analysis, and similar issues.

● **Unknown Sources:** As discussed earlier in this document, several investigators have speculated that the identification of CDD/F sources may be incomplete on the basis of mass balance analyses comparing emissions to deposition. It is not clear whether this type of mass balance can ever be refined to the point where definitive conclusions can be drawn. However, it remains one of the few methods of evaluating the possibility that unknown sources exist. Thus, research is needed to refine both emission and deposition estimates. Research to better characterize known sources is discussed above.   Deposition estimates can be improved via a combination of further field measurements and modeling.   Industrial sectors which are likely candidates for dioxin emissions can be identified from knowledge about industrial processes, feed materials and theories on formation.

● **Emissions Monitoring:**   Currently the monitoring of CDD/Fs in stack gas emissions from combustion sources cannot be conducted continuously or on a real-time basis. The test method (EPA Method 23) requires sampling in the stack for 5 or more hours, and several weeks or months lead time in developing laboratory results of the sample. This situation raises concerns about the representativeness of the sample and about the inability to detect variability in emissions.   From a public health perspective, a method of continually and instantaneously measuring emissions would be desirable. This situation suggests two areas of research. The first area would be to develop CDD/F stack measurement/laboratory techniques which provide quicker results. The second area would be to identify an easily monitored combustion parameter that strongly correlates with the magnitude of dioxin emissions. Such parameters may be measured inside or outside the furnace, and may include: temperature, carbon dioxide, carbon monoxide, oxygen, total hydrocarbons, and particulates.

● **Emission Controls:**   Engineering research is needed to develop process changes or emission controls which reduce dioxin emissions. For example, pollution prevention research is needed to determine if dioxin releases can be reduced via reductions in chlorine content of

feed material, changes in operating temperatures or other techniques.

● **Combustor Ash and Scrubber Residues:**   Municipal waste combustor ash and cement kiln dust/clinker have been tested for CDD/F content. Ash from other combustor types such as coal utilities and medical waste combustors have not been tested. No data was found on CDD/F levels in effluent from scrubbers. Research is needed on the levels of CDD/F in these materials and the potential for their release to the environment.

● **Source-Receptor Relations:**   Studies are also needed to evaluate whether CDD/F sources contribute to human exposure in proportion to their overall contribution to environmental loading, or whether some sources contribute disproportionally to general population exposure. For example, it has been speculated that diesel exhaust emissions which occur as extensive line sources at ground level may cause higher exposure (per unit emission) than stack emissions from stationary sources (Jones, 1993).   One way to link sources to receptors is on the basis of congener profiles. Each combustion source technology may routinely emit a distinctive pattern of CDD/F congeners. This has been referred to as a congener profile, and could provide a means whereby emissions from a variety of combustion sources can be distinguished from one another.   Thus research is needed to determine whether distinctive congener profiles can be developed for various sources.

● **Non-Combustion Sources:**   The above discussion has focused on combustion sources. It is important, however, to study non-combustion sources. Relatively little effort has been spent characterizing non-combustion sources (one notable exception is the pulp and paper industry). Similarly, little information has been collected on CDD/F levels in most products other than paper. In general this research should parallel the areas identified above for combustors, i.e. formation, source testing, identification of unknown sources, monitoring, controls, process residues/wastes and source-receptor relationships.   This research should focus on the following non-combustion sources:

> **- Chlorophenol production:**   The two compounds in this class historically of concern are pentachlorophenol (PCP) and trichlorophenol. Although, production and use of these compounds are now limited, new testing is needed of products and waste streams to confirm CDD/F levels.

> **- Chlorobenzene production:**   Studies in Germany have measured the presence of CDD/Fs in these compounds. No United States data could be

found.

- Aliphatic chlorine production: CDD/Fs can be released during the production of vinyl chloride, however the size of these emissions have not been independently confirmed. As discussed earlier in this document, Greenpeace has suggested that such releases could be large and the vinyl chloride industry have strongly disputed these claims. The Greenpeace estimates are based on information about European plants. No data from the United States could be found.

- Pesticide production: EPA has sponsored data call-ins which has provided some assurance that many pesticides have low CDD/F levels. Not all requested data has been received, however, and independent testing of products and waste streams may be needed to confirm levels.

- Sewage treatment: Effluent and sludge from sewage treatment plants have been shown to contain CDD/F residues. More research is needed characterizing these levels and studying formation mechanisms/controls.

● **Reservoir Sources:** Rerelease of CDD/F from reservoir sources could occur by dust resuspension, erosion, volatilization, etc. The impact of these reservoir emissions compared to current emissions on the human food chain is unknown. Research is needed to evaluate the magnitude of these releases and their impact on the food chain.

IV.2. ENVIRONMENTAL FATE, TRANSPORT, AND BIOACCUMULATION

Understanding the environmental fate of CDD/Fs is central to evaluating human exposure. Empirical measurements of inter-media transfers, environmental degradation/clearance rates, and bioaccumulation are fundamental to designing mathematical models that simulate these events. Environmental fate models are a valuable tool for evaluating impacts from specific sources and evaluating the proportionality between magnitude of emissions and subsequent exposures. Although much is known about environmental fate and transport of CDD/Fs, a number of issues remain that require further research. Key areas include:

● **Environmental Monitoring:** Knowledge of environmental levels is fundamental to

understanding how CDD/Fs behave in the environment. More data is needed on CDD/F levels in air, wet/dry deposition, sediments, soils, plants and animals. As discussed below, this information can be used to improve model formulation, parameter assignments and model validation.

● **Vapor/Particulate Partitioning:**   The modeling analysis of Volume III concluded that the transfer of dioxin-like compounds to vegetation which animals consume was the principal cause for terrestrial animal food chain impact. Thus, a better understanding of the extent to which these compounds partition between vapor and particle phases in ambient air in rural and urban environments is important. A second issue is whether this partitioning is different for stack emissions versus volatilized residues from soil. While the volatiles are initially in the vapor form, do they remain as such or do they sorb to airborne particles?

● **Vapor Transfers to Vegetation:**   As noted above, vapor transfers to vegetation largely explain terrestrial food chain impact. Further research is needed to refine the algorithms presented in this document, with particular attention paid to: differences in transfer rates among different congeners, the potential for photodegradation when sorbed onto vegetative surfaces, and the impacts of shifting wind patterns, variable crop densities, sunlight conditions, and other real world conditions.

● **Photodegradation/Transformations of Vapor-Phase Dioxins:**   Some studies have suggested that photodegradation of dioxin-like compounds may occur under natural conditions. This process is not expected to occur for sorbed dioxins, and there is very limited data on photodegradation of dioxins while airborne in the vapor-phase. Laboratory studies have demonstrated that CDD/Fs undergo photolysis, typically following first order kinetics, in the presence of a suitable hydrogen donor such as oil or an organic solvent. Study results, when extrapolated to environmental conditions, indicate half-lives ranging from hours to days. There is some evidence of reductive dechlorination, or the transformation of dioxins of higher chlorine content to dioxins of lower chlorine content. This suggests the possibility that photodegradation can be both a destruction and a formation mechanism. In general, it was decided that these processes are not sufficiently well understood to explicitly incorporate into the procedures of this document. The procedures in Volume III assume no degradation of vapor-phase dioxins during transport from stacks. Photodegradation is partially accounted for in the transfer of vapor-phase dioxins to vegetations in the air-to-leaf transfer factor, B_{vpa}. The

assignment of values for this parameter is based on the air-to-leaf experiments of Bacci, et al. (1990; 1992), with an empirical adjustment developed from the experiments of McCrady and Maggard (1993), who measured the impact of photodegradation in the transfer of vapor phase 2,3,7,8-TCDD to grass leaves.   In summary, research is needed which provides 1) photodegradation rate constants for these compounds in the air and on plant surfaces, 2) information on the formation products of photodegradation of dioxins in air and on plant surfaces, and 3) procedures to incorporate this knowledge into fate models. It is important that this research be conducted in ways that convincingly simulate real world conditions and hence provide practical results for incorprating into fate models.

● **Soil Volatilization and Dispersion:**   The models for soil volatilization and subsequent dispersion to estimate air concentrations for food chain modeling and inhalation exposures have not been verified. Some empirical evidence described in Volume III suggest that these algorithms may be underestimating air concentrations of dioxin-like compounds (see also the entry titled, "Predicted vs. observed air concentrations" in Table III-5 of this Volume).

● **Soil Dissipation Rates:**   A soil dissipation rate of 0.0693 yr^{-1}, corresponding to a 10-year half-life, is assumed for all dioxin-like compounds delivered to an exposure site as deposited particles from a stack emission source, or as delivered via erosion from a site of soil contamination. Some empirical evidence described in Volume III suggests that delivered contaminants may be more persistent and that this is a low half-life (see also the entry titled, "Predicted vs. observed beef concentrations" in Table III-5 of this Volume). Further evaluation of this dissipation assumption is recommended.

● **Overland Transport Mechanisms:**   The process of soil erosion was assumed to transport soil-bound residues from a site of contamination to a site of exposure. Soil erosion was also assumed to transport residues bound to watershed soils to surface water bodies. Other mechanisms of soil-bound transport were not modeled, such as wind erosion followed by deposition. Two factors that were modeled but are uncertain is the sediment delivery ratio, which reduced potential erosion based on the deposition of eroded particles prior to their destination, and the enrichment ratio, which increased the concentration of dioxins on eroded soil based on the assumption that eroded materials are finer and higher in organic matter as compared to in-situ soil.

● **Water Body Processes:**   Because of their affinity for organic carbon, the fate and

transport of dioxin-like compounds in water bodies is likely to be more a function of sediment-related processes rather than water-related processes. Key sediment processes in water bodies include: sorption/desorption, importance and prevalence of dissolved organic materials in the water column, deposition/suspension/resuspension, and downstream sediment transport. Although procedures for sediment modeling in surface water bodies is presented in the exposure document, the models are fairly simplistic and more development is recommended, especially for evaluating point source discharges.

● **Ground Water:**   The occurrence of these compounds in ground water is expected to be minimal, based on strong sorption to soils. Ground water impacts were not assessed in this document. Dioxin-like compounds, particularly PCBs, have been found, however, in ground water below and near sites of industrial contamination. Co-occurrence with other organic compounds, co-occurrence with solvents, and transport associated with oils have been cited as causes of enhanced mobility in these settings. The possibility that dioxins may impact ground water in certain circumstances should be evaluated further.

● **Beef Food Chain Modeling:** This document proposes the hypothesis that the air-to-food pathway is the principal mechanism by which dioxin-like compounds enter the food chain. The air-to-beef model developed in this assessment is examined in Chapter 7 of Volume III with a validation exercise which provides preliminary evidence that it will predict beef concentrations that are consistent with observations (see also the entry titled, "Predicted vs. observed beef concentrations" in Table III-5 of this Volume). Given the importance of this pathway, however, further validation work is recommended. More information is needed on several of the components of the model to estimate beef and milk concentrations. Such information includes: cattle soil ingestion rates, pasture grass concentrations and mechanisms of transfer from the air/soil to pasture grass (and other feeds such as corn, hay, etc), the impact of cattle production practices to cattle food product concentrations, models and data to further develop the bioconcentration factor (termed BCF in exposure document) and assessment of differences in bioavailability between soil and vegetative intakes.

● **Bioaccumulation in Fish:**   Several approaches have been suggested for estimating uptake in fish. The approach in this assessment is based on the organic carbon normalized concentration in water body sediments. One parameter used is termed the Biota to Sediment Accumulation Factor, or BSAF. This is defined as the ratio of the concentration in fish lipids

to the organic carbon normalized concentration in bottom sediments. The BSAF represents uptake by all mechanisms. Another sediment-based parameter used in this assessment is the BSSAF, or the Biota Suspended Sediment Accumulation Factor. This is defined similarly to the BSAF, except it is based on the organic carbon normalized concentration in suspended sediments. Other parameters that have been used include the Bioconcentration Factor, or BCF, which is based on ratios between levels in fish to levels in water and represents only uptake from water, and the Bioaccumulation Factor, or BAF, which is based on ratios between levels in fish and water and representing uptake by all mechanisms. Further research is needed to develop congener specific values for these factors, develop procedures explaining how to apply these factors and to validate these procedures with field data. A key issue that has been identified is whether BSAFs that have been developed for one species and water body are generalizable to another species and another water body. This question will be difficult to answer because of the several uncertainties associated with BSAF development: fish migratory patterns, variability in fish lipid content and other differences within and between species, study design with regard to fish and sediment sampling, ecosystem differences, and so on. However, after careful examination of existing data sets and considering key differences between species (invertebrates vs. vertebrates, fresh water vs. salt water, bottom feeders vs. water column feeders, etc.), it may be possible to develop a workable system for BSAF assignment based on key considerations.

● **Other Food Products:** This document did not present site-specific assessment procedures to evaluate all terrestrial exposure pathways. For example, models are not presented to estimate concentrations in such products as eggs, chicken, and pork. Further research is needed to develop these procedures.

IV.3. CHEMICAL/PHYSICAL PROPERTIES

Chemical specific inputs are needed for all fate models and can contribute as much uncertainty to impact estimates as the conceptual formulation of the model itself. Throughout the exposure document, the lack of congener-specific data is cited as a major source of uncertainty. For example, congener-specific data is lacking for basic chemical properties such as octanol-water partition coefficients, degradation rates, and vapor pressures. Also, data is lacking for estimation of congener-specific incinerator emission factors, metabolic rate

constants, and bioavailability and biotransfer factors. Thus, gathering more data on congener-specific properties is a high priority for further research.

IV.4. EXPOSURE

Key areas for exposure research are outlined below.

● **Levels in Food Products:** This report estimates that about 90% of human exposure to CDD/Fs occurs via food ingestion. Research is needed to determine associations between levels in food to sources and agricultural practices. Data are severely lacking on concentrations in foods identified as critical - beef, milk, other dairy products, eggs, pork, poultry and marine fish.   Thus, future exposure research should emphasize issues related to levels in animal product foods. Key questions for further research include:

1)   What are representative concentrations of dioxin-like compounds in these food products?

2)   Are there regional differences in the level of food contamination? Can these be correlated to local sources or animal raising practices?

3)   Are there differences in body burden between: range-fed and feedlot cattle, free ranging or caged chickens, or other alternate practices for other animals?

4)   What is the immediate source of animal contamination?

- CDD/F incorporated within grains or other feeds

- surface contamination on grasses and other feeds

- contaminated dirt on grasses and other feeds

- dirt eaten by animals while grazing

- food additives

- other chemicals associated with animals or crops

5)   Are there any significant opportunities to reduce exposure to animals by changing feeding practices?

● **Other Products:** This document presents data showing that, in some circumstances, dioxin can migrate into food from paper products such as milk containers. The paper industry has presented data indicating that recent reductions in dioxin levels in bleached pulp suggest that

such migration is minimal. Independent testing of paper products used in food packaging is needed to confirm these claims.

Researchers in Germany (Horstmann and McLachlan, 1994) have found that some textiles contain high levels of CDD/Fs and that they can be transferred from the textiles to human skin.   The researchers speculated that the source of these dioxins was pentachlorophenol preservatives used on cotton during sea transport. More research is needed on the levels of CDD/Fs in textiles, the sources of contamination and their potential for human exposure.

● **Highly Exposed Populations:** This document reports that CDD/Fs have been measured in human breast milk and could contribute a significant portion of a person's body burden. Key questions to address in future research in this area include:

1) What is the relative rates of exposure for nursing infants from breast feeding versus formula feeding?
2) Is there much variation in CDD/F levels for mother's milk and if so, do these variations correlate with any observable factors?
3) Is there anything nursing mothers or women of child-bearing age can do to reduce exposure to their children?

Other subpopulations, such as subsistence fishers and farmers, have been identified as potentially highly exposed. More research is needed to identify these groups and determine their level of exposure. Finally, studies should also be conducted examine whether socio-economic factors can influence dioxin exposure.

IV.5. PHARMACOKINETICS

The use of pharmacokinetics in body burden analysis has shown great potential for estimating exposure levels. In order to reduce the uncertainty in these procedures, increased collection of biological samples and improvements in PK model structure and input parameters are recommended. In addition, further research should be conducted on the application of these procedures to estimating target organ dose, absorbed dose, lactational/placental

transfers, and effects on offspring.

IV.6. COPLANAR PCBs

This document does present some information on the chemical/physical properties of some coplanar PCBs, brief qualitative information on possible sources, some information on environmental occurrence levels, and nothing on background exposures. The fate and transport models presented in the document would be generally applicable to these compounds, but the chemical specific inputs need further development.

The available information does suggest that total PCB levels are commonly much higher in soils and sediments than the other dioxin-like compounds. Most environmental data are reported as total PCBs or as an Aroclor mixture. Since congener specific data are largely unavailable, it is not clear what portion of these PCBs are coplanar. Congener specific sampling and analysis protocols need to be evaluated. Also, there is not yet a concurrence on Toxicity Equivalency Factors (TEF) schemes, so even if estimates of concentrations of coplanar PCB were made, it is not yet clear how to convert these to a 2,3,7,8-TCDD comparable basis. Thus the first goal of this research would be to derive preliminary estimates of what portion of the total PCBs present in the environment are the coplanar congeners. This would involve reviewing the limited congener specific data that is currently available and evaluating how representative it may be of PCBs in other locations. The various TEF schemes that have been proposed could be used to further assess the potential importance of these compounds. The next logical step would be to conduct a large sampling and analysis program to confirm the levels of these compounds in the environment. As TEF schemes are refined they should be incorporated into this effort.

Other research questions specific to PCBs include:

1) Are there any current sources releasing coplanar PCBs to the environment? Under what conditions are coplanar PCBs formed in industrial and combustion processes? What are the emission factors are what are the locations for major sources?

2) What are the background exposure levels to these compounds? Evaluation could be done using both a forward analysis, starting with diet information, and in a reconstructive manner, starting with body burdens.

3) How persistent are the coplanar PCBs relative to the other PCBs?

4)   Is most of the body burden derived from "old PCBs" recirculating around in the environment or is current and future body burden significantly effected by more recently released materials?

5)   What is the relative contribution of controlled large sources (HD electrical equipment) versus the more uncontrolled dispersed small sources such as small capacitors and fluorescent light ballasts?

6)   Are the pathways of exposure for dioxin-like PCBs different than for CDD/Fs?

7)   Do PCB sources contribute to human exposure proportional to the overall contribution to environmental loading, or do some sources contribute disproportionally to general population exposure?

IV.7. NON-CHLORINE HALOGENATED FORMS OF DIBENZODIOXIN/FURANS AND COPLANAR BIPHENYLS

Considerable uncertainty remains concerning the health effects of these compounds as well as basic exposure issues such as environmental occurrence, background exposure levels, chemical/physical properties, and sources. Other than some discussion on chemical/physical properties, these compounds are not addressed in the current document. The fate and transport models presented in the document would be generally applicable to these compounds, but the chemical specific inputs would need further development. No TEF schemes have been published or adopted for these compounds. As with the coplanar PCBs, the first goal of the research in this area would be to estimate the levels of these compounds in the environment and human body burdens. This estimate should initially be attempted on basis of existing data, but very likely a sampling and analysis program will be needed to collect sufficient data for even initial estimates. Congener specific sampling and analysis protocols need to be evaluated. The next steps would be to identify/evaluate sources and pathways of exposure and to estimate background exposure levels.

IV.8. GLOBAL IMPACTS

This document presents environmental and human body burden data showing that the dioxin-like compounds are found all around the world. Atmospheric deposition has been measured in remote locations such as the Arctic indicating that long range transport of these

compounds occur. It is important to better understand the geographic extent of exposure to these compounds and how far impacts from particular sources may spread. Thus, further research is needed to compare local, regional and global impacts.

REFERENCES FOR RECOMMENDATIONS SECTION

Bacci, E.; Calamari, D.; Gaggi, C.; Vighi, M. (1990) Bioconcentration of Organic Chemical Vapors in Plant Leaves: Experimental Measurements and Correlation. Environ. Sci. Technol. 24: 885-889.

Bacci, E.; M.J. Cerejeira; C. Gaggi; G. Chemello; D. Calamari; M. Vighi (1992) Chlorinated Dioxins: Volatilization from Soils and Bioconcentration in Plant Leaves. Bull of Env. Cont. and Tox. 48(3):401-408.

Horstmann, M.; McLachlan, M.S. (1994) Textiles as a source of polychlorinated dibenzo-p-dioxins and dibenzofurans (CDD/CDF) in human skin and sewage sludge. Environ. Sci. and Poll. Res. 1(1):15-20.

Jones, K. (1993) Diesel truck emissions, an unrecognized source of CDD/CDF exposure in the United States. J. Risk analysis 13(3):245-252.

McCrady, J.K.; Maggard, S.P. (1993) Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Env. Sci. Technol. 27:343-350.