# Estimation of Air-Toxic Emissions from Highway Vehicles in the Motor Vehicle Emissions Simulator (MOVES 2014)

# DRAFT REPORT

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Disclaimer

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## Table of Contents

# 1 Background

This document describes the data and methods used to estimate emissions of toxic compounds emitted from for highway vehicles in the MOVES2014 database and model. The current release of the MOVES database (MOVES2014) includes substantial updates to inputs and structures used to estimate toxic emissions, incorporating data from recent programs conducted on recently manufactured vehicles employing current technologies. It also includes the capability to estimate emissions for ethanol blends containing more than 10% ethanol, including E15, E20, E70, and E85 (71-100% ethanol).

For light-duty vehicles manufactured prior to 2001, exhaust emissions for several compounds (including benzene, 1,3-butadiene, acetaldehyde and formaldehyde), are estimated using algorithms developed for the Complex Model for Reformulated Gasoline, developed in the early 1990's for the Federal Reformulated Gasoline Rule.[1] These algorithms are used to calculated toxic to volatile organic compound (VOC) ratios based on fuel composition, and the ratios are then applied to VOC mass. For vehicles manufactured in 2004 and later, emissions of selected toxics are estimated through calculations based on models developed using data generated by EPAct program. These algorithms were developed to provide the capability to account for changes in toxic emissions attributable to changes in fuel properties, as specified by users.

Compounds emitted as constituents of exhaust but not included in the Complex or EPAct models were estimated using simpler approaches that do not explicitly account for changes in fuel properties.

For emissions through evaporative processes, simpler approaches were used. In some cases, these approaches account for two fuel properties, but typically do not account for fuel properties.

## 1.1 Air Toxics

Through MOVES, users can estimate inventories for all compounds emitted from highway vehicles that are also identified as air toxics in the National Emission Inventory (NEI) and National Air Toxics Assessment (NATA), and for which there are adequate data to develop emission estimates. This list of pollutants is provided in Table 1.1. These pollutants are organized into four categories:

1) Gaseous hydrocarbons
2) Polycyclic aromatic hydrocarbons (PAHs): This class is defined as hydrocarbons containing fused aromatic rings. These compounds can be found in the gaseous phase, particulate phase, or both, depending on properties of the compound, particle characteristics and atmospheric conditions
3) Dioxins and furans – polychlorinated organic compounds which are persistent and bioaccumulative

4) Metals

The pollutant "xylenes" represents the sum of emissions from three isomers of xylene: o-xylene, m-xylene, and p-xylene. MOVES also reports three forms of mercury: elemental gaseous, divalent gaseous (a reactive form) and particulate phase. Moreover, arsenic is reported as the total mass of all organic and inorganic arsenic compounds. However, emissions data for mobile sources all come from measurements of elemental arsenic mass.

**Table 1. Gaseous Hydrocarbons included in MOVES2014.**

| Pollutant | pollutantID | CAS Number |
|---|---|---|
| 1,3-Butadiene | 24 | 106990 |
| 2,2,4-Trimethylpentane | 40 | 540841 |
| n-Hexane | 55 | 110543 |
| Acetaldehyde | 26 | 75070 |
| Formaldehyde | 25 | 50-00-0 |
| Propionaldehyde | 58 | 123386 |
| Acrolein | 27 | 107028 |
| Methyl-Tertiary-Butyl Ether (MTBE) | 22 | 1634044 |
| Ethanol | 21 | 64175 |
| Ethyl Benzene | 52 | 100414 |
| Styrene | 60 | 100425 |
| Benzene | 20 | 71-43-2 |
| Toluene | 61 | 108883 |
| Xylenes | 62 | 1330207 |

**Table 2. Polycyclic Aromatic Hydrocarbons included in MOVES2014.**

| Pollutant | pollutantID | CAS Number |
|---|---|---|
| Acenaphthene | 41 | 83329 |
| Acenaphthylene | 42 | 208968 |
| Anthracene | 44 | 120127 |
| Benz(a)anthracene | 45 | 56553 |
| Benzo(a)pyrene | 46 | 50328 |
| Benzo(b)fluoranthene | 47 | 205992 |
| Benzo(g,h,i)perylene | 48 | 191242 |
| Benzo(k)fluoranthene | 49 | 207089 |
| Chrysene | 50 | 218019 |
| Dibenzo(a,h)anthracene | 51 | 53703 |
| Fluoranthene | 53 | 206440 |
| Fluorene | 54 | 86737 |
| Indeno(1,2,3,c,d)pyrene | 56 | 193395 |
| Naphthalene | 23 | 91203 |
| Phenanthrene | 57 | 85018 |
| Pyrene | 59 | 129000 |

**Table 3. Dioxins and Furans included in MOVES2014**

| Pollutant | pollutantID | CAS Number |
|---|---|---|
| 2,3,7,8-Tetrachlorodibenzo-p-Dioxin | 301 | 17466016 |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 302 | 40321764 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 303 | 39227286 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | 304 | 57653857 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | 305 | 19408743 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | 306 | 35822469 |
| Octachlorodibenzo-p-dioxin | 307 | 3268879 |
| 2,3,7,8-Tetrachlorodibenzofuran | 308 | 51207319 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 309 | 67562394 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 310 | 55673897 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 311 | 70648269 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 312 | 57117449 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 313 | 72918219 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 314 | 57117416 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 315 | 60851345 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 316 | 57117314 |
| Octachlorodibenzofuran | 317 | 39001020 |

**Table 4. Metals included in MOVES2014.**

| Pollutant | pollutantID | CAS Number |
|---|---|---|
| Mercury (elemental gaseous) | 201 | 200 |
| Mercury (divalent gaseous) | 202 | 201 |
| Mercury (particulate) | 203 | 202 |
| Arsenic compounds | 204 | 93 |
| Chromium (Cr3+) | 205 | 16065831 |
| Chromium (Cr6+) | 206 | 18540299 |
| Manganese | 207 | 7439965 |
| Nickel | 208 | 7440020 |

Toxics inputs for MOVES are not explicitly designed to vary by temperature. However, emissions estimated for the various hydrocarbon species do vary by temperature implicitly in that they are estimated in relation to inventories for VOC, or organic carbon (OC2.5) which are in turn estimated from total hydrocarbons (THC), which is adjusted by temperature for the start emissions process. However, for the running emissions process, THC emissions are not adjusted for temperature, and therefore most toxic emissions are also not temperature dependent, either implicitly or explicitly.

As metals are estimated directly through emission rates, these rates are assumed to be independent of operating mode and temperature. Data to account for impacts of these parameters are inadequate to model these effects in MOVES.

For 2004 and later vehicles, toxic to PM ratios differ for start versus running emissions for benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein and ethanol.

During model runs, emissions of toxic compounds, except for metals and dioxins/furans, are estimated as fractions of the emissions of volatile organic compounds (VOC), or in some cases organic carbon ($OC_{2.5}$). Metals and dioxins/furans are estimated using distance-specific emission rates. Emissions of VOC are themselves calculated from emissions of total hydrocarbons (THC). The available data and methods used to estimate toxic fractions vary for different groups of compounds. For some compounds, the toxic emissions are estimated using "complex" fractions, meaning that the fraction varies with levels of other fuel properties, such as ethanol, aromatics or RVP. For other sets of compounds, "simple" fractions are used, meaning that the fractions are constants and do not vary with other fuel properties. Note that the generalizations made here apply to evaporative as well as to exhaust emissions.

# 2 Exhaust Emissions

## 2.1 Light-Duty Vehicles (gasoline-powered): Model Year 2000 and Earlier

### 2.1.1 Gaseous Hydrocarbons

#### 2.1.1.1 Vehicles operating on Fuel blends containing 0-20% Ethanol

For three sets of compounds, Table 5 summarizes the methods used to estimate toxic fractions. The specific data and methods used for each are described in further detail below.

**Table 5. Calculation Methods for Gaseous hydrocarbons**

| Compound | Fraction Type | Basis for Estimation |
|---|---|---|
| Benzene | complex | Complex Model |
| 1,3-Butadiene | complex | Complex Model |
| Acetaldehyde | complex | Complex Model |
| Formaldehyde | complex | Complex Model |
| Methyl-tert-butyl ether | complex | Derived from Complex Model Databasse |
| 2,2,4-Trimethylpentane | simple | |
| Acrolein | simple | |
| Ethylbenzene | simple | |
| n-Hexane | simple | |
| Propionaldehyde | simple | |
| Styrene | simple | |
| Xylene(s) | simple | |
| Ethanol | simple | |

Use of Algorithms Developed for the Complex Model

For the first four compounds listed in Table 5, "complex" toxic fractions were estimated through application of algorithms developed for the Complex Model for Reformulated Gasoline.1 The equations are based on about 1,800 observations collected on vehicles equipped with three-way or three-way-plus-oxidation catalysts. The algorithms are applied by stratifying the light-duty gasoline fleet into ten Technology Groups and applying the algorithms individually to each group (this formulation is known as the unconsolidated Complex Model). The ten groups are formed as a combination of fuel system, catalyst type, Air injection (yes/no), EGR, and Normal / High emitter status. The first nine groups represent only normal emitting vehicles. The tenth group represents all "high emitters," regardless of technology. The algorithms are weighted together using model year specific weights obtained from MOBILE6.

The Complex Model algorithms are applied to running, start and extended idle emissions for gasoline fueled vehicles for all 2000 and earlier model years for these four pollutants. While MOBILE6 applied separate equations for older technologies not included in the Complex Model, such as vehicles without catalysts or vehicles with oxidation catalyst, these algorithms were not included in MOVES since these vehicles now comprise such a small portion of the fleet. For 1974 and earlier model years, 1975 weightings are used. In addition, while MOBILE6.2 relied on very limited data from heavy-duty gasoline vehicles, MOVES applies Complex Model algorithms to both light-duty and heavy-duty gasoline vehicles. The general structure of this section and all subsequent ones will be to describe and discuss the calculation algorithms in mathematical terms, show the underlying equation coefficients and present some limited results in graphical form for selected cases

#### 2.1.1.1.1 Overview of the Complex Model

The Complex model is so called because it was designed to model the "complex" behavior of selected emissions in relation to changes in a set of selected fuel properties, so as to facilitate the calculation of "complex fractions," as defined above.

The underlying dataset included measurements collected on sample of vehicles manufactured in MY1990 or earlier, and reflecting "Tier 0" standards, over a variety of gasoline formulations.

The complex model is composed of sets of models for each pollutant. The models are statistical models fit to sets of emissions measurements on a set of fuels with widely varying properties. For each pollutant, 10 models were fit, with each representing a specific combination of fuel-delivery, catalyst, air injection and emissions-control technology. The technology groups are described in Table 6. As an aggregate, these sets of models are referred to as the "unconsolidated complex model."

In fitting the complex models, the measurements for all fuel properties were "centered," meaning that the mean of all measurements for the property was subtracted from each individual measurement. This step aids in scaling the dataset so that each fuel property is centered on a mean of 0.0. Thus, if $\ln Y$ is the natural logarithm of a specific compound, such as acetaldehyde, the model is fit as shown in Equation 1, using terms for oxygenate, sulfur and E300 as examples.

$$\ln Y = \beta_0 + \beta_{\text{oxy}}\left(x_{\text{oxy},i} - \bar{x}_{\text{oxy}}\right) + \beta_{\text{S}}\left(x_{\text{S},i} - \bar{x}_{\text{S}}\right) + \cdots + \beta_{\text{E300}}\left(x_{\text{E300},i} - \bar{x}_{\text{E300}}\right) \qquad \textbf{Equation 1}$$

The mean values used for centering all values are presented in Table 7. Sets of coefficients for models by technology group, are presented for acetaldehyde, formaldehyde, benzene and 1,3-butadiene in Table 8 toTable 11.

**Table 6. Technology Groups included in the Complex Model.**

| Technology Group | Fuel System[1] | Catalyst[2] | Air Injection | Exhaust-gas Recirculation |
|---|---|---|---|---|
| 1 | PFI | 3-Way | No | Yes |
| 2 | PFI | 3-Way | No | No |
| 3 | TBI | 3-Way | No | Yes |
| 4 | PFI | 3-Way + Oxy | Yes | Yes |
| 5 | PFI | 3-Way | Yes | Yes |
| 6 | TBI | 3-Way | Yes | Yes |
| 7 | TBI | 3-Way + Oxy | Yes | Yes |
| 8 | TBI | 3-Way | No | No |
| 9 | carburetor | 3-Way + Oxy | Yes | Yes |
| 10 ("High Emitters") | ALL | ALL | ALL | ALL |

[1] Fuel System: PFI = port fuel Injection, TBI = throttle body injection.
[2] Catalyst type: "3-way" = three-way catalyst, "Oxy" = oxidation catalyst.

**Table 7. Mean Fuel-Property Values used for centering Terms in the Complex Models.**

| Property | Units | Mean Value |
|---|---|---|
| Sulfur | ppmW | 204.5779 |
| Aromatics | Vol. % | 28.26110 |
| Olefins | Vol. % | 7.318716 |
| Methyl-tertiary-butyl-ether (MTBE)[1] | Wt.% | 0.947240 |
| Ethyl-tertiary-butyl-ether (ETBE)[1] | Wt.% | 0.023203 |
| Ethanol[1] | Wt.% | 0.314352 |
| Tertiary-amyl-methyl-ether (TAME)[1] | Wt.% | 0.016443 |
| Oxygenate[2] | Wt.% | 1.774834 |
| RVP | Psi | 8.611478 |
| E200 | % | 46.72577 |
| E300 | % | 85.89620 |

[1] Species-specific values used in the aldehyde models.
[2] Aggregate value used for the butadiene and benzene models.

**Table 8. Complex Model Coefficients for Acetaldehyde, by Technology Group.**

| Technology Group | Fuel Property | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sulfur | Aromatics | Olefins | MTBE | ETBE | EtOH | TAME | RVP | E200 | E300 |
| 1 | 0.000263 | -0.05548 | - | -0.03646 | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 2 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 3 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 4 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 5 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 6 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 7 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 8 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 9 | 0.000263 | -0.05548 | - | - | 0.316467 | 0.249326 | - | - | - | -0.01216 |
| 10 | 0.000263 | -0.05548 | - | -0.05598 | 0.316467 | 0.249326 | - | - | - | -0.01216 |

**Table 9. Complex Model Coefficients for Formaldehyde, by Technology Group.**

| Technology Group | Fuel Property | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sulfur | Aromatics | Olefins | MTBE | ETBE | EtOH | TAME | RVP | E200 | E300 |
| 1 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 2 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 3 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 4 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 5 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 6 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 7 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 8 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 9 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |
| 10 | - | -0.00717 | - | 0.046213 | - | - | - | - | - | -0.01023 |

**Table 10. Complex Model Coefficients for Exhaust Benzene, by Technology Group.**

| Technology Group | Fuel Property | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Sulfur | Aromatics | Olefins | Oxygenate | Fuel Benzene | RVP | E200 | E300 |
| 1 | 0.001054 | 0.02588 | - | - | 0.222318 | - | -0.00948 | - |
| 2 | 0.000337 | 0.02588 | - | - | 0.222318 | - | - | - |
| 3 | 0.001187 | 0.02588 | - | - | 0.222318 | - | -0.00578 | - |
| 4 | 0.000337 | 0.02588 | - | - | 0.222318 | - | - | - |
| 5 | 0.000337 | 0.04859 | - | - | 0.222318 | - | - | - |
| 6 | 0.000337 | 0.02588 | - | - | 0.222318 | - | - | - |
| 7 | 0.000337 | 0.02588 | - | - | 0.222318 | - | - | - |
| 8 | - | | - | - | 0.222318 | - | - | - |
| 9 | -0.00195 | 0.02588 | - | - | 0.222318 | - | - | - |
| 10 | 0.000337 | 0.01188 | - | -0.09605 | 0.222318 | - | - | 0.011251 |

**Table 11. Complex Model Coefficients for 1,3-Butadiene, by Technology Group.**

| Technology Group | Fuel Property | | | | | |
|---|---|---|---|---|---|---|
| | Sulfur | Aromatics | Oxygenate | RVP | E200 | E300 |
| 1 | 0.000506 | -0.00401 | - | - | -0.00731 | -0.01678 |
| 2 | - | -0.00401 | - | - | -0.00731 | -0.01678 |
| 3 | 0.000544 | -0.00401 | - | - | -0.00731 | -0.01678 |
| 4 | -0.00041 | -0.00401 | - | - | -0.00731 | -0.01678 |
| 5 | - | -0.00401 | - | - | -0.00731 | -0.01678 |
| 6 | - | -0.00401 | - | - | -0.00731 | -0.01678 |
| 7 | - | -0.00401 | - | - | -0.00731 | -0.01678 |
| 8 | - | -0.00401 | - | - | -0.00731 | -0.01678 |
| 9 | - | -0.00401 | - | - | -0.00731 | -0.01678 |
| 10 | - | -0.00401 | -0.06077 | | -0.00731 | -0.00806 |

For each compound, the model equations as shown in Equation 1, are evaluated for a "base" and a "target" fuel. The base fuel represents a fuel(s) that corresponds to the emission rates used to calculate the emissions estimates, and which serves as a basis for fuel adjustments. The target fuel is represented by a set of properties from the MOVES database and which represents a fuel "in-use" in the geographic area(s) and season(s) being modeled. <see: signpost to fuel adj doc.>

Initially, an adjustment for the difference in emissions of the compound modeled on the target fuel relative to the base fuel is calculated. If the model, as shown in Equation 1, can be conveniently expressed, using matrix notation, as $\mathbf{X\beta_{target}}$ **and** $\mathbf{X\beta_{base}}$ for estimates on the target and base fuels, then the fractional difference in emissions is given by

$$f_{\text{adj}} = \frac{\exp\left(\mathbf{X}\boldsymbol{\beta}_{\text{target}}\right)}{\exp\left(\mathbf{X}\boldsymbol{\beta}_{\text{base}}\right)} - 1.0 \qquad \textbf{Equation 2}$$

The expression in Equation 2 is evaluated for target and base fuels for each of the ten technology groups. A mean value of the adjustment is then calculated as a weighted average of the values for the groups, with the weights representing the prevalence of each technology combination, as shown in Equation 3. Note that the weights applied to each technology group differ by vehicle age, as shown in Table 12. Note that the use of varying weights in applying the complex model in MOVES differs from the original application in which the weights were invariant.

$$f_{\text{adj,mean}} = \sum_{Group=1}^{10} w_{\text{Group}} f_{\text{adj,Group}} \quad ; \quad \sum_{Group=1}^{10} w_{Group} = 1.0 \qquad \textbf{Equation 3}$$

The mean adjustment calculated in Equation 3 is then applied to estimate the air-toxic emission on the target fuel absent any other adjustments ($E_{\text{relative,toxic}}$), while incorporating the effect on the emissions of the toxic due to the changes in fuel properties between the target and base fuels. If the target and base fuels were identical, the value of $f_{\text{adj,mean}}$ would be 0.0.

$$E_{\text{relative,toxic}} = E_{\text{base,toxic}}\left(1 + f_{\text{adj,mean}}\right) \qquad \text{Equation 4}$$

The values of $E_{\text{relative,toxic}}$ are the air toxic emission rates in units of grams per mile, and are a function of month of the year. They were taken directly from the Complex Model Spreadsheet "*CM Final.xls*". They are the base air-toxic emissions for the Base Fuel in the air toxics model. These base emissions were calculated from air toxic emission data from the Tier 0 vehicles in the original air toxic / fuel effects studies on which the Complex Model was based.

The calculations in Equation 1 to Equation 4 are also applied to VOC Emissions, ending with the generation of a value of $E_{\text{relative,VOC}}$. This value for VOC is then combined with that for each toxic to calculate a fraction used to estimate the total mass of emissions for each toxic during a model run. These fractions are denoted as $f_{\text{toxic}}$ and calculated as shown in Equation 5.

$$f_{\text{toxic}} = \frac{E_{\text{relative,toxic}}}{E_{\text{relative,VOC}}} \qquad \textbf{Equation 5}$$

As a final step, the mass emissions of each toxic during a model run are estimated by multiplying the mass of VOC emissions estimated by MOVES $I_{\text{VOC}}$ by the values of $f_{\text{toxic}}$.

$$I_{\text{toxic}} = f_{\text{toxic}} I_{\text{VOC}}$$ **Equation 6**

Note that the algorithm as described here is based on an assumption that within each technology group, the relations of air-toxic emissions to changes in fuel properties has remained stable as emissions standards transitioned from Tier 0 to Tier 1 levels.

**Table 12. Weights Applied to Complex Model coefficients for Technology Groups, by Age.[a]**

| Age | Technology Group | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* |
| 0 | 0.2360 | 0.2829 | 0.1806 | 0.1814 | 0.0290 | 0.0042 | 0.0556 | 0.0 | 0.0203 | 0.0100 |
| 1 | 0.2339 | 0.2803 | 0.1789 | 0.1797 | 0.0287 | 0.0042 | 0.0551 | 0.0 | 0.0201 | 0.0190 |
| 2 | 0.2315 | 0.2774 | 0.1771 | 0.1779 | 0.0284 | 0.0041 | 0.0546 | 0.0 | 0.0199 | 0.0290 |
| 3 | 0.2272 | 0.2723 | 0.1738 | 0.1746 | 0.0279 | 0.0041 | 0.0536 | 0.0 | 0.0196 | 0.0470 |
| 4 | 0.2229 | 0.2672 | 0.1706 | 0.1713 | 0.0274 | 0.0040 | 0.0525 | 0.0 | 0.0192 | 0.0650 |
| 5 | 0.2189 | 0.2623 | 0.1675 | 0.1682 | 0.0269 | 0.0039 | 0.0516 | 0.0 | 0.0188 | 0.0820 |
| 6 | 0.2148 | 0.2574 | 0.1644 | 0.1651 | 0.0264 | 0.0038 | 0.0506 | 0.0 | 0.0185 | 0.0990 |
| 7 | 0.2110 | 0.2529 | 0.1614 | 0.1621 | 0.0259 | 0.0038 | 0.0497 | 0.0 | 0.0182 | 0.1150 |
| 8 | 0.2072 | 0.2483 | 0.1585 | 0.1592 | 0.0254 | 0.0037 | 0.0488 | 0.0 | 0.0178 | 0.1310 |
| 9 | 0.2036 | 0.2440 | 0.1558 | 0.1565 | 0.0250 | 0.0036 | 0.0480 | 0.0 | 0.0175 | 0.1460 |
| 10 | 0.2000 | 0.2397 | 0.1530 | 0.1537 | 0.0246 | 0.0036 | 0.0471 | 0.0 | 0.0172 | 0.1610 |
| 11 | 0.1967 | 0.2357 | 0.1505 | 0.1512 | 0.0241 | 0.0035 | 0.0464 | 0.0 | 0.0169 | 0.1750 |
| 12 | 0.1934 | 0.2317 | 0.1479 | 0.1486 | 0.0237 | 0.0035 | 0.0456 | 0.0 | 0.0166 | 0.1890 |
| 13 | 0.1903 | 0.2280 | 0.1456 | 0.1462 | 0.0234 | 0.0034 | 0.0448 | 0.0 | 0.0164 | 0.2020 |
| 14 | 0.1872 | 0.2243 | 0.1432 | 0.1438 | 0.0230 | 0.0033 | 0.0441 | 0.0 | 0.0161 | 0.2150 |
| 15 | 0.1843 | 0.2209 | 0.1410 | 0.1416 | 0.0226 | 0.0033 | 0.0434 | 0.0 | 0.0159 | 0.2270 |
| 16 | 0.1814 | 0.2174 | 0.1388 | 0.1394 | 0.0223 | 0.0032 | 0.0428 | 0.0 | 0.0156 | 0.2390 |
| 17 | 0.1786 | 0.2140 | 0.1366 | 0.1372 | 0.0219 | 0.0032 | 0.0421 | 0.0 | 0.0154 | 0.2510 |
| 18 | 0.1760 | 0.2109 | 0.1346 | 0.1352 | 0.0216 | 0.0031 | 0.0415 | 0.0 | 0.0151 | 0.2620 |
| 19 | 0.1736 | 0.2080 | 0.1328 | 0.1334 | 0.0213 | 0.0031 | 0.0409 | 0.0 | 0.0149 | 0.2720 |
| 20 | 0.1712 | 0.2052 | 0.1310 | 0.1315 | 0.0210 | 0.0031 | 0.0403 | 0.0 | 0.0147 | 0.2820 |
| 21 | 0.1688 | 0.2023 | 0.1291 | 0.1297 | 0.0207 | 0.0030 | 0.0398 | 0.0 | 0.0145 | 0.2920 |
| 22 | 0.1664 | 0.1994 | 0.1273 | 0.1279 | 0.0204 | 0.0030 | 0.0392 | 0.0 | 0.0143 | 0.3020 |
| 23 | 0.1643 | 0.1969 | 0.1257 | 0.1262 | 0.0202 | 0.0029 | 0.0387 | 0.0 | 0.0141 | 0.3110 |
| 24 | 0.1624 | 0.1946 | 0.1242 | 0.1248 | 0.0199 | 0.0029 | 0.0383 | 0.0 | 0.0140 | 0.3190 |
| 25 | 0.1602 | 0.1920 | 0.1226 | 0.1231 | 0.0197 | 0.0029 | 0.0378 | 0.0 | 0.0138 | 0.3280 |
| 26 | 0.1602 | 0.1920 | 0.1226 | 0.1231 | 0.0197 | 0.0029 | 0.0378 | 0.0 | 0.0138 | 0.3280 |
| 27 | 0.1602 | 0.1920 | 0.1226 | 0.1231 | 0.0197 | 0.0029 | 0.0378 | 0.0 | 0.0138 | 0.3280 |
| 28 | 0.1602 | 0.1920 | 0.1226 | 0.1231 | 0.0197 | 0.0029 | 0.0378 | 0.0 | 0.0138 | 0.3280 |
| 29 | 0.1602 | 0.1920 | 0.1226 | 0.1231 | 0.0197 | 0.0029 | 0.0378 | 0.0 | 0.0138 | 0.3280 |
| 30 | 0.1602 | 0.1920 | 0.1226 | 0.1231 | 0.0197 | 0.0029 | 0.0378 | 0.0 | 0.0138 | 0.3280 |

a. Note that in the MOVES database, these weights are stored in the table FuelModelWtFactor.

#### 2.1.1.1.2 Estimating Emissions of Methyl-tertiary-butyl-ether (MTBE)

As of calendar year 2008, MTBE (pollutantID = 22) has been almost completely phased-out of the fuel supply of the United States due to concerns related to contamination of ground water. Thus, its inventory levels in the MOVES output from default inputs should be very small if not zero in future years. It is present in the MOVES model as mostly a legacy pollutant for calendar years 1990 and 1999 – 2005. However, the MTBE fuel volume is a user input, and MOVES has the capability to calculate MTBE emissions for any calendar year.

For MTBE, a fuel-effects model based on the Complex Model database and applied in MOBILE6.2 was used.[2,3] This model is based on algorithms from underlying data of nearly 900 observations. However, instead of using model equations directly, MOBILE6.2 was run at different fuel MTBE volumes ($V_{MTBE}$). Using the results, MTBE fractions were calculated and related to MTBE levels using simple regression. A quadratic equation fixed at the origin was found to give the best fit. This curve was then used in MOVES. The equation is shown in Equation 7 and the parameters are shown in Table 1. The same equation is used for both start and running processes and is shown in Equation 7.

$$f_{MTBE} = AV_{MTBE} + BV_{MTBE}^2 \qquad \textbf{Equation 7}$$

The coefficients $A$ and $B$ take the values shown in Table 13. As with the other toxic emissions, the fraction $f_{MTBE}$ is multiplied by the mass of VOC to estimate MTBE emissions, as shown in Equation 6.

**Table 13. Exhaust Calculation Coefficients for MTBE (see Equation 7 ).**

| Pollutant Process | polProcessID | A (coeffA) | B (coeffB) |
|---|---|---|---|
| Running Exhaust | 2201 | 0.00007809 | 0.00007537 |
| Start Exhaust | 2202 | 0.00007809 | 0.0007809 |

It should be noted that the sulfur effects terms in the equations were not included; rather, sulfur effects on toxic emissions were assumed to be proportional to the sulfur impacts on total VOC estimated by MOVES.

Data were not available to develop algorithms for ETBE and TAME blends; thus, the algorithms for ethanol oxygenated gasoline were used for ETBE blends, and the algorithms for MTBE oxygenated gasoline were used for MTBE blends.

#### 2.1.1.1.3 Simple Fractions

Table 14 lists toxic fractions for a set of additional hydrocarbons designed to represent toxic emissions for several fuel blends containing different oxygenates. For gasoline fuels containing 0 and 10% ethanol (E0 and E10), fractions were developed by Sierra Research using speciation profiles estimated from EPA's SPECIATE 4.2 database. [4] The fractions for E10 are also used to represent blends in which the oxygenate is ethyl-tertiary-butyl-ether (ETBE) at levels of 5 vol.% or greater.

For blends containing methyl-tertiary-butyl ether (MTBE), however, fractions were adopted from National County Database for the National Mobile Inventory Model (NMIM). The fractions used in NMIM were derived for the 1999 National Emission Inventory (NEI) for

HAPS, version 3, and summarized in Volume 1, Appendix D, Table 1 of the documentation. These ratios were based on older speciation profiles than the E0 and E10 data. One set of fractions represents winter fuels containing MTBE at 12 vol. % or more , or tertiary-amyl-methyl-ester (TAME) at levels of 13% or more (winter). A second set represents reformulated gasoline fuels containing MTBE at levels between 5.0 and 13.0 vol.% or TAME at levels between 5.0 and 13.0 vol.% (RFG). Separate ratios are used for each of the following four categories of gasoline blends:

Emissions of ethanol in exhaust are estimated for gasoline blends containing ethanol at levels of 0 to 10 vol.%. For vehicles running on 10% ethanol, ethanol was estimated to comprise 2.39% of exhaust VOC. This estimate is based on results measured on nine vehicles in four test programs.[5, 6, 7, 8] The fraction of ethanol in exhaust VOC for blends containing 5.0% and 8.0% ethanol is estimated by interpolating linearly between the fractions for 0.0% and 10.0% ethanol. No data exist for 2000 and earlier vehicles running on E15 or E20. Thus, toxics ratios for 2001 and later vehicles are used.

**Table 14. Toxic Fractions for Selected Air Toxics, Representing Gasoline and Ethanol Blends ("Gasohol").**

| Compound | pollutantID | Fuel Blend (by Ethanol Level) | |
|---|---|---|---|
| | | 0% (E0) | 10% (E10) |
| 2,2,4-Trimethylpentane | 40 | 0.01823 | 0.01849 |
| Acrolein | | 0.0006 | 0.0006 |
| Ethyl Benzene | 41 | 0.02147 | 0.01932 |
| n-Hexane | 42 | 0.01570 | 0.01593 |
| Propionaldehyde | 43 | 0.00086 | 0.00086 |
| Styrene | 44 | 0.00108 | 0.00097 |
| Toluene | 45 | 0.09619 | 0.08657 |
| Xylene | 46 | 0.07814 | 0.07032 |
| Ethanol | | | 0.0239 |

**Table 15. Toxic Fractions for Selected Air Toxics , Representing Gasolines containing MTBE.**

| Compound | pollutantID | MTBE | |
|---|---|---|---|
| | | Winter | RFG |
| 2,2,4-Trimethylpentane | 40 | 0.04327 | 0.04327 |
| Acrolein | | 0.0006 | 0.0006 |
| Ethyl Benzene | 41 | 0.01398 | 0.01484 |
| n-Hexane | 42 | 0.00861 | 0.00888 |
| Propionaldehyde | 43 | 0.00073 | 0.00073 |
| Styrene | 44 | 0.00328 | 0.00340 |
| Toluene | 45 | 0.09873 | 0.10494 |
| Xylene | 46 | 0.05557 | 0.05910 |

In the MOVES database, these inputs are stored in the table "minorHAPratio." In the label, the term "HAP" refers to "hazardous air pollutant." A description of the table is provided in Table 16.

**Table 16. Description of the Database Table "minorHAPRatio."**

| Field | Description | RelevantValues |
|---|---|---|
| polProcessID | Identifies the pollutant (1st two digits and Emissions Process (last two digits). | Pollutants are identified in the table above; Relevant processes include:<br>"Running Exhaust" (processID = 1)<br>"Start Exhaust" (processID = 2) |
| fuelTypeID | Identifies broad classes of fuels, e.g., "gasoline." "diesel." | 1 = "Gasoline"<br>2 = "Diesel"<br>5 = "Ethanol" |
| fuelSubTypeID | Identifies specific fuel classes within the fuelTypeID | 10 = "Conventional Gasoline"<br>11 = "Reformulated Gasoline"<br>12 = "Gasohol (E10)"<br>13 = "Gasohol (E8)"<br>14 = "Gasohol (E5)"<br>15 = "Gasohol (E15)"<br>18 = "Gasohol (E20)"<br>51 = "Ethanol (E85)"<br>52 = "Ethanol (E70)" |
| modelYearGroupID | Identifies a set of model years covered by a specific value of atRatio. | 1960-1970<br>1971-1977<br>1978-1995<br>1996-2003<br>2004-2050 |
| atRatio | Fraction, or "ratio" of the toxic relative to total VOC. | |
| atRatioCV | "Coefficient of Variation of the Mean" or "relative standard error" of the atRatio. | |
| dataSourceID | Indicates source data and methods used to estimate atRAtio. | |

#### 2.1.1.2 Vehicles operating on Fuel blends containing 70-100% Ethanol

Toxic fractions for vehicles running on fuels containing 70-100% ethanol were derived from measurements on four flexible fuel vehicles, conducted during the EPAct program (Phase 3). The vehicles were tested on a single E85 gasoline. Since no tests were done on an E70 blend, more typically used in winter and blends above E85, the same toxic to VOC ratios are used for blends containing 70-100% ethanol.

Of the fractions shown in Table 17 , those with pollutantID from 40-46 are stored in the database table "minorHAPRatio" (see Table 16, page 19). Those with pollutantID from 20-27 are stored in the database table "ATRatioNonGas" (see Table 18).

**Table 17. Toxic Fractions for vehicles running on E70/E85**

| Pollutant (pollutantID) | Toxic Fraction |
|---|---|
| 2,2,4-Trimethylpentane (40) | 0.0078 |
| Ethyl Benzene (41) | 0.0055 |
| Hexane (42) | 0.0045 |
| Propionaldehyde (43) | 0.0025 |
| Styrene (44) | 0.0003 |
| Toluene (45) | 0.0177 |
| Xylene(s) (46) | 0.0185 |
| 1,3-Butadiene (24) | 0.0011 |
| Acetaldehyde (26) | 0.1644 |
| Acrolein (27) | 0.0010 |
| Benzene (20) | 0.0170 |
| Ethanol (21) | 0.3724 |
| Formaldehyde (25) | 0.0291 |

**Table 18. Description of the Database Table "ATRatioNonGas," as Applied to Light-Duty Vehicles.**

| Field | Description | RelevantValues |
|---|---|---|
| polProcessID | Identifies the pollutant (1st two digits and Emissions Process (last two digits). | Pollutants are identified in the table above; Relevant processes include:<br>"Running Exhaust" (processID = 1)<br>"Start Exhaust" (processID = 2)<br>"Extended Idle Exhaust" (processID = 90)<br>"Auxiliary Power Exhaust" (processID = 91) |
| sourceTypeID | Identifies types of vehicles, classified by function | Motorcycle (11)<br>Passenger Car (21)<br>Passenger Truck (31)<br>Light Commercial Truck (32) |
| fuelSubTypeID | Identifies specific fuel classes within the fuelTypeID | 51 = "Ethanol (E85)"<br>52 = "Ethanol (E70)" |
| modelYearGroupID | Identifies a set of model years covered by a specific value of atRatio. | |
| atRatio | Fraction, or "ratio" of the toxic relative to total VOC. | |
| atRatioCV | "Coefficient of Variation of the Mean" or "relative standard error" of the atRatio. | |
| dataSourceID | Indicates source data and methods used to estimate atRAtio. | |

### 2.1.2 Polycyclic Aromatic Hydrocarbons (PAH)

Emissions of PAH are estimated through the use of fractions in a manner similar to that used for gaseous hydrocarbons as described in the previous section. However, for PAH, the process is complicated by the fact that these compounds are emitted in both the gaseous and particulate phases. Accordingly, emissions in the gaseous phase are estimated as fractions of total VOC, and emissions in the particulate phase as fractions of organic carbon (less than 2.5 microns in diameter, $OC_{2.5}$). as ratios to the VOC and $OC_{2.5}$ exhaust and crankcase emissions.

The fractions are estimated from a set of 99 vehicles measured in the Kansas City Light-duty Vehicle Emissions Study (KCVES)[9] . These vehicles were included in a subsample selected for chemical speciation. For each vehicle, emissions of total hydrocarbons (THC) and PM2.5 were measured. Fleet-average fractions of PAH/THC and PAH/PM2.5 were calculated with each sample weighted according to total emissions, vehicle-miles traveled (VMT), and an equal weight between summer and winter.[10] We used the THC measurements to represent VOC emission rates, and we corrected the PAH/PM2.5 by the fraction of OC measured in the start (42.6%) and running emission processes (55.7%) to produce PAH/$OC_{2.5}$ emission rates[10]. At this stage in the analysis, the PAHs are not allocated to gas or particle phase. The next paragraphs discuss how these fractions were then adjusted to allocate the PAHs to the gaseous or particle phases.

The true gas-particle partitioning of PAHs emissions in the atmosphere depends on particle and gas concentrations, exhaust temperature and other factors. However, in preparing inputs for MOVES, we developed one set of allocation factors for gasoline sources and another for diesel sources under all conditions in order to streamline data processing, and to be consistent with the PAH data as measured in test programs. The sampling conditions set forth in EPA regulations for particulate and hydrocarbons differ for light-duty and heavy-duty vehicles which impacts the phase partitioning of the PAH emissions.

The allocations of PAH into gaseous and particulate phases are based on measurement samples analyzed by Desert Research Institute (DRI) on a subset of vehicles in the KCVES that were measured with dilution air at both low and high temperatures.[11] One of the purposes of this follow-up study was to examine the impact of sampling conditions on PAH emission measurements. DRI measured PAH species with Teflon-impregnated glass filters (TIGF) and backup glass cartridges with Amberlite XAD-4 adsorbent resins over the LA-92 cycle. Relative concentrations of individual PAH were measured on the TIGF and the XAD with dilution temperatures of 20°C and 47°C for four composite samples of vehicles. Table 19 reports the TIGF/XAD phase allocation factors measured at 47°C (which was the measurement temperature for the Kansas City Light-duty Vehicle Emissions Study), for the composite class referred to as the 'medium-emitters.' This class contained a 1989 Camry and 1992 Voyager. In MOVES2014, we used the PAH phase-partitioning of this sample to estimate the relative gas and particle portioning of all gasoline-source emissions. Note that the PAH species partitioning was heavily dependent on molar mass (molecular weight); compounds with the smallest molar masses (e.g., naphthalene) were measured almost entirely in the gaseous phase, whereas compounds with the highest molar masses were measured almost entirely in the particulate phase (e.g. dibenzo(a,h)anthracene).

**Table 19. Gasoline PAH phase allocation factors.**

| PAH species | Molar Mass (g/mol) | Phase Fraction | |
|---|---|---|---|
| | | Gaseous | Particulate |
| Naphthalene | 128 | 0.9996 | 0.0004 |
| Acenaphthylene | 152 | 0.9985 | 0.0015 |
| Acenapthene | 154 | 1.0000 | 0.0000 |
| Fluorene | 166 | 1.0000 | 0.0000 |
| Anthracene | 178 | 0.9915 | 0.0085 |
| Phenanthrene | 178 | 0.9953 | 0.0047 |
| Fluoranthene | 202 | 0.9822 | 0.0178 |
| Pyrene | 202 | 0.9831 | 0.0169 |
| Benz(a)anthracene | 228 | 0.6721 | 0.3279 |
| Chrysene | 228 | 0.7307 | 0.2693 |
| Benzo(a)pyrene | 252 | 0.0426 | 0.9574 |
| Benzo(b)fluoranthene | 252 | 0.5546 | 0.4454 |
| Benzo(k)fluoranthene | 252 | 0.5546 | 0.4454 |
| Benzo(g,h,i)perylene | 276 | 0.0000 | 1.0000 |
| Indeno(1,2,3-cd)pyrene | 276 | 0.0000 | 1.0000 |
| Dibenzo(a,h)anthracene | 278 | 0.0000 | 1.0000 |

We multiplied the phase allocation factors in Table 19 by the PAH/VOC and PAH/OC2.5 ratios from the KCVES to obtain the ratios in Table 20 used in MOVES2014. These ratios are applied to all gasoline fuels with ethanol content less than 20%. In the MOVES database, these fractions are stored in two tables. Fractions for the gaseous phase are stored in the table "pahgasratio" and those for the particulate phase are stored in the table "pahparticleratio." The two tables have the same structure which is presented in Table 20.

**Table 20. Toxic Fractions for PAH Compounds, in Gaseous and Particulate Phases.**

| PAH species | pollutantID | CAS | Fraction (PAH/VOC) | Fraction ($PAH/OC_{2.5}$) | |
|---|---|---|---|---|---|
| | | | | Start | Running |
| Naphthalene | 23 | 91203 | 1.77E-03 | 1.68E-04 | 1.29E-04 |
| Acenaphthylene | 42 | 208968 | 1.55E-04 | 5.01E-05 | 3.83E-05 |
| Acenaphthene | 41 | 83329 | 3.41E-05 | 0E+00 | 0E+00 |
| Fluorene | 54 | 86737 | 6.91E-05 | 0E+00 | 0E+00 |
| Anthracene | 44 | 120127 | 2.86E-05 | 5.19E-05 | 3.97E-05 |
| Phenanthrene | 57 | 85018 | 1.83E-04 | 1.81E-04 | 1.39E-04 |
| Fluoranthene | 53 | 206440 | 4.79E-05 | 1.83E-04 | 1.40E-04 |
| Pyrene | 59 | 129000 | 5.47E-05 | 1.98E-04 | 1.52E-04 |
| Benz(a)anthracene | 45 | 56553 | 4.62E-06 | 4.76E-04 | 3.64E-04 |
| Chrysene | 50 | 218019 | 5.17E-06 | 4.02E-04 | 3.08E-04 |
| Benzo(a)pyrene | 46 | 50328 | 2.52E-07 | 1.19E-03 | 9.13E-04 |
| Benzo(b)fluoranthene | 47 | 205992 | 3.43E-06 | 5.81E-04 | 4.45E-04 |
| Benzo(k)fluoranthene | 49 | 207089 | 3.43E-06 | 5.81E-04 | 4.45E-04 |
| Benzo(g,h,i)perylene | 48 | 191242 | 0E+00 | 3.23E-03 | 2.47E-03 |
| Indeno(1,2,3,c,d)pyrene | 56 | 193395 | 0E+00 | 1.21E-03 | 9.28E-04 |
| Dibenzo(a,h)anthracene | 51 | 53703 | 0E+00 | 2.79E-05 | 2.13E-05 |

### 2.1.3 Metals

Emissions of metals in vehicle exhaust result from trace-level contamination of fuel and engine oil, as well as attrition from engine, exhaust system, and emission control components. MOVES estimates metal emissions for five metal species, including two valence forms of chromium and 3 forms of mercury, using emission rates expressed on a distance-specific basis (g/mile). Emission rates for chromium, magnesium and nickel are developed from the 99 vehicles sampled for chemical composition in the KCVES. The average g/mile rates are calculated by averaging the metal measured on bag 2 of the LA-92, with a weighted-average computed to be representative of the on-road vehicle fleet.[10] We used bag 2, so the emission rates for these metals are consistent with the $PM_{2.5}$ emission profile for running gasoline discussed in the MOVES2014 TOG and PM Speciation Report. $PM_{2.5}$ emissions are much more enriched in metals during hot-stabilized running conditions than during start emissions. We compared the g/mi emission rates from bag 2 to the average of the entire LA-92; the difference in the bag 2 emission rates from the average of the LA-92 is 38%, -2% and -16% for manganese, chromium, and nickel. Thus, in using bag 2 emission rates for metal emission rates we are both consistent with the $PM_{2.5}$ speciation running emission profile, and conservative when compared to using the cycle average.

Eighteen percent of chromium was assumed to be hexavalent, based on combustion data from stationary combustion turbines burning diesel fuel.[12]). Emission factors for arsenic were developed from data reported for tunnel tests.[13] Emission factors for mercury were obtained from

a 2005 EPA test program. Documentation describing development of these emission factors can be found in Appendix A. Metal emission rates do not vary among fuel types. Rates are presented in Table 21. These values are stored in the database table "metalEmissionRate," which is described in Table 22.

**Table 21. Metal emission Rates for gasoline vehicles and trucks.**

| Pollutant | Emission Rate (g/mi) |
|---|---|
| Chromium, hexavalent (6+) | 7.32E-07 |
| Chromium, trivalent (3+) | 3.34E-06 |
| Manganese | 1.33E-06 |
| Nickel | 1.50E-06 |
| Mercury, Elemental (Gaseous Phase) | 1.10E-07 |
| Mercury, Reactive (Gaseous Phase) | 9.90E-09 |
| Mercury, Particulate Phase | 4.00E-10 |
| Arsenic | 2.30E-06 |
| | |

**Table 22. Description of the Database Table "metalEmissionRate."**

| Field | Description | RelevantValues |
|---|---|---|
| polProcessID | Identifies the pollutant (1st two digits and Emissions Process (last two digits). | Pollutants are identified in the table above; Relevant processes include:<br>1 = "Running Exhaust" |
| fuelTypeID | Identifies broad classes of fuels, e.g., "gasoline." "diesel." | 1 = "Gasoline"<br>2 = "Diesel"<br>5 = "Ethanol" |
| sourceTypeID | Identifies vehicle types, classified by function | Motorcycles (11)<br>Passenger Cars (21)<br>Passenger Trucks (31)<br>Light Commercial Trucks (32) |
| modelYearGroupID | Identifies a set of model years covered by a specific value of atRatio. | 1960-1970<br>1971-1977<br>1978-1995<br>1996-2006<br>2007-2050 |
| Units | Identifies units in which the meanBaseRate is expressed. | grams/mile |
| meanBaseRate | Average emission rate for a combination of process, fuel type, sourceType and modelYearGroup. | |
| meanBaseRateCV | "Coefficient of Variation of the Mean" or "relative standard error" of the meanBaseRate. | |
| dataSourceID | Indicates source data and methods used to estimate atRAtio. | |

### 2.1.4 Dioxins and Furans

MOVES estimates emissions for 17 dioxin and furan congeners in mg/mi toxic equivalents (TEQs). The emissions are estimated using distance-specific emission rates multiplied by World Health Organization 2005 toxic equivalency factors (TEFs; Table 23).[14] Thus, emission rates for the various congeners are expressed as TEQs of the most toxic congener (2,3,7,8 TCDD)(Table 23)These emission factors were obtained from a tunnel study and used in EPA's dioxin assessment.[15,16] They do not vary among fuel types. The rates are stored in the database table "dioxinEmissionRate," which is described in Table 25.

**Table 23. Dioxin/Furan Toxic Equivalency Factors (World Health Organization)**

| Pollutant | TEF |
|---|---|
| 2,3,7,8-TCDD TEQ | 1.0 |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 1.0 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 0.10 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | 0.10 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | 0.10 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | 0.01 |
| Octachlorodibenzo-p-dioxin | 0.0003 |
| 2,3,7,8-Tetrachlorodibenzofuran | 0.10 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 0.030 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 0.3 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 0.1 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 0.01 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 0.01 |
| Octachlorodibenzofuran | 0.0003 |

**Table 24. Dioxin emission Rates for gasoline vehicles.**

| Pollutant | TEQ (mg/mi) |
|---|---|
| 2,3,7,8-Tetrachlorodibenzo-p-Dioxion (TCDD) | 8.27E-10 |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 3.70E-10 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 3.87E-11 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | 7.92E-11 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | 4.93E-11 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | 5.95E-11 |
| Octachlorodibenzo-p-dioxin | 1.41E-11 |
| 2,3,7,8-Tetrachlorodibenzofuran | 2.76E-10 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 3.96E11 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 2.90E-10 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 1.09E-10 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 1.16E-10 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 3.17E-11 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 1.36E-10 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 1.21E-10 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 3.87E-12 |
| Octachlorodibenzofuran | 4.11E-12 |

**Table 25. Description of the Database Table "DioxinEmissionRate."**

| Field | Description | RelevantValues |
|---|---|---|
| polProcessID | Identifies the pollutant (1st two digits and Emissions Process (last two digits). | Pollutants are identified in the table above; Relevant processes include:<br>1 = "Running Exhaust" |
| fuelTypeID | Identifies broad classes of fuels, e.g., "gasoline." "diesel." | 1 = "Gasoline"<br>2 = "Diesel"<br>5 = "Ethanol" |
| modelYearGroupID | Identifies a set of model years covered by a specific value of atRatio. | 1960-2050<br>1960-2006<br>2007-2009<br>2010-2050 |
| Units | Identifies units in which the meanBaseRate is expressed. | grams/mile |
| meanBaseRate | Average emission rate for a combination of process, fuel type, sourceType and modelYearGroup. | |
| meanBaseRateCV | "Coefficient of Variation of the Mean" or "relative standard error" of the meanBaseRate. | |
| dataSourceID | Indicates source data and methods used to estimate atRAtio. | |

## 2.2 Light-Duty Vehicles (gasoline powered): Model-year 2001 and later

For vehicles manufactured in MY2001 and later, and certified to NLEV or Tier 2 standards, recently collected data was available. As before, toxic emissions are estimated as fractions of VOC, with toxic fractions for various compounds estimated using differing datasets and methods. For some compounds and processes, models were developed to estimate "complex" fractions (responding to fuel properties), whereas for others, "simple" fractions were estimated (not responding to fuel properties). An additional feature for these fractions is that in some cases, different fractions could be estimated for the start and running emission processes. For the compounds included in MOVES, data sources and estimation methods are summarized in Table 26.

**Table 26. Data Sources and Estimation Methods Used in Estimation of Toxic Fractions for Gaseous Hydrocarbons.**

| Compound | Process | Fraction Type | Basis for Estimation |
|---|---|---|---|
| Acetaldehyde | Start | complex | application of EPAct models |
| | Running | complex | application of EPAct models1 |
| Formaldehyde | Start | complex | application of EPAct models |
| | Running | complex | application of EPAct models |
| Acrolein | Start | complex | application of EPAct models |
| | Running | simple | Data from EPAct Project (Phase 3)[2] |
| Ethanol | Start | complex | application of EPAct models |
| | Running | complex | application of EPAct models |
| Benzene | Start | complex | application of EPAct models |
| | Running | simple | Data from EPAct Project (Phase 3) |
| 1,3-Butadiene | Start | complex | application of EPAct models |
| | Running | simple | Data from EPAct Project (Phase 3) |
| 2,2,4-Trimethylpentane | Both | simple | Speciation Profile (EPAct Phase 1)[3] |
| Ethylbenzene | Both | simple | Speciation Profile (EPAct Phase 1) |
| N-Hexane | Both | simple | Speciation Profile (EPAct Phase 1) |
| Propionaldehyde | Both | simple | Speciation Profile (EPAct Phase 1) |
| Styrene | Both | simple | Speciation Profile (EPAct Phase 1) |
| Xylene(s) | Both | simple | Speciation Profile (EPAct Phase 1) |

[1] Derived from models fit to data from EPAct Phase 3 Results.
[2] Derived from data collected in EPAct Phase 3.
[3] Derived from data collected in EPAct Phase 1.

### 2.2.1 Application of the Results of the EPAct Program

An important function of mobile source air pollution inventory models, including MOBILE6 and MOVES, is to account for the effects of different fuel properties on exhaust emissions. For this purpose, MOBILE6 relied on previously existing fuel- effect models, known as the "EPA Predictive Model" and the "Complex Model". While these models are still in use in MOVES to estimate fuel effects for vehicles manufactured prior to model year 2001 their applicability to vehicles employing more recent engine and emission control technologies has been questioned. Since the initiation of the MOVES project, it has become clear that an updated fuel-effects model representing Tier-2 certified vehicles would be needed. In addition, Congress provided for the development of such a model in the 2005 Energy Policy Act (EPAct).

To meet this goal, EPA entered a partnership with the Department of Energy (DOE) and the Coordinating Research Council (CRC) to undertake the largest fuels research program conducted since the Auto/Oil program in the early 1990's, aimed specifically at understanding the effects of fuel property changes on exhaust emissions on recently manufactured Tier 2 vehicles. The

resulting research program was dubbed the "EPAct/V2/E-89" program (or "EPAct" for short), with the three components of the label denoting the designation given to the study by the EPA, DOE and CRC, respectively.

The program was conducted in three phases. Phases 1 and 2 were pilot efforts involving measurements on 19 light-duty cars and trucks on three fuels, at two temperatures. These preliminary efforts laid the groundwork for design of a full-scale research program, designated as Phase 3.

Initiated in March 2009, the Phase 3 program involved measurement of exhaust emissions from fifteen high-sales-volume Tier-2 certified vehicles (model year 2008), using twenty-seven test fuels spanning wide ranges of five fuel properties (ethanol, aromatics, vapor pressure, and two distillation parameters: T50 and T90). The properties of the test fuels were not assigned to represent in-use fuels, but rather to allow development of statistical models that would enable estimation of relative differences in emissions across the ranges of fuel properties expected in the U.S. fuel pool. A fuel matrix was designed for Phase 3 to span the ranges of the five selected properties seen in commercially available fuels.

An initial sample of 19 test vehicles was chosen with the intent of representing the latest-technology light-duty vehicles being sold at the time the program was launched (model year 2008). The 19 vehicles represented a high fraction of vehicle sales at the time. The sample was to conform on average to Tier-2 Bin-5 exhaust levels and employ a variety of emission control technologies, to be achieved by including a range of vehicle sizes and manufacturers. Due to budget constraints, the sample was reduced from 19 to 15 vehicles for the Phase-3 program.

The LA92 test cycle was used with emissions measured over three phases analogous to those in the Federal Test Procedure (FTP), at an ambient temperature of 75°F. In MOVES, the EPAct results are applied at temperatures higher and lower than this level, under an assumption that effects for fuels and temperature are independent and multiplicative.

Emissions measured include carbon dioxide ($CO_2$), carbon monoxide (CO), total hydrocarbons (THC), methane (CH4), oxides of nitrogen ($NO_x$), and particulate matter ($PM_{2.5}$). In addition, hydrocarbons were speciated for subsets of vehicles and fuels, allowing calculation of derived parameters such as non-methane organic gases (NMOG) and non-methane hydrocarbons (NMHC). Speciation also allowed independent analyses of selected toxics including acetaldehyde, formaldehyde, acrolein, benzene and 1,3-butadiene.

Phase 3 data collection was completed in June 2010. Dataset construction and analysis was conducted between January 2010 and November 2012. This process involved ongoing collaboration among EPA staff, DOE staff and contractors, and CRC representatives. Following the completion of data collection, construction of the dataset involved intensive evaluation and quality assurance. The analysis involved several iterations between analysis and additional physical and chemical review of the data. Successive rounds of statistical modeling were applied to the data, to achieve several goals, including identification of potential candidate models, identification and review of outlying observations, identification and review of subsets of data from influential vehicles, and identification of models including subsets of terms that best explain the results obtained.

The EPAct exhaust research program and analysis are extensively documented in the "EPAct Test Program Report[17]" and "EPAct Analysis Report.[18]"

This document describes how the data and statistical models developed during the EPAct study are applied in the MOVES model (MOVES2014).

#### 2.2.1.1 Standardizing Fuel Properties

In applying the EPAct models to estimate emissions effects for a given fuel, it is necessary to first "center" and "scale" the properties for the fuel, also known as "standardization." This process simply involves first "centering" the measured fuel properties by subtracting the given value from the sample mean, and then "scaling" by then dividing the centered values by their respective standard deviations, as shown in Equation 8. Note that the means and standard deviations are calculated from the fuel set used for the program (see Table 26, page 28).The result is a "Z score," representing a "standard normal distribution" with a mean of 0.0 and a standard deviation of 1.0.

$$Z_i = \frac{x_i - \bar{x}}{s} \qquad \textbf{Equation 8}$$

For the linear effects in the model, standardization is performed using the values of each fuel property, each in their respective scales (vol. %, psi, °F.). Using aromatics as an example, the standardization of the linear term is shown in Equation 9.

$$Z_{\text{arom}} = \frac{x_{\text{arom}} - \bar{x}_{\text{arom}}}{s_{\text{arom}}} \qquad \textbf{Equation 9}$$

For second-order terms, however, the process is not performed on the values of the fuel properties themselves. Rather, quadratic and interaction terms are constructed from the Z scores for the linear terms, and the process is repeated. Using the quadratic term for ethanol as an example (etOH×etOH), the standardized value, denoted by $ZZ_{\text{etOH}\times\text{etOH}}$, is calculated as shown in Equation 10, where $m_{Z_{\text{etOH}}Z_{\text{etOH}}}$ and $s_{Z_{\text{etOH}}Z_{\text{etOH}}}$ are the mean and standard deviation of the quadratic term constructed from the Z score for the linear effect.

$$ZZ_{\text{etOH}\times\text{etOH}} = \frac{Z_{\text{etOH}}Z_{\text{etOH}} - m_{Z_{\text{etOH}}Z_{\text{etOH}}}}{s_{Z_{\text{etOH}}Z_{\text{etOH}}}} \qquad \textbf{Equation 10}$$

Standardized terms for interaction effects are constructed similarly. For example, Equation 11 shows the standardization of an interaction term between ethanol and aromatics.

$$ZZ_{\text{etOH}\times\text{eArom}} = \frac{Z_{\text{etOH}} Z_{\text{Arom}} - m_{Z_{\text{etOH}} Z_{\text{Arom}}}}{s_{Z_{\text{etOH}} Z_{\text{Arom}}}} \qquad \textbf{Equation 11}$$

### 2.2.1.2 Application of EPAct Statistical Models

The approach for toxics estimates the emissions of the toxic as a fraction of emissions for VOC, on the same fuel. So, to model the behavior of the fraction with respect to changes in fuel properties, it was necessary to develop models for NMOG and Ethane, as well as the toxics, because MOVES estimates VOC as NMOG minus Ethane.

The models generated using EPAct results allow estimation of emissions effects related to five fuel properties: ethanol content (vol.%), aromatics content (vol.%), RVP (psi), T50 (°F) and T90 (°F), as well as selected interaction terms among these five parameters. The statistical models generated from the EPAct exhaust data follow the general structure shown in Equation 12 below. In this example equation, $\beta$ denotes a model coefficient, $Z_{\text{etOH}}$ denotes a "standardized" fuel term for this property, and $Z_{\text{etOH}\times\text{Arom}}$ denotes a "standardized" etOH×Arom interaction term.[b] For simplicity, the terms for ethanol and the etOH×Arom interaction have been shown; linear and interaction terms for the remaining three properties are not shown in this example. Finally, the term $s_\varepsilon^2$ represents the residual error or "mean square error" for the model. Note that the subsets of the potential terms vary by emission and process, depending on the results of the statistical model fitting.

When the data was sufficient, two sets of exhaust fuel effect coefficients were employed for each pollutant; one set representing start emissions and a second set representing hot-running emissions. In some cases fuel effects estimated for these two processes differed substantially, as the effects of fuel properties on start emissions are dominated by changes in combustion and catalyst warm-up, while the impact of running emissions is dictated by catalyst efficiency when fully operational.

$$\begin{aligned}\text{Emissions (g/mi)} &= e^{\mathbf{X\beta}} \\ &= \exp\begin{pmatrix}\beta_0 + \beta_{\text{etOH}} Z_{\text{etOH}} + [\textit{other linear terms}] + \beta_{\text{etOH}\times\text{Arom}} Z_{\text{etOH}\times\text{Arom}} + \\ [\textit{other 2nd-order terms}] + 0.5 s_\varepsilon^2\end{pmatrix}\end{aligned} \qquad \textbf{Equation 12}$$

Thus, if we let $\mathbf{X\beta_{toxic}}$, $\mathbf{X\alpha_{NMOG}}$ and $\mathbf{X\theta_{ethane}}$ represent models for a selected toxic compound, NMOG and ethane, respectively, calculated by applying Equation 12 to each compound for a specified fuel, the toxic emissions as a fraction of VOC emissions is given by

b Note that these coefficients apply to fuel properties that have been "standardized," i.e., centered on their means and scaled by their standard deviations, based on the fuel-property matrix used to develop the models. To properly apply the models, this process must be applied for the specific fuels under consideration. For more information on this technique, please see the EPAct analysis report.

$$\text{Toxic Fraction} = f_{\text{toxic}} = \frac{e^{\mathbf{X}\boldsymbol{\beta}_{\text{toxic}}}}{e^{\mathbf{X}\boldsymbol{\alpha}_{\text{NMOG}}} - e^{\mathbf{X}\boldsymbol{\theta}_{\text{ethane}}}} \qquad \textbf{Equation 13}$$

For these compounds, the calculation shown in Equation 13 is applied in the GeneralFuelRatioExpression table. Table 28 and Table 29 show coefficients for statistical models for ethanol and the five toxics representing "cold start" and "hot-running" emissions, respectively.

At this point, two important aspects of the EPAct Phase 3 program must be noted. As resources available for the project limited the number of tests for which hydrocarbons could be speciated, some models were developed using smaller subsets of data representing fewer vehicles and fuels and are thus simpler in structure, including only the four linear terms ethanol, aromatics, T50 and T90, and no second-order terms. For simplicity, the smaller set of vehicles and fuels is termed the "reduced" design, in contrast to the "full" design. In addition, it is necessary to note that the fuel terms for models fit to the "reduced" design are standardized differently than those fit under the "full" design. The fuel property statistics for the reduced design are presented below in Table 27.

Coefficients for start emissions are presented in Table 30, as start emissions for four compounds were measured on the "full design", with two compounds measured on the "reduced design." However, as all models representing running emissions were developed using the reduced design, representing 5 vehicles measured on 11 fuels, these models are presented separately in Table 31.

In addition, because VOC are calculated as non-methane organic gases (NMOG) minus ethane ($H_3CCH_3$), it was necessary to develop analogous models for both NMOG and ethane. Coefficients for these two models are shown in Table 30 and Table 31 for start and running emissions, respectively. Models for these two compounds were calculated in the same manner as those for the toxic compounds. Note that models for both start and running ethane were developed using the reduced design, as with some of the toxics models.

In calculating toxic fractions, we elected to use models for NMOG and ethane fit using study designs and datasets similar to those for the toxic compounds. That is to say, if the toxic model was fit with the reduced design, we combined it with the NMOG and ethane models also fit with the reduced design. We followed this approach to prevent the calculation and propagation of artifacts in the estimated fractions resulting from differing levels of information and complexity in the numerator and denominator in Equation 13. In this context we considered it important to apply "information parity" to the toxic model in the numerator and the NMOG model in the denominator, as the vast majority of VOC mass is represented by NMOG, with ethane comprising only a small fraction.

**Table 27. Means and Standard deviations for Fuel Properties, based on the Fuel Matrix in the EPAct Phase-3 Project.**

| Model Term | Full Design[1] | | Reduced Design[2] | |
|---|---|---|---|---|
| | Mean | Standard Deviation | Mean | Standard Deviation |
| Ethanol (%) | 10.3137 | 7.87956 | 10.3137 | 7.87956 |
| Aromatics (%) | 25.6296 | 10.0154 | 25.6296 | 10.0154 |
| RVP (psi) | 8.5178 | 1.61137 | | |
| T50 (°F) | 190.611 | 28.5791 | 190.611 | 28.5791 |
| T90 (°F) | 320.533 | 19.4801 | 320.533 | 19.4801 |
| etOH × etOH | 0.962963 | 0.802769 | | |
| T50 × T50 | 0.962963 | 0.739766 | | |
| etOH × Arom | -0.03674 | 0.978461 | | |
| etOH × RVP | -0.099235 | 0.999615 | | |
| etOH × T50 | -0.541342 | 0.769153 | | |
| etOH × T90 | 0.0163277 | 0.972825 | | |

[1] Applies to models fit with data from 13-15 vehicles measured on 27 fuels.
[2]Applies to models fit with data from five vehicles measured on 11 fuels.

**Table 28. Models representing "Cold-start" Emissions for Selected Air Toxics.**

| Model term | Compound | | | | | |
|---|---|---|---|---|---|---|
| | Acetaldehyde[1] | Formaldehyde[1] | Acrolein[1] | Ethanol[1] | Benzene[2] | 1,3-Butadiene[2] |
| Intercept | -5.2323 | -5.9771 | -7.9338 | -4.9080 | -4.1029 | -5.8371 |
| etOH | 0.81449 | 0.2299 | 0.2476 | 1.4627 | -0.00468 | -0.01729 |
| Arom | 0.03483 | 0.02822 | 0.1122 | | 0.4056 | 0.02673 |
| RVP | -0.04170 | -0.04718 | -0.06450 | -0.06054 | | |
| T50 | 0.08670 | 0.1672 | 0.1880 | 0.07029 | 0.04242 | 0.1247 |
| T90 | 0.03801 | 0.1302 | 0.2489 | -0.09923 | 0.01133 | 0.1004 |
| etOH × etOH | -0.1669 | | -0.08310 | -0.4970 | | |
| T50 × T50 | 0.06665 | 0.05262 | | 0.1108 | | |
| etOH × Arom | 0.01840 | 0.01651 | | | | |
| etOH × RVP | 0.02194 | | | | | |
| etOH × T50 | | -0.01627 | -0.1186 | | | |
| etOH × T90 | | 0.02004 | 0.04617 | | | |
| T50 × T90 | 0.03959 | 0.03489 | 0.05986 | | | |
| Variance ($s^2_\varepsilon$) | 0.2034 | 0.4765 | 0.4661 | 0.7013 | 0.4614 | 0.3281 |

[1] Models fit under the full design, including 15 vehicles measured on 27 fuels. See Table 27.
[2] Models fit under the reduced design, including 15 vehicles measured on 11 fuels. Note that these models do not include a linear term for RVP, and do not include any 2nd –order terms.

**Table 29. Models representing "Hot-Running" Emissions for Selected Air Toxics[1].**

| Model term | Acetaldehyde | Formaldehyde | Acrolein | Ethanol | Benzene | 1,3-Butadiene |
|---|---|---|---|---|---|---|
| Intercept | -9.4189 | -8.6574 | | -9.3072 | | |
| etOH | 0.1520 | 0.08456 | NO | 0.9233 | NO | NO |
| Arom | 0.07991 | 0.01575 | MODEL | -0.3772 | MODEL | MODEL |
| T50 | -0.02997 | 0.01863 | | -0.01910 | | |
| T90 | -0.07836 | -0.08138 | | -0.3017 | | |
| Variance ($s^2_\varepsilon$) | 0.4379 | 0.4583 | | 1.4596 | | |

[1] Models fit using data from 5 vehicles measured on 11 fuels.

**Table 30. NMOG and Ethane (Bag 1):**

**Models representing "Cold-start" Emissions under Full and Reduced Designs.**

| Model term | Full Design[1] | Reduced Design[2] | |
|---|---|---|---|
| | NMOG | NMOG[3] | Ethane[4] |
| Intercept | -0.95209 | -0.8943 | -4.3079 |
| etOH | 0.08019 | 0.1040 | 0.1204 |
| Arom | 0.08782 | 0.09435 | -0.1728 |
| RVP | -0.04224 | | |
| T50 | 0.1345 | 0.1527 | 0.2169 |
| T90 | | 0.02127 | 0.09531 |
| etOH × etOH | 0.04432 | | |
| T50 × T50 | 0.07579 | | |
| etOH × Arom | 0.01693 | | |
| etOH × RVP | | | |
| etOH × T50 | 0.04653 | | |
| etOH × T90 | -0.95209 | | |
| Variance ($s^2_\varepsilon$) | 0.2012 | 0.1982 | 0.6377 |

[1] Represents 15 vehicles measured on 27 fuels; this model is used with the "full-design" models for Acetaldehyde, Formaldehyde, Acrolein and Ethanol, shown in Table 28 above.
[2] Represents 15 vehicles measured on 11 fuels.
[3] This model used with models for Benzene and 1,3-butadiene shown in Table 28 above.
[4] This model used with all models shown in Table 28; note that ethane was measured only under the reduced design.

**Table 31. NMOG and Ethane (Bag 2):**

**Models representing "Hot-Running" Emissions under the Reduced Design**

| Model Term | Model[1] | |
|---|---|---|
| | NMOG | Ethane |
| Intercept | -4.7775 | -7.7241 |
| etOH | 0.01778 | 0.07345 |
| Arom | 0.03320 | -0.1260 |
| T50 | 0.04258 | 0.1815 |
| T90 | 0.09051 | 0.1322 |
| Variance ($s^2_\varepsilon$) | 1.2431 | 2.8243 |

[1]These models used with all models listed in Table 29.

### *2.2.1.3 Estimating Simple Fractions for Running Emissions*

In Table 29 above, note that models representing running emissions are not available for three compounds: acrolein, benzene and 1,3-butadiene. For these compounds, the relevant subsets of data were inadequate to allow model fitting. Therefore, for these compounds, running emissions were represented as "simple" (constant) fractions of VOC, with values derived from the available data.

Thus, for acrolein, benzene and 1,3-butadiene, the values of the fractions were 0.00077, 0.047 and 0.0, respectively. These values were derived as "ratios of means" (ROM), in which the toxic and VOC values were averaged first by vehicle and then across vehicles, as described below. The ROM approach is generally preferred as it provides an unbiased estimator of the true fraction as the sample size increases[19].

For benzene, results were available for four vehicles, differing widely in their benzene and VOC levels, and also in numbers of available measurements, as shown in Table 32. The averaging was performed in two steps so that the vehicle(s) with the greatest numbers of measurements would not dominate the overall mean. In the first step, the benzene and VOC values were averaged for each vehicle. In the second step, the four vehicle means were averaged to give an overall mean. Finally, the overall mean for benzene was divided by that for VOC to give a simple ratio estimator for benzene as a fraction of VOC.

**Table 32. Benzene (Running):**

**Derivation of a Ratio-of-Means Estimator for Benzene as a Fraction of VOC.**

| Vehicle | *n* | Benzene (mg) | VOC (mg) | Ratio of means (ROM)[1] |
|---|---|---|---|---|
| Corolla | 2 | 0.053752 | 2.2694 | |
| F150 | 10 | 2.2241 | 28.427 | |
| Impala | 3 | 0.10825 | 10.670 | |
| Silverado | 4 | 0.29381 | 16.216 | |
| All vehicles | 4 | 0.669971 | 14.396 | 0.0465 |

[1] This value is a simple average of the means for all four vehicles, as listed above.

The VOC fraction for acrolein was derived similarly (Table 33). For this compound results were available for five vehicles. Values for acrolein are considerably lower than for benzene, so results are expressed in µg, rather than mg. The resulting fraction is two orders of magnitude lower than that for benzene.

**Table 33. Acrolein (Bag 2):**

**Derivation of a Ratio-of-Means Estimator for Acrolein as a Fraction of VOC.**

| Vehicle | *n* | Acrolein (µg) | VOC (µg) | Ratio of means (ROM) |
|---|---|---|---|---|
| Civic | 3 | 5.4190 | 3,038.9 | |
| Corolla | 5 | 2.8934 | 2,929.6 | |
| F150 | 5 | 8.3558 | 24,321 | |
| Impala | 6 | 8.0180 | 10,408 | |
| Silverado | 10 | 19.662 | 17,192 | |
| All vehicles | 5 | 8.8696[1] | 11,578 | 0.0007661 |

[1] This value is a simple average of the means for all five vehicles, as listed above.

For 1,3-butadiene in hot-running operation, measurements were extremely low; in fact, we considered the dataset so heavily affected by "left-censoring" that we did not consider it adequate for either model fitting or development of ratio estimators. Accordingly, for modeling purposes, we have adopted an assumption that this compound is not emitted during hot-running operation, i.e., the ROM estimator is 0.0.

#### *2.2.1.4 Post-Model Adjustments*

For two compounds, benzene and 1,3-butadiene, additional refinements were applied to supplement the study design of the EPAct fuel set. These adjustments are applied to both start and running emissions.

For benzene, the issue is that the fuel matrix included aromatics generally, but not benzene specifically. As we considered it inadequate to model benzene in exhaust without explicitly accounting for benzene levels in fuel, we developed a "*post-model*" refinement using data external to the EPAct program. In this case the source was a program conducted in support of the 2007 MSAT2 rule. This program performed measurements on nine Tier-2 certified vehicles on fuels with benzene levels ranging from 0.6 to 1.1 percent by weight.[20,21] With benzene represented as a fraction of VOC (as in Equation 13) denoted as $f_{benzene}$, a value modified to account for benzene levels in different fuels ($f^*_{benzene}$) is calculated as shown in Equation 14 where $x_{benzene}$ is the benzene level for the fuel modeled (weight percent), $A$ is the mean benzene level in the EPAct exhaust program fuel set (0.66 weight percent), and $B$ is an empirical coefficient, taking a value of 0.24.

$$f^*_{benzene} = \left[\left(x_{benzene} - A\right)\cdot B \cdot f_{benzene}\right] + f_{benzene} \qquad \textbf{Equation 14}$$

Similarly, given the importance of olefins to estimation of emissions for 1,3-butadiene, and that the EPAct exhaust program study design did not incorporate olefins as a factor, we considered it appropriate to develop a post-model adjustment explicitly accounting for olefin level. This adjustment was derived by varying olefin levels in the Complex Model1 and fitting a polynomial trend to the results.[22] Starting with an unadjusted toxic fraction for 1,3-butadiene ($f_{buta}$), the modified fraction $f^*_{buta}$ is calculated using Equation 15, in which $x_{olefin}$ is the olefin

level, and $A$, $B$, $C$ and $D$ are coefficients, taking values of 0.000008, 0.0002, 0.0069 and 0.008823, respectively.

$$f^{*}_{buta} = f_{buta}\left(\frac{Ax^{2}_{olefin} + Bx_{olefin} + C}{D}\right) \qquad \textbf{Equation 15}$$

### 2.2.2 Gaseous Hydrocarbons

#### 2.2.2.1 Vehicles operating on Fuel blends containing 0-20% Ethanol

##### 2.2.2.1.1 Additional Air Toxics

For fuel blends with 0%, 10% and 15% ethanol, composite speciation profiles developed from the results of EPAct (Phase 1) were used to develop toxic fractions for the hazardous air toxics included in Table 34.[c] These profiles were based on averaging results of tests from 3 vehicles.[23,24] Toxic fractions for E10 are used for all gasolines containing ethanol levels of 5 vol.% or greater. For fuel blends containing 20% ethanol fractions were developed using a composite speciation profile developed using results from the EPAct (Phase 3) program. The fractions are also presented in Table 34. For blends containing MTBE, no data were available for Tier 2 vehicles; thus the toxic to VOC ratios for Tier 1 and earlier vehicles were used (See Table 14, page 17). The values shown in the Table 34 are stored in the database table minorHAPRatio (see Table 16, page 19).

c Phase 1 testing was done using fuels more representative of in-use fuels, in contrast to the orthogonal matrix used for EPAct Phase 3.

**Table 34. Toxic fractions for Selected Compound, Representing Model years 2004 and Later.**

| Pollutant (pollutantID)[1] | Fuel Blends (Gasoline & "Gasohol") | | | |
|---|---|---|---|---|
| | 0% (E0) | 10% (E10)** | 15% (E15) | 20% (E20) |
| 2,2,4-Trimethylpentane (40) | 0.03188 | 0.01227 | 0.02199 | 0.004625 |
| Ethyl Benzene (41) | 0.01683 | 0.01660 | 0.01568 | 0.022199 |
| Hexane (42) | 0.002790 | 0.02911 | 0.0110 | 0.02497 |
| Propionaldehyde (43) | 0.00122 | 0.00054 | 0.0005984 | 0.0006607 |
| Styrene (44) | 0.00085 | 0.00083 | 0.004588 | 0.004096 |
| Toluene (45) | 0.07542 | 0.07440 | 0.0727 | 0.09646 |
| Xylene(s) (46) | 0.06127 | 0.06047 | 0.06902 | 0.09302 |

[1] For fuels containing 0-20% ethanol, fractions for ethanol, benzene, acetaldehyde, formaldehyde, 1,3-butadiene, and acrolein were estimated using methods described in 2.2.1.2 - 2.2.1.4.

**Values also applied for fuels containing 5% and 8% ethanol, (E5 and E8).

### 2.2.2.2 Vehicles operating on Fuel blends containing 70-100% Ethanol

#### 2.2.2.2.1 Major Hazardous Air Pollutants (HAPs)

For major HAPs, instead of deriving toxic fractions, adjustment factors were developed based on the analysis of EPAct (phase 3) program, National Renewable Energy Laboratory (NREL) E40[25], Coordinating Research Council (CRC) E-80[26], and PM Speciation Program[27]. All programs measured emissions from LA92 test cycle on both E10 and E85, except CRC E-80 which tested E6 and E85. Only the vehicles tested on both E10 (E6) and E85 were included in the analysis. The number of vehicles from each program is summarized in Table 35.

**Table 35. Number of vehicles included in the analysis of major HAPs**

| Test Program | Number of Vehicles |
|---|---|
| EPAct (phase 3) | 3 |
| NREL E40 | 9 |
| CRC E-80 | 7 |
| PM Speciation | 2 |

Consistent emission trends were observed across datasets and thus, all available datasets were pooled to examine the effect of E85 on emissions compared to E10. First, the test of significance of differences between E10 and E85 was performed using Student's paired t-tests. Next, when there was a statistically significant difference in emissions between E10 and E85, the adjustment factors were calculated using Equation 16. The adjustment factor was set to zero when the differences in emissions were not statistically different (i.e., acrolein).

$$E85\ adjustment\ factor = \frac{\frac{Toxics_{E85}}{VOC_{E85}}}{\frac{Toxics_{E10}}{VOC_{E10}}} \qquad \textbf{Equation 16}$$

The resulting adjustment factors are shown in Table 36, and are stored in the database table, "GeneralFuelRatioExpression", for fuelTypeID = 5.

**Table 36. E70/E85 adjustment factors for major HAPs**

| Pollutant (pollutantID) | Adjustment Factor for E70/E85 |
|---|---|
| Benzene (20) | 0.6672 |
| Ethanol (21) | 7.587 |
| 1,3-butadiene (24) | 0.2167 |
| Formaldehyde (25) | 1.572 |
| Acetaldehyde (26) | 7.126 |
| Acrolein (27) | 0 |

#### 2.2.2.2.2 Additional Air Toxics

Toxic fractions for additional air toxics (pollutantID from 40-46) for model year 2001 and later are identical to the fractions for model year 2000 and earlier, as shown in Table 34.

### 2.2.3 Polycyclic Aromatic Hydrocarbons (PAH)

#### *2.2.3.1 Vehicles operating on Fuel blends containing 0-20% Ethanol*

In the absence of additional data, the fractions for more recently manufactured vehicles were assumed to be similar to those for vehicles employing older technologies. See Table 20, page 23.

#### *2.2.3.2 Vehicles operating on Fuel blends containing 70-85% Ethanol (E70/E85)*

Limited emissions data exist for PAH emissions from vehicles running on E85. Thus, toxic fractions for PAH relative to $OC_{2.5}$ VOC were estimated by multiplying the fractions for E0 fuels (Table 20) by the fraction of gasoline in E85 fuel. We assumed that annual average ethanol content of E85 is 74%. Thus, E0 fractions were multiplied by 0.26. This approach assumes that no PAH emissions result from ethanol combustion. The resulting fractions presented in Table 37

**Table 37. Toxic Fractions for PAH Species for Vehicles running on E85 blends, by Phase and Process.**

| Species | pollutantID | CAS | Toxic fraction | | |
|---|---|---|---|---|---|
| | | | Gaseous Phase | Particulate Phase | |
| | | | | Start | Running |
| Naphthalene | 23 | 91203 | 4.60E-02 | 4.37E-03 | 3.35E-03 |
| Acenaphthylene | 42 | 208968 | 4.03E-03 | 1.30E-03 | 9.97E-04 |
| Acenaphthene | 41 | 83329 | 8.87E-04 | 0.00E+00 | 0.00E+00 |
| Fluorene | 54 | 86737 | 1.80E-03 | 0.00E+00 | 0.00E+00 |
| Anthracene | 44 | 120127 | 7.44E-04 | 1.35E-03 | 1.03E-03 |
| Phenanthrene | 57 | 85018 | 4.77E-03 | 4.71E-03 | 3.61E-03 |
| Fluoranthene | 53 | 206440 | 1.24E-03 | 4.77E-03 | 3.65E-03 |
| Pyrene | 59 | 129000 | 1.42E-03 | 5.16E-03 | 3.95E-03 |
| Benz(a)anthracene | 45 | 56553 | 1.20E-04 | 1.24E-02 | 9.48E-03 |
| Chrysene | 50 | 218019 | 1.34E-04 | 1.05E-02 | 8.01E-03 |
| Benzo(a)pyrene | 46 | 50328 | 6.54E-06 | 3.10E-02 | 2.37E-02 |
| Benzo(b)fluoranthene | 47 | 205992 | 8.91E-05 | 1.51E-02 | 1.16E-02 |
| Benzo(k)fluoranthene | 49 | 207089 | 8.91E-05 | 1.51E-02 | 1.16E-02 |
| Benzo(g,h,i)perylene | 48 | 191242 | 0.00E+00 | 8.39E-02 | 6.42E-02 |
| Indeno(1,2,3,c,d)pyrene | 56 | 193395 | 0.00E+00 | 3.15E-02 | 2.41E-02 |
| Dibenzo(a,h)anthracene | 51 | 53703 | 0.00E+00 | 7.24E-04 | 5.55E-04 |

### 2.2.4 Metals

Since metal emissions can result from trace level contamination of fuel and engine oil, as well attrition from exhaust emission components, there is no way to estimate metal emissions for vehicles running on E85 or E70 fuel in the absence of data. Thus metal emission rates were assumed to remain unchanged from those applicable to vehicles with earlier fuel delivery and emissions control technologies (see Table 21, page 24).

### 2.2.5 Dioxins and Furans

#### 2.2.5.1 Vehicles operating on Fuel blends containing 0-20% Ethanol

In the absence of additional data, the fractions for more recently manufactured vehicles were assumed to be similar to those for vehicles employing older technologies. See Table 24, page 26.

#### 2.2.5.2 Vehicles operating on Fuel blends containing 70-85% Ethanol (E70/E85)

No emissions data exist for dioxin and furan emissions from vehicles running on E85 or E70. Thus dioxin emission factors for E85 and E70 were estimated by multiplying fractions for vehicles running on E0 fuels (Table 24) by the fraction of gasoline in the fuel, assuming no emission of dioxins or furans resulting from the combustion of ethanol. Resulting ratios are given in Table 38.

**Table 38. Emission Factors for Dioxins and Furans, for Vehicles Operating on E85 Blends.**

| Congener | Emission rate (mg/mile) |
|---|---|
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin | 2.15E-10 |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 9.61E-11 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 1.01E-11 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | 2.06E-11 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | 1.28E-11 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | 1.55E-11 |
| Octachlorodibenzo-p-dioxin | 3.67E-12 |
| 2,3,7,8-Tetrachlorodibenzofuran | 7.19E-11 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 1.03E-11 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 7.55E-11 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 2.84E-11 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 3.02E-11 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 8.24E-12 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 3.52E-11 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 3.16E-11 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 1.01E-12 |
| Octachlorodibenzofuran | 1.07E-12 |

## 2.3 Heavy-Duty Diesel Vehicles: MY 2007 and Earlier

Toxic fractions and metal emission rates were developed for exhaust emissions from heavy-duty diesel vehicles and applied to all diesel vehicle categories. There are no separate emission ratios or factors for diesel engines running on biodiesel fuels or synthetic diesel fuels, due to very limited data.

The composition of hydrocarbons emissions for heavy-duty diesel engines lacking the advanced control technologies applied in more recently manufactured vehicles differ substantially. Thus, we developed one set of toxic fractions for pre-2007 diesel engines and another set for engines manufactured in 2007 and later.

### 2.3.1 Gaseous Hydrocarbons

To estimate toxic fractions for vehicles in this model-year group EPA relied on a database compiled for the Coordinating Research Council and the National Renewable Energy Laboratory (NREL) (CRC E-75).[28] This database was developed from a literature survey and compiled data collected in 13 different studies. The studies included were conducted in a number of different countries, included heavy-duty and light-duty engines, a variety of diesel and biodiesel fuels, and a number of different operating modes and cycles.

For 2,2,4-trimethylpentane, n-hexane, propionaldehyde, and toluene, toxic fractions were developed by Sierra Research. Their analysis of CRC E-75 data is described in detail in their technical report. Data from tests using non-conventional diesel fuel (Fischer-Tropsch, bioDiesel, ethanol-Diesel blends, emulsified fuel, European blends, and other obvious research fuels) were excluded, as were data from non-heavy duty engines. The fractions are provided in Table 39.

Toxic fractions for other compounds in Table 39 were developed by EPA from the E-75 database. We relied on data collected in the United States from heavy-duty diesel engines running on conventional diesel fuels, collected on test-cycles representative of real world operation. Some studies reported results on a distance-specific basis (g/mi) whereas others reported results on a brake-specific basis (g/hp-hr). For both subsets of data, we calculated mean emissions for each toxic and for VOC, and then calculated mean fractions for each reporting basis. We then calculated an overall mean fraction using the respective sample sizes to weight the two fractions. The resulting ratios are also provided in Table 39.

**Table 39. Toxic Fractions for pre-2007 Diesel Engines.**

| Pollutant | Toxic fraction |
|---|---|
| 1,3-Butadiene | 0.002918 |
| 2,2,4-Trimethylpentane | 0.001808 |
| Acetaldehyde | 0.035559 |
| Acrolein | 0.006622 |
| Benzene | 0.007835 |
| Ethyl Benzene | 0.002655 |
| Formaldehyde | 0.078225 |
| n-Hexane | 0.00197 |
| Propionaldehyde | 0.00468 |
| Styrene | 0.001312 |
| Toluene | 0.00433 |
| Xylenes | 0.003784 |

### *2.3.2 Polycyclic Aromatic Hydrocarbons*

As with gasoline emissions, PAH mass emissions from diesel engines were apportioned into gaseous and particulate phases, using a single set of allocation factors for all temperature conditions. The partitioning factors for diesel PAHs were developed by Sierra Research[29] using estimates from EPA's SPECIATE 4.2 database[30] and information on compounds' physical and chemical properties. The allocations from SPECIATE were based on medium duty diesel engine data.[31]. The phase-partitioning factors are shown in Table 40. Compared to the partitioning for gasoline (Table 19, page 22**Error! Bookmark not defined.**), the fraction of PAH in the particulate phase is higher for diesel emissions, which is consistent with the higher concentrations of particles in diesel exhaust.

**Table 40. Phase-Partition Fractions for Emissions of Polyaromatic Hydrocarbons from Diesel Engines.**

| PAH species | Molar Mass (g/mol) | Phase Fraction | |
|---|---|---|---|
| | | Gaseous | Particulate |
| Napthalene | 128 | 1.0 | 0.0 |
| Acenaphthylene | 152 | 1.0 | 0.0 |
| Acenapthene | 154 | 1.0 | 0.0 |
| Fluorene | 166 | 0.785 | 0.215 |
| Anthracene | 178 | 0.534 | 0.466 |
| Phenanthrene | 178 | 0.665 | 0.335 |
| Fluoranthene | 202 | 0.484 | 0.516 |
| Pyrene | 202 | 0.448 | 0.552 |
| Benz(a)anthracene | 228 | 0.277 | 0.723 |
| Chrysene | 228 | 0.177 | 0.823 |
| Benzo(a)pyrene | 252 | 0.0 | 1.0 |
| Benzo(b)fluoranthene | 252 | 0.0 | 1.0 |
| Benzo(k)fluoranthene | 252 | 0.0 | 1.0 |
| Benzo(g,h,i)perylene | 276 | 0.227 | 0.773 |
| Indeno(1,2,3-cd)pyrene | 276 | 0.0 | 1.0 |
| Dibenzo(a,h)anthracene | 278 | 0.0 | 1.0 |

Emissions of PAH in the gaseous and particulate phases were estimated as fractions of total VOC and Organic carbon emissions ($OC_{2.5}$), respectively. Toxic fractions were calculated using results from the E-75 database. For the particulate phase, a fraction was first calculated with respect to total $PM_{2.5}$, and then converted to a fraction of total $OC_{2.5}$ using estimates of OC as a fraction of total $PM_{2.5}$. Note that the OC:PM fractions differed by emissions process, with separate fractions applied for start, running and extended-idle emissions.

In estimating fractions, we relied on data collected in the United States on heavy-duty diesel engines running on conventional diesel fuels, measured on test-cycles representative of real world operation. It should be noted that for some compounds, substantially more data was available than for others; thus the level of confidence in emission rates varies among individual compounds. For instance, while data from 66 tests were available for acenaphthene, data from only two tests were available for dibenz(a,h)anthracene. Table 41 shows fractions for PAH emissions relative to OC and VOC, by emissions process.

The PAH fractions for exhaust emissions are also applied to crankcase emissions. Because the PAH emissions are applied to the OC emissions, the total $PM_{2.5}$ crankcase emissions in MOVES are more enriched with PAHs than tailpipe $PM_{2.5}$ emissions, due to the large fraction $OC/PM_{2.5}$ emissions in crankcase emissions. Research suggests that PM emissions from the crankcase are more enriched with PAHs than emissions from the exhaust.[32]

**Table 41. Toxic Fractions for PAH Species, by Phase and Process, for pre-2007 Heavy-Duty Diesel Engines.**

| Compound | Particulate Phase ($OC_{2.5}$) | | | Gaseous Phase (VOC) |
|---|---|---|---|---|
| | Start | Extended Idle | Running (crankcase) | |
| Naphthalene | 0.0 | 0.0 | 0.0 | 0.009046 |
| Acenaphthylene | 0.0 | 0.0 | 0.0 | 0.000501 |
| Acenaphthene | 0.0 | 0.0 | 0.0 | 0.000321 |
| Fluorene | 0.000280 | 0.000254 | 0.000849 | 0.000591 |
| Anthracene | 0.000163 | 0.000148 | 0.000494 | 0.000235 |
| Phenanthrene | 0.000644 | 0.000586 | 0.001956 | 0.001945 |
| Fluoranthene | 0.000624 | 0.000568 | 0.001896 | 0.000611 |
| Pyrene | 0.000902 | 0.000821 | 0.002740 | 0.000758 |
| Benzo(a)anthracene | 0.000323 | 0.000294 | 0.000981 | 0.000045 |
| Chrysene | 0.000204 | 0.000186 | 0.000620 | 0.000024 |
| Benzo(a)pyrene | 0.000121 | 0.000110 | 0.000369 | 0.0 |
| Benzo(b)fluoranthene | 0.000036 | 0.000033 | 0.000110 | 0.0 |
| Benzo(k)fluoranthene | 0.000005 | 0.000005 | 0.000015 | 0.0 |
| Indeno(1,2,3-cd)pyrene | 0.000009 | 0.000008 | 0.000028 | 0.0 |
| Benzo(g,h,i)perylene | 0.000006 | 0.000005 | 0.000018 | 0.0000276 |
| Dibenz(a,h)anthracene | 0.000005 | 0.000004 | 0.000015 | 0.0 |

### *2.3.3 Metals*

Emission rates for selected metals representing pre-2007 heavy-duty diesel engines were based on data from the CRC E-75 program, with the exception of rates for mercury and arsenic. Emission rates for these metals were obtained from the same tunnel study used to supply the arsenic rates for gasoline vehicles (see Table 21, page 24). They do not vary with emission control technology. Table 42 provides metal emission factors for pre-2007 heavy duty engines.

**Table 42. Emission Rates for Selected Metals, for pre-2007 Heavy-Duty Diesel Engines.**

| Pollutant | Emission Rate (g/mi) |
|---|---|
| Chromium III | $5.6\times10^{-6}$ |
| Chromium VI | $1.2\times10^{-6}$ |
| Manganese | $8.0\times10^{-6}$ |
| Nickel | $1.4\times10^{-5}$ |
| Mercury, Elemental Gaseous Phase | $6.2\times10^{-9}$ |
| Mercury, Reactive Gaseous Phase | $3.2\times10^{-9}$ |
| Mercury, Particulate Phase | $1.6\times10^{-9}$ |
| Arsenic | $2.3\times10^{-6}$ |

### *2.3.4 Dioxins and Furans*

To represent emissions of dioxins and furans from pre-2007 heavy-duty diesel engines, emissions rates for 17 congeners were calculated from the results of an EPA diesel dioxin/furan study of legacy engines[33] In this study, dioxin emissions from three heavy-duty engines were measured, manufactured in model year 1984 (GM 6.2 L), 1987 (Detroit Diesel 6V92) and 1993 (Cummins L10). The emission factors in mg/mi TEQ are shown in Table 43.

**Table 43. Emission Rates for Dioxin/Furan Congeners, for pre-2007 Heavy-duty Diesel engines.**

| Congener | Emission Rate (mg/mi TEQ) |
|---|---|
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) | $2.23 \times 10^{-10}$ |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 0 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 0 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | $1.03 \times 10^{-11}$ |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | $4.78 \times 10^{-11}$ |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | $4.18 \times 10^{-11}$ |
| Octachlorodibenzo-p-dioxin | $4.84 \times 10^{-12}$ |
| 2,3,7,8-Tetrachlorodibenzofuran | $6.50 \times 10^{-10}$ |
| 1,2,3,7,8-Pentachlorodibenzofuran | $4.16 \times 10^{-11}$ |
| 2,3,4,7,8-Pentachlorodibenzofuran | $6.69 \times 10^{-10}$ |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | $8.02 \times 10^{-11}$ |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | $4.24 \times 10^{-11}$ |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 0.0 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | $3.03 \times 10^{-11}$ |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | $2.16 \times 10^{-11}$ |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 0.0 |
| Octachlorodibenzofuran | $5.56 \times 10^{-13}$ |

## 2.4 Heavy-Duty Diesel Vehicles: MY 2007 and later

### 2.4.1 Gaseous Hydrocarbons

For heavy-duty diesel engines manufactured in 2007 and later, and light-duty diesel engines meeting Tier 2 emissions standards, advanced emission controls change the composition of

VOCs. For these engines, we relied on speciated emissions data from the Advanced Collaborative Emissions Study (ACES), directed by the Health Effects Institute and Coordinating Research Council, with participation from a range of government and private-sector sponsors.[34] In this study detailed emissions measurements were performed on four engines operated on low-sulfur diesel fuel over several test cycles. We made use of data from a 16-hour transient cycle. Toxic fractions calculated from the ACES data are provided in Table 44.

**Table 44. Toxic Fractions for Heavy-duty Diesel Engines manufactured in 2007 and later.**

| Pollutant | Toxic fraction |
|---|---|
| 1,3-Butadiene | 0.00080 |
| 2,2,4-Trimethylpentane | 0.00782 |
| Acetaldehyde | 0.06934 |
| Acrolein | 0.00999 |
| Benzene | 0.01291 |
| Ethyl Benzene | 0.00627 |
| Formaldehyde | 0.21744 |
| N-Hexane | 0.00541 |
| Propionaldehyde | 0.00314 |
| Styrene | 0.00000 |
| Toluene | 0.02999 |
| Xylenes | 0.03800 |

### 2.4.2 Polyaromatic Hydrocarbons

For heavy-duty diesels manufactured in 2007 and later, advanced emission controls reduce the total mass of PAH emitted and change the composition of these compounds. For these engines, we relied on speciated emissions data from the ACES study. Toxic fractions applicable to these engines are shown in Table 45, in which the fractions are differentiated by phase but not by emissions process. For the particulate phase, a single fraction is provided for all processes (similar to HC) because the OC/PM fraction in MOVES for 2007+ diesel is a single fraction for all emission processes. The OC/PM fraction is derived from measurements made on a 16-hour drive cycle that composes multiple driving modes as documented in the MOVES2014 TOG and PM Speciation Report.

**Table 45. Toxic Fractions for Polyaromatic Compounds, by Phase, for Heavy-duty Diesel Engines manufactured in 2007 and later.**

| Compound | Particulate Phase ($OC_{2.5}$) | Gaseous Phase (VOC) |
|---|---|---|
| Naphthalene | 0 | 0.0163278 |
| Acenaphthylene | 0 | 0.0000853 |
| Acenaphthene | 0 | 0.0000526 |
| Fluorene | 0.0002409 | 0.0001963 |
| Anthracene | 0.0001187 | 0.0000304 |
| Phenanthrene | 0.0019187 | 0.0008507 |
| Fluoranthene | 0.0002181 | 0.0000457 |
| Pyrene | 0.0002091 | 0.0000379 |
| Benzo(a)anthracene | 0.0000036 | 0.0000003 |
| Chrysene | 0.0000112 | 0.0000005 |
| Benzo(a)pyrene | 0.0000148 | 0 |
| Benzo(b)fluoranthene | 0.0000063 | 0 |
| Benzo(k)fluoranthene | 0.0000063 | 0 |
| Indeno(1,2,3-cd)pyrene | 0.0000022 | 0 |
| Benzo(ghi)perylene | 0.0000009 | 0.0000002 |
| Dibenz(a,h)anthracene | 0.0000045 | 0 |

### *2.4.3 Metals*

Emissions rates for selected metals representing heavy-duty diesel engines manufactured since 2007 were developed from data from the ACES program, with the exception of rates for mercury and arsenic. Rates for these two metals are identical to those used for gasoline engines (Table 21, page 24). Rates are presented in Table 46.

**Table 46. Emission Rates for Metals, for Heavy-Duty Diesel Engines manufactured in 2007 and Later.**

| Pollutant | Emission Rate (g/mi) |
|---|---|
| Chromium III | $1.6\times10^{-6}$ |
| Chromium VI | $3.4\times10^{-7}$ |
| Manganese | $5.5\times10^{-7}$ |
| Nickel | $6.5\times10^{-7}$ |
| Mercury, Elemental Gaseous Phase | $6.2\times10^{-9}$ |
| Mercury, Reactive Gaseous Phase | $3.2\times10^{-9}$ |
| Mercury, Particulate Phase | $1.6\times10^{-9}$ |
| Arsenic | $2.3\times10^{-6}$ |

### 2.4.4 Dioxins and Furans

The data used to calculate the emission rates for engines manufactured in 2007 and later were obtained from the EPA diesel dioxin study of 2007 and later engines.[35] The results represent measurements of transient tests conducted on a MY2008 Cummins ISB over 48 tests on the FTP cycle in a 1:23 cold:hot start ratio, combined with several emission-control technologies. To represent emissions from engines manufactured between 2007-2009, the results for the diesel oxidation catalyst plus catalyzed diesel particulate filter were used. For engines manufactured in 2010 and later, the results for the diesel oxidation catalyst plus catalyzed diesel particulate filter coupled with flow through copper zeolite selective catalytic reduction and urea and ammonia slip catalyst were used. Rates are presented in Table 47.

**Table 47. Emission Rates for Dioxins and Furans, for Heavy-duty Diesel Engines manufactured in 2007 and later**

| Congener | 2007 - 2009 | 2010 and later |
|---|---|---|
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) | 0.0 | 0 |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 0.0 | 0 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 0.0 | 0 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | 0.0 | 0 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | $4.11 \times 10^{-12}$ | 0 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | $2.58 \times 10^{-12}$ | 1.05 × 10-11 |
| Octachlorodibenzo-p-dioxin | 2.79 × 10-13 | 2.09 × 10-12 |
| 2,3,7,8-Tetrachlorodibenzofuran | 0.0 | 5.09 × 10-12 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 0.0 | 3.21 × 10-12 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 1.89 × 10-11 | 9.73 × 10-11 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 0.0 | 2.20 × 10-11 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 0.0 | 2.43 × 10-11 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 0.0 | 0 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 0.0 | 1.80 × 10-11 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 3.00 × 10-12 | 9.94 × 10-12 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 0.0 | 5.81 × 10-13 |
| Octachlorodibenzofuran | 2.12 × 10-13 | × 10-13 |

## 2.5 Light-duty Diesel and Auxiliary Power Units

Since extended idle emissions associated with auxiliary power units (APUs) are not subject to 2007 standards, toxic to VOC ratios for pre-2007 diesel engines were used for them[36]. Since light-duty diesels comprise a very small portion of the fleet, the heavy-duty ratios were applied to light-duty diesel vehicle classes to streamline modeling.

## 2.6 Compressed Natural Gas Emissions

Currently, MOVES2014 only models compressed natural gas (CNG) fueled transit buses. For simplification, all CNG-powered light-duty and heavy-duty vehicles are assumed to be fueled by gasoline of diesel. This section describes the development of toxic emission rates applied to CNG transit buses.

### 2.6.1 Gaseous Hydrocarbons

We used hydrocarbon speciation measurements from the testing by the California Air resources Board[37] (Ayala et al. 2003) using measurements from the 2000 MY Detroit Diesel Series 50G engine with and without an oxidation catalyst collected on the CBD cycle. As discussed in the MOVES2014 heavy-duty report, we used the uncontrolled tests to represent speciation from pre-2002 CNG transit buses, and the oxidation catalyst tests to represent 2002 and later buses. We also used the Central Business District (CBD) cycle to be consistent with the criteria pollutant measurements.

The toxic fractions derived from this set of measurements are displayed in Table 48. The total VOC emissions rates are reduced by 70% from pre-2002 levels and the 2002-2006 model year groups in MOVES. As shown in Table 48, formaldehyde emissions are preferentially reduced by the oxidation catalyst. Formaldehyde contributes to over 50% of the VOC emissions for the uncontrolled CNG bus, but only 16.2% of the VOC emissions for the CNG bus equipped with an oxidation catalyst. The MOVES toxics not measured in this study are assumed to be negligible, and are modeled as 0.

**Table 48. Toxic Fractions for CNG Transit Buses.**

| | No control (pre-2002) | With oxidation catalyst (2002+) |
|---|---|---|
| 1,3 Butadiene | 2.34E-04 | 0 |
| Benzene | 1.35E-03 | 2.53E-03 |
| Toluene | 6.91E-04 | 7.86E-03 |
| Ethylbenzene | 8.41E-05 | 1.31E-03 |
| Xylenes | 8.23E-04 | 6.34E-03 |
| Formaldehyde | 0.517 | 0.162 |
| Acetaldehyde | 0.0305 | 0.138 |
| Acrolein | 2.35E-03 | 0 |
| Propionaldehyde | 0.0153 | 0 |

### 2.6.2 Polycyclic Aromatic Hydrocarbons

The PAH toxic fractions for compressed natural gas are derived from tests on a MY2000 DDC Series 50G engine on a New Flyer CNG transit bus tested by the California Air Resources Board.[38] Emissions were measured in two stages (the bus was re-tested after 3 months of service

in the Los Angeles County Metropolitan Transit Authority. The PAH emissions were measured in the semi-volatile phase using PUF-XAD, and measured in the particulate phase on Teflon-coated glass fiber filters. VOC emissions are derived from the NMHC and speciated hydrocarbon emissions. The OC emissions rates were provided to EPA by CARB. We estimated the volatile PAH emissions by calculating PAH/VOC fractions from the PUF-XAD measurements, and particle-phase PAH/OC fractions using the filter-based measurements for both stages of the study. For use in MOVES, we averaged the ratios estimated from both stages of the testing. The average ratios are displayed in Table 49.

**Table 49. PAH Ratios to volatile organic carbon (volatile PAHs), and to organic carbon (particle-phase.**

| Compound | VOC ratio | OC ratio |
|---|---|---|
| Naphthalene | 9.554E-06 | 2.114E-05 |
| Acenaphthylene | 4.230E-06 | ND |
| Acenaphthene | 1.243E-06 | 1.886E-05 |
| Fluorene | 2.986E-06 | 3.301E-05 |
| Anthracene | 1.164E-06 | 1.644E-06 |
| Phenanthrene | 8.356E-06 | 2.043E-05 |
| Fluoranthene | 1.936E-06 | 2.874E-05 |
| Pyrene | 3.743E-06 | 5.350E-05 |
| Benz(a)anthracene | 1.682E-07 | 9.390E-06 |
| Chrysene/triphenylene | 2.441E-07 | 1.911E-05 |
| Benzo(a)pyrene | ND | ND |
| Benzo(b)fluoranthene | ND | ND |
| Benzo(k)fluoranthene | ND | ND |
| Indeno(1,2,3-cd)pyrene | ND | ND |
| Benzo(g,h,i)perylene | ND | 5.502E-06 |
| Dibenz(a,h)anthracene | ND | ND |

ND = not detected, fractions set to 0.

### 2.6.3 Metals

We used the chromium and nickel emission rates reported from the uncontrolled 2000 MY DDC Series 50G[39]. We used the uncontrolled bus to be consistent with the $PM_{2.5}$ speciation profile and because this was the only bus in the study that detected both pollutants. The chromium emissions were not significantly different between the uncontrolled and controlled DDC engine. The isotope split of chromium is based on the same assumptions used for gasoline [12].

The other metal emission rates produced by MOVES were not available in the published literature. As such, we used the same g/mile emission rates as gasoline.

**Table 50. Metal emission rates and sources used for CNG Transit buses in MOVES.**

| Pollutant | Emission Rate (g/mi) | Source |
|---|---|---|
| Chromium 6+ | 1.26E-08 | Okamoto et al. (2006) |
| Chromium 3+ | 5.74E-08 | Okamoto et al. (2006) |
| Manganese | 1.33E-06 | Same as gasoline |
| Nickel | 1.00E-08 | Okamoto et al. (2006) |
| Elemental Gas Phase Hg | 1.10E-07 | Same as gasoline |
| Reactive Gas Phase Hg | 9.90E-09 | Same as gasoline |
| Particulate Hg | 4.00E-10 | Same as gasoline |
| Arsenic | 2.30E-06 | Same as gasoline |

### 2.6.4 Dioxins and Furans

No published dioxin and furan emission rates for CNG vehicles were available to the US EPA. As such, we are using the dioxin emission rates for gasoline reported in Table 24 (page 7).

# 3 Evaporative Emissions

## 3.1 Light-Duty Vehicles (Gasoline-powered): MY???? <2.1>

As with exhaust emissions, emissions of toxics emitted through evaporation of unburned fuel as also estimated as fractions of total (evaporative?) VOC. Again, fractions for some compounds are estimated as complex fractions based on fuel properties such as oxygenate content and vapor pressure. For other compounds, simple fractions are estimated. For the compounds modeled, fraction types and data sources are summarized in Table 51.

### 3.1.1 Non-permeation processes

Algorithms used to generate complex fractions were adapted from those used in MOBILE6.2.[40] However, as the conceptual basis for modeling evaporative emissions has changed in MOVES, the equations are applied to the emission processes considered most closely analogous. Thus, algorithms for hot soak in MOBILE6.2 are used for vapor venting and refueling vapor loss, and algorithms for running loss are used for fuel leaks and refueling spillage loss. The equations are applied for fuels containing up to 10% ethanol, and are presented in Table 52.

Simple Fractions for other air toxics in evaporative non-permeation emissions were obtained from profiles developed for EPA by Environ Corporation, using data from the Auto/Oil program conducted in the early 1990's.[41] The fractions for these compounds are the same for all pollutant processes (except permeation) and are presented in Table 53.

Ratios for naphthalene and ethanol are derived from <source?>, and are also shown in Table 53.

The ratios for 10% ethanol are used for all fuels with greater than or equal to 5% ethanol and less than 12%.

Conventional gasoline ratios are also used for MTBE oxygenated gasoline.

For vehicles operating on fuels containing 15% ethanol (E15), no data describing evaporative emissions are available. For the vapor-venting and spillage emission processes, emission rates calculated from E15 and E10 fuel speciation data from the EPAct Program were used to adjust the E10 evaporative emissions speciation.[42] Resulting toxic fractions are provided in Table 53.

For vehicles containing 20% ethanol, toxic fractions were developed for fuel speciation profiles developed from data collected in the EPAct program. Average fractions by weight were calculated as a composite of data from the seven E20 blends included in the fuel matrix. Resulting fractions are shown in Table 53.

For vehicles operating on fuels containing high levels of ethanol, ranging from 70 to 100%, the toxic fractions were developed based on the two-day diurnal evaporative emissions test from four 2007 model year FFVs from CRC E-80 program[26]. Following the typical speciation profile procedures, the fraction of each compound in a test was first calculated by dividing its emission factors (EFs) by the sum of all EFs for that test, and the percentages for a given compound were then averaged across all tests to form the composite profile. The resulting fractions are presented in Table 53.

**Table 51. Data Sources and Estimation Methods Used in Estimation of Toxic Fractions for Evaporative Hydrocarbons.**

| Compound | Process | Fraction Type | Basis for Estimation |
|---|---|---|---|
| Benzene | Vapor venting/refueling (vapor) | complex | Adapted from MOBILE6.2 |
| | Fuel leaks/spillage | complex | Adapted from MOBILE6.2 |
| MTBE | Vapor venting/refueling (vapor) | complex | Adapted from MOBILE6.2 |
| | Fuel leaks/spillage | complex | Adapted from MOBILE6.2 |
| 2,2,4-trimethylpentane | All (except permeation) | simple | Speciation profile |
| Ethylbenzene | All (except permeation) | simple | Speciation profile |
| N-Hexane | All (except permeation) | simple | Speciation profile |
| Propionaldehyde | All (except permeation) | simple | Speciation profile |
| Toluene | All (except permeation) | simple | Speciation profile |
| Xylenes | All (except permeation) | simple | Speciation profile |
| Naphthalene | | simple | |
| Ethanol | | simple | |
| | | | |

**Table 52. Complex fractions for Evaporative Emissions of Two Compounds.**

| Pollutant | Process | Equation for Toxic Fraction |
|---|---|---|
| Benzene | Vapor venting/Refueling (vapor) | (-0.03420*OXY - 0.080274*RVP + 1.4448)*BNZ/100 |
| | Fuel Leaks/Spillage | (-0.03420*OXY - 0.080274*RVP + 1.4448)*BNZ/100 |
| MTBE | Vapor Venting/Refueling (vapor) | (24.205 - 1.746*RVP)*MTBE/1000 |
| | Fuel Leaks/Spillage | (17.8538 - 1.6622*RVP)*MTBE/1000 |

OXY = oxygen content (wt%)
RVP = Reid Vapor Pressure (psi)
BNZ = benzene content (vol.%)
MTBE = methyl-tertiary-butyl ether content (vol.%).

**Table 53. Toxic Fractions for Evaporative Emissions, for Vapor-venting and Refueling-spillage Processes.**

| Pollutant | Ethanol Level | | | | |
|---|---|---|---|---|---|
| | 0.0% (E0) | 10% (E10) | 15% (E15) | 20% (E20) | 70-100% |
| Ethanol | 0.00000 | 0.11896 | 0.1935 | 0.2227 | 0.61042 |
| Naphthalene | 0.00040 | 0.00040 | 0.0000 | ? | 0 |
| 2,2,4-Trimethylpentane | 0.01984 | 0.03354 | 0.05313 | 0.0430 | 0.00830 |
| Ethyl Benzene | 0.02521 | 0.01721 | 0.01662 | 0.0155 | 0.00124 |
| N-Hexane | 0.02217 | 0.02536 | 0.007478 | 0.0186 | 0.01276 |
| Toluene | 0.09643 | 0.14336 | 0.1406 | 0.0874 | 0.01608 |
| Xylene [a] | 0.07999 | 0.06423 | 0.05735 | 0.0711 | 0.00733 |
| Benzene | | | 0.02758 | 0.0073 | 0.00664 |

### 3.1.2 Permeation

The composition of hydrocarbons emitted through permeation differs substantially from that of hydrocarbons emitted through other processes. Work to better characterize these permeation emissions was recently conducted by Southwest Research Institute for EPA and the Coordinating Research Council.[43] Data from 3-day diurnal tests on vehicles meeting Tier 1 and near-zero evaporative emission standards were used. Fractions representing emissions of toxic compounds relative to total VOC were estimated for gasoline fuels containing 0-10% ethanol by averaging data from fuels with varying vapor pressures. Fractions are presented in Table 54, for all compounds except benzene and naphthalene.

For benzene, the diurnal emissions equation from MOBILE6.2 was used to calculate the permeation fraction $f_{benz,permeation}$, since it accounts for changes in oxygenate, vapor pressure and fuel benzene levels, as shown in Equation 17.[44] However, a study of permeation emissions

suggests that the fraction of benzene from permeation is about 1.77 times higher than the ratio associated with evaporation.[45] Thus the diurnal emissions algorithm was multiplied by 1.77.

$$f_{\text{benz,permeation}} = 1.77\left[\left(-0.02895\,\text{OXY} - 0.080274\,\text{RVP} + 1.3758\right)\text{benz}/100\right] \quad \textbf{Equation 17}$$

In the absence of data on permeation emissions for MTBE, a complex fraction $f_{\text{MTBE,permeation}}$ is calculated using the resting-loss algorithm from MOBILE6.2 (Equation 18).

$$f_{\text{MTBE,permeation}} = \left(22.198 - 1.746\,\text{RVP}\right)\text{MTBE}/1{,}000 \quad \textbf{Equation 18}$$

To estimate toxic fractions for vehicles operating on fuels containing 15% ethanol, the fractions for E10 and E20 fuels were linearly interpolated for ethanol levels of 15%. The fractions for the E10 and E20 fuels were derived from the CRC E-77-2b and CRC E-77-2c test programs.[46,47] Toxic fractions are shown in Table 54.

For vehicles operating on fuels containing 20% ethanol, fractions were developed using data from the CRC E-77-2c test program.[48] Fractions are presented in Table 54.

**Table 54. Toxic Fractions Representing Permeation Emissions as Components of Total VOC Emissions, by Ethanol Level (Source: CRC E-77-2b).**

| Pollutant | Ethanol Level | | | | |
|---|---|---|---|---|---|
| | 0.0% (E0) | 10% (E10) | 15% (E15) | 20% (E20) | 70-100% |
| 2,2,4-Trimethylpentane | 0.036 | 0.024 | 0.0172 | 0.0107 | 0. 00830[1] |
| Ethylbenzene | 0.003 | 0.001 | 0.0017 | 0.0019 | 0. 00124[1] |
| N-Hexane | 0.050 | 0.065 | 0.0472 | 0.0308 | 0. 01276[1] |
| Toluene | 0.110 | 0.101 | 0.0666 | 0.0354 | 0. 01608[1] |
| Xylene(s) | 0.016 | 0.011 | 0.0127 | 0.0140 | 0. 00733[1] |
| Ethanol | 0.000 | 0.202 | 0.2694 | 0.3296 | 0. 61042[1] |
| Naphthalene[1] | | | 0.0000 | | 0[1] |
| Benzene | | | 0.0236 | 0.0244 | 0. 00664[1] |

[1] Identical to fractions for the vapor-venting process, based on CRC E-80 program (Table 53).

For ethanol levels less of 10% and less, the toxic fraction for non-permeation evaporative emissions was also applied to permeation.

## 3.2 Diesel Vehicles (heavy-duty, light duty?)

For diesel-fueled vehicles, evaporative emissions are estimated for the refueling-spillage process only. As no results describing the speciation of spilled diesel fuel, we developed toxic fractions of total VOC based on a diesel "headspace" profile. In which the headspace is the empty space above the liquid fuel in a tank. The profile used was no. 4547 from the SPECIATE database.[49] The fractions are shown in Table 55.

**Table 55. Toxic Fractions for the fuel-spillage Process, for Diesel fuel.**

| Pollutant | Toxic fraction |
|---|---|
| 2,2,4-Trimethylpentane | 0.00974 |
| Ethyl Benzene | 0.00324 |
| N-Hexane | 0.01076 |
| Toluene | 0.01419 |
| Xylene | 0.01222 |
| Benzene | 0.00410 |

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# Appendix A: Development of Motor Vehicle Emission Factors for Mercury

## Calculation of Mercury Emission Factors from Vehicle Tests

In 2005, the USEPA National Exposure Research Laboratory (NERL) collected mercury samples in the raw exhaust from 14 light-duty gasoline vehicles and two heavy-duty diesel vehicles. The work plan for this project includes details of the methods used that are not reproduced here including quality assurance and quality control for Hg collection and analysis. This information can be obtained from EPA upon request. Briefly, mercury and regulated pollutant data were collected during two sets of three consecutive LA92 drive cycles for each vehicle. The morning set of LA92 cycles began with one 'cold start' and the afternoon set of three LA92 cycles began with a 'hot start'. The intake air was filtered through charcoal to greatly reduce background mercury concentrations entering the vehicle intake. Separate sample lines were used for gaseous and particulate mercury species. Samples analyzed for mercury were drawn from raw exhaust at a constant flow rate and fixed dilution. Carbon dioxide measurements were also taken in the exhaust stream where mercury samples were collected.

Mercury samples were collected in raw exhaust since previous data suggested that mercury levels might be sufficiently low to challenge mercury detection limits. This sampling method imposed a challenge in calculating emission factors since it assumes that the exhaust flow rate from the vehicle is constant. Calculation of exhaust flow and its application to the development of mercury emission rates is described below.

Evaporative losses of mercury from motor vehicles and loss of mercury during refueling were not measured. The emission of mercury through evaporative processes is expected to be negligible compared with that expected from exhaust emissions.

A description of the vehicles tested for which data were used in developing emission rates is provided in Table 1. The data collected from these vehicles in diluted exhaust in the constant volume sampler (CVS) included total hydrocarbon (THC), carbon dioxide ($CO_2$), nitrogen oxides ($NO_x$), methane ($CH_4$), and carbon monoxide (CO). In raw, undiluted exhaust, data collected included elemental and total gas-phase mercury, particulate mercury and $CO_2$. Gas-phase mercury was also measured in the intake air. Total air flow was measured for all sampling systems and corrected to standard temperature and pressure conditions. The data streams had different reporting frequencies, all due to the nature of the instrumentation. The dilute measurement of the standard emission gases (THC, $CO_2$, $NO_x$, CH4, and CO), CVS flows, and vehicle speed were reported at 1 Hertz. The gas-phase mercury samples were analyzed at 2.5 minute intervals and particle-phase mercury samples were collected cumulatively for the duration of three consecutive LA92 cycles. Gas-phase elemental mercury in the engine intake air was measured at five-minute intervals.

Table 1. Vehicles tested for Mercury Emissions

| Model Year | Make | Model | Fuel Type | Odometer (mi) | Cylinders | Displacement (L) |
|---|---|---|---|---|---|---|
| 2005 | MERCURY | GRAND MARQUIS LS | Gasoline | 9,953 | 8 | 4.6 |
| 2005 | FORD | MUSTANG CONVERTIBLE | Gasoline | 5,424 | 6 | 4.0 |
| 2003 | SATURN | L 200 | Gasoline | 29,667 | 4 | 2.2 |
| 2002 | HONDA | ACCORD EX | Gasoline | 51,824 | 4 | 2.3 |
| 2001 | HONDA | ACCORD EX | Gasoline | 88,611 | 4 | 2.3 |
| 2001 | CHRYSLER | PT CRUISER | Gasoline | 54,010 | 4 | 2.4 |
| 2000 | CHEVROLET | SUBURBAN | Gasoline | 39,787 | 8 | 6.0 |
| 2000 | JEEP | CHEROKEE SPORT | Gasoline | 48,468 | 6 | 4.0 |
| 1999 | FORD | F250 XLT | Diesel | 113,897 | 8 | 7.3 |
| 1999 | FORD | F250 XLT SD | Diesel | 109,429 | 8 | 7.3 |
| 1998 | HONDA | CIVIC DX | Gasoline | 204,983 | 4 | 1.6 |
| 1994 | CHEVROLET | SILVERADO | Gasoline | 129,521 | 8 | 5.7 |
| 1992 | CHEVROLET | S10 BLAZER | Gasoline | 162,249 | 6 | 4.3 |
| 1991 | HONDA | ACCORD EX | Gasoline | 143,289 | 4 | 2.2 |
| 1987 | CHRYSLER | FIFTH AVENUE | Gasoline | 72,573 | 8 | 5.2 |
| 1984 | FORD | F150 PICKUP | Gasoline | 36,727 | 8 | 5.8 |

Exhaust flow was integrated at the same reporting frequency as the mercury exhaust values for a particular test and then used to calculate total, elemental, and reactive gas-phase mercury mass emissions. The intake air mercury values were typically collected at half the frequency of the mercury exhaust values. There is precedent in accepting background values measurements at less frequent intervals and using them to correct exhaust measured values that are reported at higher frequencies. The particulate matter measurements were filter-based, test-level measurements and were reported in that manner.

**Calculation of Emission Rates**

The time-series for the regulated pollutants and mercury were aligned; however, emissions data were not related to vehicle specific power as the data are not to be used estimate modal emissions modeling. Emission rates were calculated separately for elemental gas-phase mercury, reactive gas-phase mercury and particulate mercury. Elemental gas-phase mercury in the exhaust was corrected for the intake air concentration of elemental mercury. To estimate the gas-phase mercury concentration in dilute exhaust from the measured mercury in raw exhaust, the dilution factor was applied. For light-duty gasoline vehicles, the dilution factor equation found in 40 CFR 90.426 (d) was used:

$$\text{Dilution factor} = 13.4 / ([CO_2\%] + ([\text{THC, ppm}] + [\text{CO, ppm}])* 0.0001)$$

Exhaust flow = (CVS flow / dilution factor)

Exhaust flow calculation was initiated when the analytical equipment indicated that the dilute exhaust $CO_2$ concentration was greater than the background $CO_2$ concentration.

To calculate exhaust flow for the diesel vehicles, the dilution factor was calculated by simply dividing $CO_2$ in the raw exhaust by $CO_2$ in the CVS. This method was used because diesel engines operate across a very wide range of fuel to air mixtures and the CFR method described above was not appropriate.

**Determination of Reactive Gas Mercury Mass in Exhaust**

Reactive gas-phase mercury (RGM) was calculated by subtracting elemental gas-phase mercury measurements from total gas-phase mercury measurements. RGM values were typically small and therefore influenced by the variability in the elemental mercury measurements. Negative RGM values for a given measurement period were observed. Values for which there was not a positive RGM measurement were treated as non-detects and were nulled in the aggregation of RGM values for the test. The measurement uncertainty for gas-phase elemental mercury was estimated from quantitative recovery of injections of known amounts of mercury into the sampling system. The uncertainty in measuring elemental mercury was applied to the total gas-phase and elemental gas-phase measurements to determine when the RGM value was above the measurement uncertainty. Values within the measurement uncertainty were not included in the emission factor calculation.

**Calculating Weighted Emission Test Results**

Highway vehicle tests on the LA92 cycle, a more aggressive chassis-dynamometer test similar in concept to the Federal Federal Test Procedure's (FTP) UDDS or LA4. Like the FTP, the LA92 includes a cold start, a hot start, and a hot stabilized phase using identical drive schedules for the starts. It was, therefore, considered appropriate to follow the precedent of calculating a weighted emission factor (representing cold start and hot start driving) for each vehicle in the same manner as the FTP, using the equation below for each test (a test consisting of all six LA92 cycles performed on each vehicle).

We summed the gas-phase mercury mass emissions for the first phase (300 seconds) of the morning test and last phase (1,135 seconds) of the individual LA92 drive schedules for all the tests (e.g., 'hot stabilized emissions'), divided by the total distance covered in these phases and multiplied by 0.43. We also summed the sum of the mass gas-phase mercury emissions of the first phase of the afternoon test and last phase (1,135 seconds) of all the tests, divided by the total distance covered in these phases and multiplied by 0.57. The two terms were summed to calculate a test level emission rate for each of the gasoline powered vehicles.

Equation used to calculate test-level emission rates:

$$\overline{E}_{\mathrm{Hg}} = 0.43\left(\frac{C+R}{C_m+R_m}\right)+0.57\left(\frac{H+R}{H_m+R_m}\right)$$

Where:
$E_{\mathrm{Hg}}$ = mean aggregate emission rate (g/mi),
$C$ = mercury mass collected in the first 300 seconds of the first morning test ('cold start', g ) ,
$C_m$ = distance covered in the cold start phase (mi),
$R$ = mercury mass collected in the last 1,135 seconds of all six cycles of the LA92 ('hot stabilized', g )
$R_m$ = cumulative distance covered in all six cycles of the LA92 ('hot stabilized ', mi )
$H$ = mercury mass collected in the first 300 seconds of the first afternoon test ('hot start', g )
$H_m$ = distance covered by the hot start (mi)

It should be noted that the 'hot start' in the afternoon typically occurred after the vehicle had been off for at least 1 hour, making this start closer to a 'cold start' than 'hot start'. Since the true cold start emissions were slightly higher than hot start emissions, it is expected that this approach would bias the emission factors high by a small amount, relative to the value expected for a cycle composite.

Particulate mercury emissions could not be apportioned into modes of operation in similar manner because filters were collected across all three LA92 cycles and could not be parsed into the three phases. A test-level emission rate was calculated by multiplying the morning particulate mercury emission rate by 0.43 and the afternoon particulate mercury emission rate by 0.57 and adding the two values together.

The average of emission factors across vehicles was calculated for each form of mercury and is reported in Table 2. A simple average was used since the data did not suggest that mercury concentrations varied by vehicle age, mileage, displacement or other factors.

Mercury emission factors for on-road diesel engines were obtained from the first 715 seconds of the morning and afternoon tests on the Ford F250 XLT SD; data from the second diesel vehicle could not be used. The first 715 seconds is approximately half of the first of the three LA92 drive cycles that made up a single test. The truncation of the test was due to sample flow problems in the mercury sampling manifold due to particulate matter restricting flow across the particulate matter filters. Graphical analysis of exhaust flow indicated that at they appeared nominal during the first LA92 cycle. It was decided that only using data collected before 715 seconds into both tests provided the most reliable data.

Table 2. Mercury Emission Factors from Mobile Sources

| Source Category | Pollutant | Pollutant ID | Emission Rate | Units |
|---|---|---|---|---|
| Gasoline motor vehicles | Elemental gas-phase | 200 | 1.1E-07 | grams/mile |
| | Reactive gas-phase | 201 | 9.9E-09 | grams/mile |
| | Particulate phase | 202 | 4.0E-10 | grams/mile |
| Diesel motor vehicles | Elemental gas-phase | 200 | 6.2E-09 | grams/mile |
| | Reactive gas-phase | 201 | 3.2E-09 | grams/mile |
| | Particulate phase | 202 | 1.6E-09 | grams/mile |
| Gasoline nonroad engines | Elemental gas-phase | 200 | 1.8E-06 | grams/gallon |
| | Reactive gas-phase | 201 | 1.7E-07 | grams/gallon |
| | Particulate phase | 202 | 6.9E-09 | grams/gallon |
| Diesel nonroad engines | Elemental gas-phase | 200 | 1.2E-07 | grams/gallon |
| | Reactive gas-phase | 201 | 6.2E-08 | grams/gallon |
| | Particulate mercury | 202 | 3.2E-08 | grams/gallon |