Air Toxic Emissions from Onroad Vehicles in MOVES201X

XX, 201X

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1 Introduction

Through MOVES, users can estimate inventories for selected compounds identified as air toxics in the National Emission Inventory (NEI) and National Air Toxics Assessment (NATA), and for which adequate data are available to develop emissions estimates. This document describes the data and methods used in MOVES201X to estimate emissions of toxic compounds emitted from highway vehicles, incorporating data from recent programs conducted on vehicles employing the latest technologies. MOVES201X includes the capability to estimate emissions for ethanol blends containing more than 10 percent ethanol, including E15, E20, and E85 (70-100 percent ethanol).

The toxics included in MOVES are classified into four categories:

1) Volatile Organic Compounds (VOC): EPA defines VOC as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity.[1]
2) Polycyclic aromatic hydrocarbons (PAHs): This category is defined as hydrocarbons containing fused aromatic rings. These compounds can be measured in the gaseous phase, particulate phase, or both, depending on properties of the compound, particle characteristics and conditions in the exhaust stream or the atmosphere.
3) Dioxins and furans: This category includes polychlorinated organic compounds which are persistent in the environment and considered bioaccumulative in aquatic and terrestrial food chains.
4) Metals: This category includes metals or metal-containing compounds in elemental, gaseous and particulate phases.

Specific compounds in each category are listed in Table 1 through Table 4. Note that each compound is identified by its pollutantID in the MOVES database. With the exception of the metal species in Table 4, each compound is also identified by its Chemical Abstracts Service Registry number (CAS number).[2] For most other compounds, the identifier for the National Emissions Inventory (NEIPollutantCode in the pollutant table) is identical to the CAS number (minus the dashes). In MOVES201X, methyl-tertiary-butyl-ether (MTBE) has been removed from the volatile organic compounds (Table 1), since it has been many years since this pollutant has been used as a gasoline additive in any significant quantity.

Table 1. Hydrocarbons and Volatile Organic Compounds Included in MOVES

Pollutant	pollutantID	CAS Number
Benzene	20	71-43-2
Ethanol	21	64-17-5
1,3-Butadiene	24	106-99-0
Formaldehyde	25	50-00-0
Acetaldehyde	26	75-07-0
Acrolein	27	107-02-8
2,2,4-Trimethylpentane	40	540-84-1
Ethyl Benzene	41	100-41-4
Hexane	42	110-54-3
Propionaldehyde	43	123-38-6
Styrene	44	100-42-5
Toluene	45	108-88-3
Xylene(s)[1]	46	1330-20-7

Note:
[1] These species represent the sum of emissions from three isomers of xylene, i.e., *ortho*-, *meta*-, and *para*-xylene.

Table 2. Polycyclic Aromatic Hydrocarbons Included in MOVES

Pollutant	pollutantID		CAS Number
	(gaseous phase)	(particulate phase)	
Acenaphthene	170	70	83-32-9
Acenaphthylene	171	71	208-96-8
Anthracene	172	72	120-12-7
Benz(*a*)anthracene	173	73	56-55-3
Benzo(*a*)pyrene	174	74	50-32-8
Benzo(*b*)fluoranthene	175	75	205-99-2
Benzo(*g,h,i*)perylene	176	76	191-24-2
Benzo(*k*)fluoranthene	177	77	207-08-9
Chrysene	178	78	218-01-9
Dibenzo(*a,h*)anthracene	168	68	53-70-3
Fluoranthene	169	69	206-44-0
Fluorene	181	81	86-73-7
Indeno(1,2,3,*c,d*)pyrene	182	82	193-39-5
Naphthalene	185	23	91-20-3
Phenanthrene	183	83	85-01-8
Pyrene	184	84	129-00-0

Table 3. Dioxins and Furans Included in MOVES

Pollutant	pollutantID	CAS Number
2,3,7,8-Tetrachlorodibenzo-p-Dioxin	142	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-Dioxin	135	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	134	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	141	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	130	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin	132	35822-46-9
Octachlorodibenzo-p-dioxin	131	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran	136	51207-31-9
1,2,3,4,6,7,8-Heptachlorodibenzofuran	144	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran	137	55673-89-7
1,2,3,4,7,8-Hexachlorodibenzofuran	145	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran	140	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran	146	72918-21-9
1,2,3,7,8-Pentachlorodibenzofuran	139	57117-41-6
2,3,4,6,7,8-Hexachlorodibenzofuran	143	60851-34-5
2,3,4,7,8-Pentachlorodibenzofuran	138	57117-31-4
Octachlorodibenzofuran	133	39001-02-0

Table 4. Metals Included in MOVES

Pollutant	pollutantID
Mercury (elemental gaseous)	60
Mercury (divalent gaseous)	61
Mercury (particulate)	62
Arsenic compounds	63
Chromium (Cr6+)	65
Manganese compounds	66
Nickel compounds	67

Toxics are emitted through exhaust, crankcase and evaporative processes, and by both light-duty and heavy-duty vehicles, operating on gasoline, diesel and compressed natural gas (CNG) fuels. MOVES estimates emissions from vehicles representing relevant combinations of technology and fuel; however, the availability and comprehensiveness of data acquired and used varied widely. Consequently, the methods and approaches used to develop model inputs also varied as necessary to incorporate the latest and best data into the model.

During MOVES runs, emissions of toxic compounds (except for metals and dioxins/furans), are estimated as fractions of the emissions of VOC, or for toxic species in the particulate phase, fractions of total organic carbon < 2.5 μm ($OC_{2.5}$). Emissions of VOC themselves are calculated from emissions of total hydrocarbon (THC). All toxic fractions are mass-based (as opposed to using molar-ratios).

For some compounds, the toxic emissions are estimated using fractions that vary with levels of other fuel properties, such as ethanol, aromatics or Reid Vapor Pressure (RVP). Fractions that vary according to fuel properties are termed “complex” by MOVES. For other sets of compounds, “simple” fractions are used, meaning that the fractions are constants and do not vary

with fuel properties. Note that the generalizations made here apply to evaporative as well as to exhaust emissions. In addition, in some cases, available data were sufficient to model emission as a function of two different combustion processes, e.g., start and running exhaust emissions. However, in other cases, available data were not adequate for this purpose, with the result that single sets of inputs are used to represent both start and running emissions. Similarly, for evaporative emissions, inputs were developed to distinguish "permeation" and "non-permeation" processes. Finally, fractions vary with the levels of emission control (e.g., pre-Tier 2 versus Tier 2), and for pre-2001 vehicles, catalyst type and fuel delivery system.

The approach differs for estimation of emissions of metals and dioxin/furans. These species are estimated directly through application of emission rates that are assumed to be independent of operating mode. Rates for metals and dioxins/furans are expressed on a distance-specific basis (g/mile).

It should be noted that metals and dioxin emission rates are only produced from the 'running' exhaust emission process with the g/mile rates. Due to a lack of data, MOVES does not estimate their emissions explicitly from other exhaust emission processes such as start, extended idle, auxiliary power unit usage, and crankcase processes. However, in some cases, the start emissions for these pollutants are included in the driving cycle used to derive distance-based emission factors as discussed in the report.

For gasoline fuels containing ethanol between 70 and 100 volume percent (vol. percent), a uniform approach was used to develop a set of inputs to estimate toxics emissions. The data used for this purpose were typically measured on "E85" blends, containing 70 to 85 vol. percent ethanol.

It is important to note that the inputs used to estimate emissions of toxics do not vary by temperature (i.e., the ambient temperature simulated during a run). However, the inventories of toxic compounds estimated by the model may vary by ambient temperatures for specific runs because VOC and $OC_{2.5,}$ do vary by temperature, and as described above, emissions of toxics compounds are estimated as fractions of VOC or $OC_{2.5}$ emissions.

1.1 Overview

The report first considers exhaust emissions from gasoline vehicles, covered in Section 2. The data used to develop the emission rates are based on light-duty gasoline vehicles. However, the light-duty gasoline emission rates are applied to all gasoline vehicles, including motorcycles and heavy-duty gasoline trucks. For volatile organic compound toxic emissions, the rates are derived from two broad groups of gasoline vehicles, incorporating differences in vehicle technologies, emission-control technologies and emissions standards, as well as subsets of available data and analytic methods. These two groups are defined as "model year 2000 and earlier," and "model year 2001 and later." The "model year 2001 and later" group represents emissions starting with light-duty gasoline vehicles regulated under the National Low Emission Vehicle (NLEV) program, which began with 2001 model year vehicles, followed by the Tier 2 Light-duty vehicle emission standards[3], which began with 2004 model year vehicles.

For other toxic emissions from gasoline vehicles (PAHs, metals, and dioxins), we estimated fleet-average toxic emission ratios, with no distinction for vehicle technology or model year, as discussed in Sections 2.2, 2.3, and 2.4.

Next, the report considers exhaust emissions from diesel vehicles, covered in Section 3. The development of inputs for diesel vehicles are defined as "pre-2007", "model year 2007 through 2009", and "2010 and later" based on technology and emissions standards for heavy-duty vehicles. This distinction is made because emission controls on 2007 through 2009 and 2010 and later engines differ, and have a substantial effect on composition of emissions. In addition, due to a lack of applicable data, the toxic emission rates developed from heavy-duty trucks are used to represent light-duty diesel vehicles, as well as small diesel engines used as auxiliary power units, as noted in Section 3. This report documents updates made to the toxics emission rates for diesel engines meeting 2010 and later heavy-duty engine standards in MOVES201X, using recently published speciation data from Phase 2 of the Advanced Collaborative Emissions Study.[40]

Section 4 contains the derivation of the toxic emission rates for CNG-powered heavy-duty vehicles in MOVES. Toxic emissions from evaporative emission processes and crankcase emission processes from all vehicle and fuel types are addressed in Sections 5 and 6.

2 Gasoline Exhaust

The following sections describe methods and data used to estimate VOCs (Section 2.1), PAHs (Section 2.2), metals (Section 2.3), and dioxins and furans (Section 2.4) in gasoline vehicle exhaust.

2.1 Volatile Organic Compounds

Within VOCs, there are separate subsections for vehicles operating on gasoline containing low ethanol percentages (Section 2.1.1) and high-ethanol percentages (Section 2.1.2).

2.1.1 Vehicles Operating on Fuel Blends Containing 0-20 percent Ethanol

Within this sub-section, we further delineate the methods and data used for estimating VOCs from 2000 and earlier vehicles (Section 2.1.1.1) and 2001 and later model year vehicles (Section 2.1.1.2).

2.1.1.1 2000 and Earlier Model Year Vehicles

Table 5 summarizes the methods used to estimate VOC toxic fractions. The specific data and methods used for each are described in further detail below.

Table 5. Calculation Methods for VOC

Compound	Fraction Type	Basis for Estimation
Benzene	complex	Complex Model
1,3-Butadiene	complex	Complex Model
Acetaldehyde	complex	Complex Model
Formaldehyde	complex	Complex Model
2,2,4-Trimethylpentane	Simple	SPECIATE profile
Acrolein	Simple	SPECIATE profile
Ethylbenzene	Simple	SPECIATE profile
n-Hexane	Simple	SPECIATE profile
Propionaldehyde	Simple	SPECIATE profile
Styrene	Simple	SPECIATE profile
Xylene(s)	Simple	SPECIATE profile
Ethanol	Simple	4 test programs outlined in Section 2.1.1.3

2.1.1.1.1 Overview of the Complex Model

For the first four compounds listed in Table 5, "complex" toxic fractions of VOC were estimated through application of equations developed for the Complex Model for Reformulated Gasoline.[4] The equations are based on about 1,800 observations collected on vehicles equipped with three-way or three-way-plus-oxidation catalysts.[a] The equations were developed by stratifying the light-duty gasoline fleet into ten technology groups and fitting statistical models to subsets of data for each group. The resulting sets of equations are known collectively as the "unconsolidated Complex Model." The ten groups were assigned as combinations of fuel system, catalyst type, air injection (yes/no), exhaust-gas recirculation (EGR), and normal/high emitter status. The first nine groups were intended to represent the "normal–emitting" vehicles. The tenth group represents the "high emitters," regardless of technology.
The Complex Model was designed to model the "complex" behavior of selected emissions in relation to changes in a set of selected fuel properties. The underlying dataset included measurements collected on sample of vehicles manufactured in model year (MY) 1990 or earlier, and reflecting "Tier 0" standards over a variety of gasoline formulations.

The Complex Model is composed of sets of statistical models for each pollutant that were fit to emission measurements on different 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 Model, 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,

[a] While more recent emissions data are available for Tier 1 and earlier vehicles, such as data from the Kansas test program mentioned earlier, testing was not done on a matrix of fuels which enable development of a fuel effects model.

the model is fit as shown in Equation 1, using terms for oxygenate (wt. percent), aromatics (vol. percent) and RVP (psi) as examples.

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

The mean values used for centering all individual fuel-property values are presented in Table 7. Sets of coefficients (β values in Equation 1) for models by technology group are presented for acetaldehyde, formaldehyde, benzene and 1,3-butadiene in Table 8 to Table 11. Dashes in table cells indicate no coefficient was fit for that property. It should be noted that the sulfur effects terms in the original Complex Model were not included when the model was adapted for inclusion in MOVES; rather, the sulfur effects on toxic emissions are assumed to be proportional to the effects of sulfur on total VOC, as estimated by MOVES.

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

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

Table 7. Mean Fuel-Property Values Used for Centering Terms in the Complex Model

Property	Units	Mean Value
Aromatics	Vol. %	28.26110
Olefins	Vol. %	7.318716
Ethyl-tertiary-butyl-ether (ETBE)[1]	Wt. %	0.023203
Ethanol (EtOH)[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

Notes:
[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							
	Aromatics	Olefins	ETBE	EtOH	TAME	RVP	E200	E300
1	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
2	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
3	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
4	-0.05548	-	0.316467	0.249326	-	0.24230	-	-0.01216
5	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
6	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
7	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
8	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
9	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216
10	-0.05548	-	0.316467	0.249326	-	-	-	-0.01216

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

Technology Group	Fuel Property							
	Aromatics	Olefins	ETBE	EtOH	TAME	RVP	E200	E300
1	-0.00717	-	-	-	-	-	-	-0.01023
2	-0.00717	-	-	-	-	-	-	-0.01023
3	-0.00717	-	-	-	-	-	-	-0.01023
4	-0.00717	-	-	-	-	-	-	-0.01023
5	-0.00717	-	-	-	-	-	-	-0.01023
6	-0.00717	-	-	-	-	-	-	-0.01023
7	-0.00717	-	-	-	-	-	-	-0.01023
8	-0.00717	-	-	-	-	-	-	-0.01023
9	-0.00717	-	-	-	-	-	-	-0.01023
10	-0.00717	-0.03135	-	-	-	-	-	-0.01023

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

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

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

Technology Group	Fuel Property				
	Aromatics	Olefins	Oxygenate	E200	E300
1	-0.00401	0.028238	-	-0.00731	-0.01678
2	-0.00401	0.028238	-	-0.00731	-0.01678
3	-0.00401	0.028238	-	-0.00731	-0.00625
4	-0.00401	0.028238	-	-0.00731	-0.01678
5	-0.00401	0.028238	-	-0.00731	-0.01678
6	-0.00401	0.028238	-	0.005786	-0.01678
7	-0.00401	0.028238	-	-0.00731	-0.01678
8	-0.00401	0.028238	-	-0.00731	-0.01678
9	-0.00401	0.028238	-	-0.00731	-0.01678
10	-0.00401	0.043696	-0.06077	-0.00731	-0.00806

2.1.1.1.2 Application of the Complex Model

In MOVES, the complex model equations are consolidated by weighting them together using model-year specific weights based on the mix of technologies in the sales fleet for each model year, as obtained from MOBILE6.2.

For each compound, Equation 1 is used to estimate the effects of both "base" and "target" fuels. We assume that vehicles were running on a specific fuel when the data underlying the base emission rates were measured. We refer to these fuels as "base" fuels and use them as reference points to estimate the effects of "target" fuels simulated during MOVES runs.[18] The "target" fuels are represented by specific sets of fuel properties and represent fuels "in-use" in the geographic area(s) and season(s) being modeled in MOVES.

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:

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

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 for each model year from 2000 back to 1970, as a weighted average of the fraction of sales in each group in each model year, for the groups, as shown in Equation 3. The weights are shown in Table 12. The weights represent the sales fractions for the ten vehicle technologies defined in Table 6 above.

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. The application of Equation 3 to each of the thirty ages listed in Table 12 gives a set of 30 adjustments that gets applied to a single model year, which represents a specific age with respect to the calendar year simulated.

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

The mean adjustments calculated in Equation 3 are then applied to estimate emissions of the toxic on the target fuel ($E_{\text{relative,toxic}}$), representing 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 values of $f_{\text{adj,mean}}$ would be 0.0.

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

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 of each toxic to calculate a fraction of VOC used to estimate the total mass of emissions for each toxic during a model run. These fractions are denoted as f_{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 (I_{toxic}) during a model run are estimated by multiplying the mass of VOC emissions estimated by MOVES (I_{VOC}) by the values of f_{toxic}.

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

The equations and parameters presented are used to estimate the fuel impacts for both Tier 0 and Tier 1 gasoline vehicles. This approach is based on the assumption that the proportional

responses of air toxic emissions to changes in fuel properties are similar for vehicles certified to both sets of standards.

The Complex Model equations are applied to running, start and extended idle emissions for gasoline-fueled vehicles for all 2000 and earlier model years for the first four pollutants listed in Table 5 (acetaldehyde, formaldehyde, benzene and 1,3-butadiene). In addition, MOVES applies the Complex Model based on light-duty gasoline vehicles to heavy-duty gasoline vehicles. This step was taken because the very limited data specific to heavy-duty gasoline vehicles used in MOBILE6.2 were considered not adequate to accurately capture the effects of fuel properties on those vehicles.

Table 12. Weights Applied to Complex Model Coefficients for Technology Groups, by Age (Vehicle Age 0 Represents Model Year 2000)[b]

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

2.1.1.1.3 Simple Fractions of VOC

Table 13 lists toxic fractions of VOC for a set of additional compounds designed to represent toxic emissions for several fuel blends containing different oxygenates. For gasoline fuels containing 0 and 10 percent ethanol (E0 and E10), toxic fractions, with the exception of ethanol, were developed by Sierra Research using speciation profiles estimated from EPA's SPECIATE 4.2 database.[5] 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. percent or greater.

[b] Note that in the MOVES database, these weights are stored in the table FuelModelWtFactor.

Emissions of ethanol in exhaust are estimated for gasoline blends containing ethanol at levels of 0 to 10 vol percent. For vehicles running on 10 percent ethanol, ethanol was estimated to comprise 2.39 percent of exhaust VOC. This estimate is based on results measured on nine vehicles in four test programs.[6,7,8,9] The fraction of ethanol in exhaust VOC for blends containing 5.0 percent and 8.0 percent ethanol is estimated by interpolating linearly between the fractions for 0.0 percent and 10.0 percent ethanol.

No data exist for 2000 and earlier vehicles running on E15 or E20. These emissions comprise a minor fraction of the inventory, as conventional vehicles do not have an EPA waiver to operate on ethanol fractions higher than 10 percent[10], and flex-fuel vehicles were manufactured only for 1999 and 2000 model years. For pollutantIDs 40 – 46, we used toxics ratios for 2001 and later vehicles, found in Table 38. For acrolein and ethanol, we simply extended the E10 toxic fractions as shown in Table 13.

Table 13. Toxic Fractions of VOC for Selected Air Toxics, Representing Gasoline and Ethanol Blends

Compound	pollutantID	Fuel Blend (by Ethanol Level)			
		0% (E0)	10% (E10)	15% (E15)	20% (E20)
Ethanol	21	0	0.024	0.024	0.024
Acrolein	27	0.00063	0.00063	0.00063	0.00063
2,2,4-Trimethylpentane	40	0.018	0.018	0.022	0.0046
Ethyl Benzene	41	0.021	0.019	0.016	0.022
Hexane	42	0.016	0.016	0.011	0.025
Propionaldehyde	43	0.00086	0.00086	0.00060	0.00066
Styrene	44	0.0011	0.0010	0.0046	0.0041
Toluene	45	0.096	0.087	0.073	0.096
Xylene	46	0.078	0.070	0.069	0.093

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 14.

Table 14. 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: "Running Exhaust" (processID = 1) "Start Exhaust" (processID = 2)
fuelTypeID	Identifies broad classes of fuels, e.g., "gasoline." "diesel."	1 = "Gasoline" 2 = "Diesel" 5 = "Ethanol"
fuelSubTypeID	Identifies specific fuel classes within the fuelTypeID	10 = "Conventional Gasoline" 11 = "Reformulated Gasoline" 12 = "Gasohol (E10)" 13 = "Gasohol (E8)" 14 = "Gasohol (E5)" 15 = "Gasohol (E15)" 18 = "Gasohol (E20)" 51 = "Ethanol (E85)" 52 = "Ethanol (E70)"
modelYearGroupID	Identifies a set of model years covered by a specific value of atRatio.	1960-1970 1971-1977 1978-1995 1996-2003 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 2001 and later model year vehicles

For vehicles manufactured in model year 2001 and later, and certified to NLEV or Tier 2 standards[3], recently-collected data were 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 15. The data used to estimate the toxic fractions were obtained from the EPAct Program which is discussed in the following section.

Table 15. Data Sources and Estimation Methods Used in Estimation of Toxic Fractions for VOCs

Compound	Process	Fraction Type	Basis for Estimation
Acetaldehyde	Start	complex	application of EPAct models[1]
	Running	complex	application of EPAct models
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)

Notes:
[1] Derived from models fit to data from EPAct Phase 3 Results[12]
[2] Derived from data collected in EPAct Phase 3[12]
[3] Derived from data collected in EPAct Phase 1[23]

2.1.1.2.1 Application of the Results of the EPAct Program

Since the initiation of the MOVES project, it was clear that application of the Complex Model to 2001 and later vehicles, as in MOVES2010b and MOBILE6.2, was no longer appropriate. Thus, an updated fuel-effects model representing Tier-2 certified vehicles was needed. 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).

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. The vehicles were selected so as to represent

the latest technologies in the market at the time the program was launched (2008). The vehicles were to reflect a majority of sales for model year 2008. In addition, the vehicles were to conform primarily to Tier-2 Bin-5 exhaust standards, and to reflect a variety of emission-control technologies, as realized through the selection of a range of vehicle sizes and manufacturers. The vehicle sample is summarized in Table 16.

Table 16. Test Vehicles for the Phase-3 EPAct Program (all vehicles in MY2008)

Make	Brand	Model	Engine Size	Tier 2 Bin	LEVII Std	Odometer
GM	Chevrolet	Cobalt	2.2L I4	5	NA	4,841
GM	Chevrolet	Impala FFV	3.5L V6	5	L2	5,048
GM	Saturn	Outlook	3.6L V6	5	L2	5,212
GM	Chevrolet	Silverado FFV	5.3L V8	5	NA	5,347
Toyota	Toyota	Corolla	1.8L I4	5	U2	5,019
Toyota	Toyota	Camry	2.4L I4	5	U2	4,974
Toyota	Toyota	Sienna	3.5L V6	5	U2	4,997
Ford	Ford	Focus	2.0L I4	4	U2	5,150
Ford	Ford	Explorer	4.0L V6	4	NA	6,799
Ford	Ford	F150 FFV	5.4L V8	8	NA	5,523
Chrysler	Dodge	Caliber	2.4L I4	5	NA	4,959
Chrysler	Jeep	Liberty	3.7L V6	5	NA	4,785
Honda	Honda	Civic	1.8L I4	5	U2	4,765
Honda	Honda	Odyssey	3.5L V6	5	U2	4,850
Nissan	Nissan	Altima	2.5L I4	5	L2	5,211

The study used a total of twenty-seven test fuels spanning wide ranges of five fuel properties (ethanol, aromatics, vapor pressure, and two distillation parameters: T50 and T90). The numbers of test points and values of each property are shown in Table 17. 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 commercially available summer fuels in the U.S. (5^{th} to 95^{th} percentiles for each property).

Table 17. Levels Assigned to Experimental Factors (Fuel parameters) for the Phase-3 EPAct Program

Factor	No. Levels	Levels		
		Low	Middle	High
Ethanol (vol.%)	4	0	10, 15	20
Aromatics (vol.%)	2	15		35
RVP (psi)	2	7		10
T50 (°F)	5	150	165, 190, 220	240
T90 (°F)	3	300		340

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. Note that throughout this chapter, the terms “start,” “cold start” and “Bag 1” will be treated as synonymous, and similarly, the terms “running,” “hot-running” and “Bag 2” will also be treated as synonymous.

The experimental design embodied in the fuel set is the product of an iterative process involving balancing among research goals, fuel-blending feasibility and experimental design. As fuel properties tend to be moderately to strongly correlated, and as the goal was to enable analysis of fuel effects as though the properties were independent (uncorrelated), it was necessary to address these issues in design and analysis. Accordingly, the fuel set was designed using a computer-generated optimal design, as modified by additional requirements such as the total number of fuels and specific properties for subsets of fuels. In addition, to generate the design, it was necessary to specify the fuel effects to be estimated by the resulting model. The fuel set was designed to allow estimation of linear effects for the five properties shown in Table 17, plus two-way interactions of ethanol and the other five properties, as shown in Equation 7, in which β represents a linear coefficient for each effect.

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 \text{etOH} + \beta_2 \text{Arom} + \beta_3 \text{RVP} + \beta_4 \text{T50} + \beta_5 \text{T90} + \\ & \beta_6 \text{T50}^2 + \beta_{11} \text{etOH}^2 \\ & \beta_7 \text{etOH} \times \text{Arom} + \beta_8 \text{etOH} \times \text{RVP} + \beta_9 \text{etOH} \times \text{T50} + \beta_{10} \text{etOH} \times \text{T90} + \\ & \varepsilon \end{aligned} \qquad \textbf{Equation 7}$$

In the equation, the linear terms (e.g., $\beta_1$etOH, etc.) describe linear associations between emissions (Y) and the value of the fuel property. The quadratic terms are used to describe some degree of curvature in the relationship between emissions and the fuel property. Note that a minimum of 3 test levels for a property is needed to assess curvilinear relationships and that the design included such effects only for ethanol and T50. Two-way interaction terms indicate that the relationship between emissions and the first fuel property is dependent on the level of the second fuel property. For example, if an etOH×Arom interaction is included in a model, it implies that the effect of ethanol on the emission Y cannot be estimated without accounting for the aromatics level, and vice versa. Note that inclusion of the 11 effects in the design does not imply that all effects will be retained in all models following the fitting process. Properties for each of the test fuels are shown in Table 18.

Emissions measured include carbon dioxide (CO_2), carbon monoxide (CO), THC, methane (CH_4), oxides of nitrogen (NO_X), and $PM_{2.5}$. 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, 1,3-butadiene and ethanol.

Due to limitations in budget, the entire study design was not applied to speciated hydrocarbons, including those discussed in this chapter. For the speciated compounds, the volume of data collected varies by bag, compound and vehicle. For selected compounds, measurements for Bag 1 were taken for all vehicles over the entire fuel set, thus encompassing the entire study as designed, including replication. However, for the remaining compounds in Bag 1 and for all compounds in Bags 2, measurements were taken for a smaller number of vehicles over a reduced set of fuels, without replication. The combinations of fuels and vehicles included for each compound analyzed are summarized in Table 19.

Throughout this chapter, the complete set of 27 fuels will be denoted as the "full design," as it includes all the fuel parameter points for which the design was optimized. Similarly, the set of 11 fuels will be denoted as the "reduced design," as it covers a set of fuel parameter points narrower than that for which the design was originally optimized. Note that Table 18 also identifies the subset of fuels included in the reduced design.

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"[11] and "EPAct Analysis Report".[12]

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

Table 18. Measured Parameters for Fuels in the Phase-3 EPAct Program

Fuel[1]	etOH (vol.%)	Aromatics (vol.%)	RVP (psi)2	T50 (°F)	T90 (°F)
1	10.03	15.4	10.07	148.9	300.2
2	0	14.1	10.2	236.7	340.1
3[3]	10.36	15.0	6.93	217.5	295.9
4	9.94	15.5	10.01	221.9	337.5
5	0	34.7	6.95	237.0	300.0
6[3]	10.56	15.0	7.24	188.5	340.4
7[3]	0	17.0	7.15	193.1	298.4
8	0	15.7	10.2	221.1	303.1
9	0	35.8	10.30	192.8	341.8
10[3]	9.82	34.0	7.11	217.1	340.2
11	10.30	35.0	9.93	189.3	298.6
12	9.83	34.8	10.13	152.2	339.8
13[3]	0	34.1	6.92	222.5	337.9
14[3]	0	16.9	7.14	192.8	338.5
15	0	35.3	10.23	189.7	299.4
16	10.76	35.6	7.12	218.8	300.6
20	20.31	15.2	6.70	162.7	298.7
21[3]	21.14	35.5	7.06	167.6	305.0
22	20.51	15.0	10.21	163.2	297.3
23[3]	20.32	15.9	6.84	162.5	338.2
24	20.51	15.3	10.12	165.1	338.1
25	20.03	35.2	10.16	166.9	337.9
26	15.24	35.6	10.21	160.3	338.7
27[3]	14.91	14.9	6.97	221.5	340.3
28[3]	14.98	34.5	6.87	216.6	298.8
30	9.81	35.5	10.23	152.9	323.8
31[3]	20.11	35.5	6.98	167.3	325.2

Notes:
[1] Note that numbering of fuels is not entirely sequential throughout.
[2] This parameter was measured as "DVPE," but for simplicity, will be referred to as "RVP" in this document.
[3] These fuels included in the "reduced design."

Table 19. Features of the Study Design Applied to Speciated Compounds Selected for Analysis

Compound	Bag 1			Bag 2		
	No. vehicles	No. Fuels	replication	No. vehicles	No. Fuels	replication
Acetaldehyde	15	27	YES	5	11	NO
Formaldehyde	15	27	YES	5	11	NO
Acrolein	15	27	YES	5	11	NO
Ethanol	15	27	YES	5	11	NO
Benzene	15	11	NO	5	11	NO
1,3-Butadiene	15	11	NO	5	11	NO
Ethane	15	11	NO	5	11	NO

2.1.1.2.2 Standardizing Fuel Properties

In model fitting, as well as in applying the resulting sets of coefficients, it is necessary to first "center" and "scale" the properties of fuels, also known as "standardization." This process

simply involves first "centering" the measured fuel properties by subtracting the sample mean from the given value, 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 18). 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. percent, 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.

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

Means and standard deviations for relevant model terms are shown in Table 20. Note that the means and standard deviations shown in the table are calculated from the fuel set itself as shown in the table; in this calculation the properties are not weighted for numbers of replicates on each fuel and emission combination. In this way, the process is simplified by using the same standardization in fitting all models, as well as in subsequent applications of the models. Note also that the reduced fuel set is standardized using a different set of parameters than the full fuel set.

The process of standardization is illustrated for three test fuels in Table 21. Overall, the process applied here is similar to the "correlation transformation" sometimes applied in multiple regression. One difference in this case is that the standardization is applied only to the predictor variables, whereas it is also possible to apply it to the response variable.[13]

Table 20. Means and Standard Deviations for Fuel Properties, Based on Fuel Matrices for the Full and Reduced Designs

Model Term	Full Design[1]		Reduced Design[2]	
	Mean	Standard deviation	Mean	Standard Deviation
Ethanol (%)	10.3137	7.87956	11.0182	8.05925
Aromatics (%)	25.6296	10.0154	24.3909	9.92426
RVP (psi)	8.5178	1.61137		
T50 (°F)	190.611	28.5791	197.000	23.4536
T90 (°F)	320.533	19.4801	323.527	19.6015
etOH × etOH	0.962963	0.802769		
T50 × T50	0.962963	0.739766		
etOH × Arom	-0.03674	0.978461		
etOH × RVP	-0.0992352	0.999615		
etOH × T50	-0.541342	0.769153		
etOH × T90	0.0163277	0.972825		

Notes:

[1] Applies to models fit with data for 15 vehicles measured on 27 fuels.

[2] Applies to models fit with data for 5 or 15 vehicles measured on 11 fuels. Note that these models have no linear term for RVP and no 2nd order terms.

Table 21. Examples of One-Stage and Two-Stage Standardization for Three Test Fuels (1, 5 and 20)

Fuel	etOH (vol.%)	Arom (vol.%)	RVP (psi)	T50 (°F)	T90 (°F)	etOH × etOH	T50 × T50	etOH × Arom	etOH × RVP	etOH × T50	etOH × T90
Fuel Properties											
1	10.03	15.4	10.07	148.9	300.2						
5	0.00	34.7	6.95	237.0	300.0						
20	20.31	15.2	6.70	162.7	298.7						
Mean[1]	10.314	25.630	8.518	190.6	320.5						
Std. Dev.[1]	7.880	10.015	1.611	28.6	19.5						
One-Stage Standardized Values (Z) (Equation 9)											
	Z_e	Z_a	Z_r	Z_5	Z_9						
1	-0.036	-1.021	0.963	-1.460	-1.044						
5	-1.309	0.906	-0.973	1.623	-1.054						
20	1.269	-1.041	-1.128	-0.977	-1.121						
Mean[2]						0.9630	0.9630	-0.0367	-0.0992	-0.5413	0.1633
Std. Dev.[2]						0.8028	0.7398	0.9785	0.9996	0.7692	0.9728
Two-Stage Standardized Values (ZZ) (Equation 10, Equation 11)											
						ZZ_{ee}	ZZ_{55}	ZZ_{ea}	ZZ_{er}	ZZ_{e5}	ZZ_{e9}
1						-1.198	1.578	0.075	0.065	0.772	0.022
5						0.935	2.260	-1.174	1.373	-2.058	1.401
20						0.805	-0.012	-1.313	-1.332	-0.907	-1.478

Notes:
[1] Mean and Standard Deviations of fuel properties for the entire fuel set. See Table 20.
[2] Mean and Standard Deviations of 2nd order terms values for the entire fuel set, constructed from the one-stage *Z* values.

2.1.1.2.3 Model Fitting

Throughout model fitting, the response variable was the natural logarithm transformation of the emissions results (ln*Y*), and the predictor variables were the one- or two-stage standardized fuel properties, as shown in Table 21. Thus, the model to be fit includes some subset of the 11 candidate terms shown in Equation 12.

$$\begin{aligned}\ln Y = {} & \beta_0 + \\ & \beta_1 Z_e + \beta_2 Z_a + \beta_3 Z_r + \beta_4 Z_5 + \beta_5 Z_9 + \\ & \beta_6 ZZ_{55} + \beta_7 ZZ_{ee} + \\ & \beta_8 ZZ_{ea} + \beta_9 ZZ_{er} + \beta_{10} ZZ_{e5} + \beta_{11} ZZ_{e9} + \\ & \varepsilon\end{aligned} \qquad \textbf{Equation 12}$$

A model containing all potential candidate terms is referred to as a "full model," whereas a model containing some subset of the candidate terms is referred to as a "reduced model." The goal of model fitting is to identify a reduced model by removing terms from the full model that do not contribute to fit.

Where the available data were sufficient, "mixed models" were fit, in which the terms listed in Table 20 were included as "fixed" terms. In addition, a "random intercept" was fit for each vehicle, which represents the high degree of variability contributed to the dataset by the vehicles measured. One way of understanding this distinction that the fuel properties are "fixed" because the fuels studied span the entire range of properties under study, and because the goal of the analysis is to estimate the effect of these parameters on the mean levels of emissions. On the other hand, "vehicle" is treated as a "random" factor because the sample of vehicles measured is but one of many samples that could have been measured. In the analysis, the emission levels of the specific vehicles are not of interest *per se*, but rather the degree of variability contributed to the analysis by the different vehicles. Analyses were performed using the MIXED procedure in the Statistical Analysis System (SAS®), version 9.2.[14]

When data were not sufficient for the mixed-model approach, models were fit by "Tobit regression." This technique was used when specific datasets were affected by low-end "censoring." For some measurements, the sample ostensibly obtained from the vehicle exhaust was lower than that attributable to background levels. In these cases, we assumed that a small but detectable mass was not measured accurately due to limitations in the sampling technique. In the Tobit model, the fitting method (maximum likelihood) is modified so as to compensate for the absence of the censored measurements. As with the mixed models, individual intercepts were fit for each vehicle; however, as the Tobit procedure does not distinguish "fixed" and "random" factors, vehicles were entered into the model as fixed factors (i.e., "dummy" variables). The Tobit models were fit using the LIFEREG procedure in SAS 9.2.[15]

Model fitting was conducted by backwards elimination, in which all terms in the full model were included at the outset. In fitting successive models, terms not contributing to fit were removed based on results of likelihood-ratio tests (LRT).[16] Note that the LRT were used for model selection because all models were fit using "maximum-likelihood" (rather than "least-squares") methods.

Model fitting results for acetaldehyde, formaldehyde, acrolein and ethanol are shown in Table 22 through Table 25. Note that these four models represent "Bag 1" or "start" emissions on the LA92 cycle, based on datasets incorporating the full design. Also note that in fitting these models, an additional six terms beyond the original 11 design terms were included in the full models. These terms included one quadratic term (T90×T90), three interaction terms for aromatics, one interaction for RVP, and one interaction for the distillation parameters (T50×T90). However, none of these additional terms were retained as significant, with the single exception of the T50×T90 term.

In MOVES, emissions of toxics are estimated as fractions of volatile organic compounds in exhaust (VOC). To allow estimation of VOC, it was necessary to develop models for non-methane organic gases (NMOG). NMOG is equivalent to VOC, plus the mass of ethane and acetone.[c] It is calculated in MOVES from non-methane hydrocarbons (NMHC) by correcting for the mass of oxygenated compounds not fully measured by the flame ionization detector used to

[c] Note that acetone was treated as negligible for purposes of these calculations.

determine NMHC.[17] EPA and CARB regulations set NMOG emission standards for motor vehicles, so NMOG is an important model output. The model representing start emissions for NMOG, fit using the full design, is shown in Table 26. This model was fit using the same methods as that for total hydrocarbons (THC), as described in the Fuel Effects Report.[18]

Table 22. Acetaldehyde (Bag 1): Coefficients and Tests of Effect for the Full and Reduced Models[1]

Effect	*Full Model*					*Reduced Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-5.2324	0.08802	15	-59.4	0.000000	-5.2323	0.08785	15	-59.6	0.000000
Z_e	0.8250	0.01297	898	63.6	0.000000	0.8145	0.01020	898	79.9	0.000000
Z_a	0.03999	0.009279	898	4.31	0.000018	0.03484	0.008249	898	4.22	0.000027
Z_r	-0.03667	0.01297	898	-2.83	0.0048	-0.04170	0.008833	898	-4.72	0.000003
Z_5	0.09927	0.01826	898	5.44	0.000000	0.08670	0.01063	898	8.16	0.000000
Z_9	0.04235	0.01115	898	3.80	0.00016	0.03801	0.007764	898	4.90	0.000001
ZZ_{ee}	-0.1716	0.01548	898	-11.09	0.000000	-0.1669	0.007849	898	-21.3	0.000000
ZZ_{55}	0.07115	0.01314	898	5.42	0.000000	0.06665	0.007993	898	8.34	0.000000
ZZ_{ea}	0.03016	0.01304	898	2.31	0.021	0.01840	0.007777	898	2.37	0.018
ZZ_{er}	0.02020	0.008769	898	2.30	0.021	0.02194	0.007845	898	2.80	0.0053
ZZ_{e5}	-0.01614	0.01673	898	-0.965	0.33					
ZZ_{e9}	-0.01486	0.01072	898	-1.39	0.17					
ZZ_{ar}	0.01738	0.01618	898	1.07	0.28					
ZZ_{a5}	0.004828	0.01729	898	0.28	0.78					
ZZ_{a9}	0.008759	0.008852	898	0.99	0.32					
ZZ_{99}	0.01270	0.01503	898	0.84	0.40					
ZZ_{59}	0.02718	0.01132	898	2.49	0.013	0.03959	0.008256	898	4.80	0.000002
ZZ_{r9}	-0.0206	0.009971	898	-2.07	0.039					
σ^2_{veh}	0.1154					0.1149				
σ^2_{ε}	0.08743					0.08850				

Note:
[1] See 9.2.2 and 8.7.3 in the Project Report.[19]

Table 23. Formaldehyde (Bag 1): Coefficients and Tests of Effect for Full and Reduced Models[1]

Effect	*Full Model*					*Reduced Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-5.9771	0.1498	15	-39.9	0.000000	-5.9771	0.1498	15	-39.9	0.000000
Z_e	0.2279	0.01234	898	18.5	0.000000	0.2299	0.009640	898	23.8	0.000000
Z_a	0.03528	0.008841	898	3.99	0.000071	0.02822	0.007979	898	3.54	0.00043
Z_r	-0.05202	0.01234	898	-4.21	0.000028	-0.04718	0.008457	898	-5.58	0.000000
Z_5	0.1577	0.01738	898	9.07	0.000000	0.1672	0.01001	898	16.7	0.000000
Z_9	0.1357	0.01064	898	12.7	0.000000	0.1302	0.007360	898	17.7	0.000000
ZZ_{ee}	-0.01498	0.01475	898	-1.02	0.31					
ZZ_{55}	0.05026	0.01251	898	4.02	0.000064	0.05262	0.008341	898	6.31	0.000000
ZZ_{ea}	0.02017	0.01241	898	1.63	0.10	0.01651	0.007340	898	2.25	0.025
ZZ_{er}	0.004100	0.008366	898	0.490	0.62					
ZZ_{e5}	-0.03686	0.01594	898	-2.31	0.021	-0.01627	0.008177	898	-1.99	0.047
ZZ_{e9}	0.02181	0.01023	898	2.13	0.033	0.02004	0.008838	898	2.27	0.024
ZZ_{ar}	0.007384	0.01535	898	0.481	0.63					
ZZ_{a5}	-0.006739	0.01645	898	-0.41	0.68					
ZZ_{a9}	-0.01036	0.008437	898	-1.23	0.22					
ZZ_{99}	0.02104	0.01435	898	1.47	0.14					
ZZ_{59}	0.03974	0.01080	898	3.68	0.00025	0.03489	0.009322	898	3.74	0.00019
ZZ_{r9}	-0.003140	0.009498	898	-0.331	0.74					
σ^2_{veh}	0.3360					0.3358				
σ^2_{ε}	0.1395					0.1406				

Note:

[1] See 9.2.2 and Appendix L.3 in the Project Report.[12]

Table 24. Acrolein (Bag 1): Coefficients and Tests of Effect for Full and Reduced Models[1]

Effect	*Full Model*					*Reduced Model (FM8)*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept[2]	-7.9337					-7.9338				
Z_e	0.2571	0.02638	15	9.74	0.000000	0.2476	0.02738	15	9.04	0.000000
Z_a	0.1149	0.02128	15	5.40	0.000074	0.1122	0.02184	15	5.14	0.00012
Z_r	-0.05815	0.01799	15	-3.23	0.0056	-0.0645	0.01364	15	-4.73	0.00027
Z_5	0.1979	0.03123	15	6.34	0.000013	0.1881	0.03554	15	5.29	0.000091
Z_9	0.2465	0.02979	15	8.28	0.000000	0.2488	0.03125	15	7.96	0.000000
ZZ_{ee}	-0.06009	0.01880	15	-3.20	0.0060	-0.08306	0.01392	15	-5.97	0.000026
ZZ_{55}	0.02735	0.01709	15	1.60	0.13					
ZZ_{ea}	0.01716	0.01838	15	0.93	0.37					
ZZ_{er}	0.01253	0.01404	15	0.89	0.39					
ZZ_{e5}	-0.09661	0.02096	15	-4.61	0.00034	-0.1185	0.02415	15	-4.91	0.00019
ZZ_{e9}	0.04178	0.01618	15	2.58	0.021	0.04618	0.01120	15	4.12	0.00091
ZZ_{ar}	0.02002	0.01562	15	1.28	0.22					
ZZ_{a5}	0.01127	0.01822	15	0.62	0.55					
ZZ_{a9}	-0.007484	0.01726	15	-0.43	0.67					
ZZ_{99}	0.0004162	0.01481	15	0.028	0.98					
ZZ_{59}	0.06274	0.01552	15	4.04	0.0011	0.05985	0.01271	15	4.71	0.00028
ZZ_{r9}	0.0002551	0.01709	15	0.015	0.99					
σ^2_{veh} [1]	0.3633					0.3629				
σ^2_{ε}	0.03206					0.3213				

Notes:

[1] See 9.2.2 and 8.7.4 in the Project Report[12]

[2] Not fit by the Tobit model, manually recalculated from intercepts for individual vehicles.

Table 25. Ethanol (Bag 1): Coefficients and Tests of Effect for Full and Reduced Models

Effect	*Full Model*					*Reduced Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept[2]			15			-4.9081				
Z_e	1.4759	0.07240	15	20.38	<0.00001	1.4643	0.07115	15	20.56	<0.00001
Z_a	-0.0067	0.04327	15	-0.16	0.88					
Z_r	-0.05004	0.04316	15	-1.16	0.26	-0.05990	0.02940	15	-2.06	0.057
Z_5	0.1050	0.03806	15	2.76	0.015	0.07188	0.02964	15	2.37	0.032
Z_9	-0.1261	0.03701	15	-3.47	0.0034	-0.09990	0.03574	15	-2.78	0.014
ZZ_{ee}	-0.4787	0.06014	15	-7.96	<0.00001	-0.4967	0.05229	15	-9.51	<0.00001
ZZ_{55}	0.1261	0.05018	15	2.51	0.024	0.1121	0.03826	15	2.90	0.011
ZZ_{ea}	-0.005952	0.03881	15	-0.15	0.88					
ZZ_{e5}	0.02820	0.05277	15	0.54	0.60					
ZZ_{e9}	0.0008509	0.06491	15	0.0090	0.99					
ZZ_{er}	0.03237	0.05103	15	0.64	0.53					
ZZ_{a5}	0.03318	0.03212	15	1.04	0.32					
ZZ_{a9}	-0.01143	0.03461	15	-0.33	0.74					
ZZ_{99}	-0.5112	0.04523	15	-1.13	0.28					
ZZ_{59}	0.05311	0.04341	15	1.22	0.24					
ZZ_{ar}	0.04136	0.02855	15	1.45	0.17					
ZZ_{r9}	-0.008676	0.04644	15	-0.20	0.85					
σ^2_{veh} [1]						0.1283				
σ^2_{ε}	0.5697					0.05739				

Notes:
[1] See 9.2.2 in the Project Report.[12]
[2] Not fit by the Tobit model, manually recalculated from intercepts for individual vehicles.

Table 26. NMOG (Bag 1): Coefficients and Tests of Effect for Full and Reduced Models[1]

Effect	*Full Model*					*Reduced Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr> *t*	Estimate	Std.Err.	d.f.	*t*-value	Pr> *t*
Intercept	-0.9520	0.09077	15	-10.49	<0.0001	-0.9521	0.09089	15	-10.48	<0.0001
Z_e	0.07981	0.01326	941	6.02	<0.0001	0.08019	0.01330	941	6.027	<0.0001
Z_a	0.08789	0.00929	941	9.46	<0.0001	0.08782	0.00932	941	9.424	<0.0001
Z_r	-0.04595	0.01053	941	-4.36	<0.0001	-0.04224	0.01046	941	-4.037	<0.0001
Z_5	0.1344	0.01329	941	10.12	<0.0001	0.1345	0.01333	941	10.09	<0.0001
Z_9	0.01593	0.00925	941	1.72	0.0855					
ZZ_{ee}	0.04594	0.01760	941	2.61	0.00918	0.04432	0.01764	941	2.513	0.012
ZZ_{55}	0.07680	0.01336	941	5.75	<0.0001	0.07579	0.01340	941	5.656	<0.0001
ZZ_{ea}	0.01635	0.00906	941	1.80	0.0714	0.01693	0.00909	941	1.862	0.063
ZZ_{er}	-	-	-	-	-					
ZZ_{e5}	0.04754	0.01893	941	2.51	0.0122	0.04653	0.01898	941	2.452	0.014
ZZ_{e9}	0.01961	0.00902	941	2.17	0.0300					
σ^2_{veh}	0.1224					0.1224				
σ^2_{ε}	0.07538					0.07538				

Note:
[1] See 9.1.2 in the Project Report[12]

2.1.1.2.4 Model development under the Reduced Design

As previously discussed, the "reduced design" involved the measurement of 11 fuels on 5 or 15 test vehicles, whereas the "full design" involved measurement of 27 fuels on 15 vehicles.

As shown in Table 19, measurements of two compounds in Bag 1, and all compounds in Bag 2, were performed under the reduced design. Supplementary analyses suggested that the reduced design was not adequate to support model fitting as described in 0 above. These results suggested that in these cases, full models retaining all four linear terms would perform as well or better than corresponding reduced models, many of which would retain only single terms. Thus, this sub-section presents results for full models under the reduced design.

Models representing start (Bag 1 on LA92) emissions are presented for benzene, 1,3-butadiene, non-methane organic gases (NMOG) and ethane in Table 27 through Table 30. These models were fit using subsets of data incorporating 15 vehicles measured over 11 fuels.

Similarly, models representing hot-running (Bag 2 on LA92) emissions are presented for acetaldehyde, formaldehyde, ethanol, NMOG and ethane in Table 31 through Table 35. These models were fit using subsets of data incorporating five vehicles measured over 11 fuels.

The development of these models is described in greater detail in sub-section 9.2.1 of the EPAct analysis report.[12]

Table 27. Benzene (Bag 1): Coefficients and Tests of Effect for the Full Model (Fit Under the Reduced Design, with 15 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-4.1019	0.1392	15	-29.48	<0.0001
Z_e	-0.004685	0.03704	161	-0.126	0.90
Z_a	0.4056	0.03389	161	11.97	<0.0001
Z_5	0.04142	0.03789	161	1.09	0.28
Z_9	0.01133	0.03255	161	0.35	0.73
σ^2_{veh}	0.2741				
σ^2_{ε}	0.1873				

Note:
[1] See 9.2.2 and Appendix O.3 to the Project Report.[12]

Table 28. 1,3-Butadiene (Bag 1): Coefficients and Tests of Effect for the Full Model (Fit Under the Reduced Design, with 15 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-5.8371	0.1235	15	-47.28	1.06×10^{-17}
Z_e	-0.01729	0.03071	160	-0.56	0.57
Z_a	0.02673	0.02730	160	0.98	0.33
Z_5	0.01247	0.03031	160	4.11	0.000062
Z_9	0.10036	0.02657	160	3.78	0.00022
σ^2_{veh}	0.2192				
σ^2_{ε}	0.1089				

Note:
[1]See 9.2.2 in the Project Report.[12]

Table 29. NMOG (Bag 1): Coefficients and Tests of Effect for the Full Models (Fit under the Reduced Design, 15 vehicles, 11 fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-0.8943	0.08668	15	-10.32	0.000000033
Z_e	0.1040	0.01921	362	5.411	0.00000011
Z_a	0.09435	0.01697	362	5.559	0.000000053
Z_5	0.1527	0.01890	362	8.079	0.000000000
Z_9	0.02127	0.01648	362	1.290	0.198
σ^2_{veh}	0.1091				
σ^2_{ε}	0.08907				

Note:
[1]See 9.2.2 in the Project Report.[12]

Table 30. Ethane (Bag 1): Coefficients and Tests of Effect for the Full Models (Fit Under the Reduced Design, with 15 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-4.308	0.09833	15.0	-43.81	2.84×10^{-17}
Z_e	0.1204	0.02075	160	5.805	3.37×10^{-8}
Z_a	-0.1728	0.01844	160	-9.373	6.51×10^{-17}
Z_5	0.2169	0.02047	160	10.59	3.30×10^{-20}
Z_9	0.09531	0.01795	160	5.311	3.60×10^{-7}
σ^2_{veh}	0.1407				
σ^2_{ε}	0.04970				

Note:

[1] See 9.2.2 in the Project Report.[12]

Table 31. Acetaldehyde (Bag 2): Coefficients and Tests of Effect for the Full Models (Fit Under the Reduced Design, with 5 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-9.4189	0.1177	5	-80.1	0.000000
Z_e	0.1520	0.06080	58	2.50	0.0152
Z_a	0.07991	0.05279	58	1.51	0.136
Z_5	-0.02997	0.05957	58	-0.503	0.617
Z_9	-0.07836	0.05153	58	-1.52	0.134
σ^2_{veh}	0.05654				
σ^2_{ε}	0.3814				

Note:

[1] See 9.2.2 and Appendix K.3 to the Project Report.[12]

Table 32. Formaldehyde (Bag 2): Coefficients and Tests of Effect for the Full Model (Fit Under the Reduced Design, with 5 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept	-8.6574	0.1372	5.01	-63.10	<0.00001
Z_e	0.08456	0.05937	58.04	1.424	0.16
Z_a	0.01575	0.05154	58.05	0.306	0.76
Z_5	0.01863	0.05815	58.03	0.320	0.75
Z_9	-0.08138	0.05031	58.16	-1.62	0.11
σ^2_{veh}	0.08205				
σ^2_{ε}	0.3762				

Note:

[1] See 9.2.2 and Appendix L.4 to the Project Report.[12]

Table 33. Ethanol (Bag 2): Coefficients and Tests of Effect for the Full Model (Fit Under the Reduced Design, with 5 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept[1]	-9.3072	0.6333	5	-15.45	0.000021
Z_e	0.9233	0.2824	5	3.27	0.022
Z_a	-0.3772	0.28499	5	-1.32	0.24
Z_5	-.01910	0.2091	5	-0.091	0.93
Z_9	-0.3017	0.2416	5	-1.25	0.27
σ^2_{veh} [1]	0.3707				
σ^2_{ε}	1.0889				

Note:

[1] See 9.2.2 and Appendix N.4 to the Project Report.[12]

Table 34. NMOG (Bag 2): Coefficients and Tests of Effect for the Full Model (Fit Under the Reduced Design, with 5 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept[1]	-4.777	0.4784	5	-9.99	0.00017
Z_e	0.01778	0.03574	124	0.497	0.62
Z_a	0.03320	0.03117	124	1.07	0.29
Z_5	0.04258	0.03494	124	1.22	0.23
Z_9	0.09051	0.03038	124	2.98	0.0035
σ^2_{veh} [1]	1.1405				
σ^2_{ε}	0.1026				

Note:

[1] See 9.2.2 in the Project Report.[12]

Table 35. Ethane (Bag 2): Coefficients and Tests of Effect for the Full Model (Fit Under the Reduced Design, with 5 Vehicles, 11 Fuels)[1]

Effect	*Full Model*				
	Estimate	Std.Err.	d.f.	*t*-value	Pr>*t*
Intercept[1]	-7.724	0.7325	5	-10.54	0.00013
Z_e	0.07345	0.05873	57	1.251	0.22
Z_a	-0.1260	0.05151	57	-2.447	0.018
Z_5	0.1815	0.05727	57	3.168	0.0025
Z_9	0.1322	0.04994	57	2.647	0.010
σ^2_{veh} [1]	2.6712				
σ^2_{ε}	0.1476				

Note:

[1] See 9.2.2 and Appendix Q.4 to the Project Report.[12]

2.1.1.2.5 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. 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 VOC is estimated as NMOG minus ethane.[d]

The models generated using EPAct results allow estimation of emissions effects related to the five fuel properties included in the study design: ethanol content (vol. percent), aromatics content (vol percent), RVP (psi), T50 (°F) and T90 (°F), as well as selected interaction terms among these five parameters.

The statistical models generated from the EPAct data follow the general structure shown in Equation 13 below, which uses the model for acetaldehyde as an example (see Table 22). Note that the subsets of the potential terms vary by emission and process, depending on the results of model fitting, as described in the previous two sub-sections.

$$\text{Emissions (g/mi)} = e^{\mathbf{X\beta}} = \exp\begin{pmatrix} \beta_0 + \beta_e Z_e + \beta_a Z_a + \beta_r Z_r + \beta_5 Z_5 + \beta_9 Z_9 + \\ \beta_{ee} ZZ_{ee} + \beta_{55} ZZ_{55} + \\ \beta_{ea} ZZ_{ea} + \beta_{er} ZZ_{er} + 0.5(s_{veh}^2 + s_\varepsilon^2) \end{pmatrix}$$

$$= \exp\begin{pmatrix} -5.23 + 0.814\, Z_e + 0.0348\, Z_a - 0.0417\, Z_r + 0.0867\, Z_5 + 0.0380\, Z_9 - \\ 0.1669\, ZZ_{ee} + 0.0667\, ZZ_{55} + \\ 0.0184\, ZZ_{ea} + 0.0219\, ZZ_{er} + 0.5(0.1149 + 0.08850) \end{pmatrix} \qquad \textbf{Equation 13}$$

Where the data were sufficient, two sets of exhaust fuel effect coefficients were employed for each pollutant; one set representing cold 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. Thus, using convenient matrix notation, the expressions $\mathbf{X\beta_{toxic}}$, $\mathbf{X\alpha_{NMOG}}$ and $\mathbf{X\theta_{ethane}}$ represent models for a selected toxic compound, NMOG and ethane, respectively, calculated by applying Equation 13 to each compound for a specified fuel. The toxic emissions as a fraction of VOC emissions (f_{toxic}) are given by

$$\text{Toxic Fraction} = f_{\text{toxic}} = \frac{e^{\mathbf{X\beta}_{\text{toxic}}}}{e^{\mathbf{X\alpha}_{\text{NMOG}}} - e^{\mathbf{X\theta}_{\text{ethane}}}} \qquad \textbf{Equation 14}$$

For all compounds, the calculation shown in Equation 14 is applied in the GeneralFuelRatioExpression table. 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. In other words, if the toxic model was fit with the reduced design, we combined it with the

[d] In MOVES, VOC is typically calculated as NMOG – ethane – acetone, but for this purpose, acetone was considered negligible, and was not subtracted.

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 14. 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.

Note that for three compounds in Bag 2, levels of "left censoring," were high enough that modeling was not considered feasible. Again, "censoring" occurs when background levels of the compounds under study were as high as or higher than levels ostensibly measurable in vehicle exhaust. Estimation of "simple" toxic fractions for these compounds is covered in the following sub-section.

2.1.1.2.6 Estimating Simple Fractions of VOC for Running Emissions

As noted in Table 19, models for 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 toxic 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 36. 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 36. 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

Note:

[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 37). 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 37. 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	8.86961	11,578	0.0007661

Note:

[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.

2.1.1.2.7 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 14) denoted as $f_{benzene}$, a value modified to account for benzene levels in different fuels ($f^*_{benzene}$) is calculated as shown in Equation 15 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.

$$f^*_{benzene} = [(x_{benzene} - A) \cdot B \cdot f_{benzene}] + f_{benzene} \qquad \textbf{Equation 15}$$

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 Model 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 16, 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.

$$f^*_{buta} = f_{buta}\left(\frac{Ax^2_{olefin} + Bx_{olefin} + C}{D}\right) \qquad \textbf{Equation 16}$$

2.1.1.2.8 Additional Air Toxics Estimated from EPAct Speciation Profiles

For fuel blends with 0 percent, 10 percent and 15 percent ethanol, composite speciation profiles developed from the results of EPAct (Phase 1) were used to develop toxic fractions of VOC for the hazardous air toxics listed in Table 38.[e] 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. percent or greater. For fuel blends containing 20 percent ethanol, fractions were developed using a composite speciation profile from the EPAct (Phase 3) program. The fractions are also presented in Table 38. The values shown in Table 38 are stored in the database table minorHAPRatio (see Table 14).

[e] 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 38. Toxic Fractions of VOC for Selected Compounds, Representing Model Years 2001 and Later

Pollutant (pollutantID)[1]	Fuel Blends (Gasoline and Ethanol)			
	0% (E0)	10% (E10)[2]	15% (E15)	20% (E20)
2,2,4-Trimethylpentane (40)	0.03188	0.01227	0.02198	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

Notes:

[1] For fuels containing 0-20 percent ethanol, fractions for ethanol, benzene, acetaldehyde, formaldehyde, 1,3-butadiene, and acrolein were estimated using methods described in the previous subsections.

[2] Values also applied for fuels containing 5 percent and 8 percent ethanol, (E5 and E8).

2.1.2 Vehicles Operating on Fuel Blends Containing 70-100 percent Ethanol

Within this sub-section, we further delineate the methods and data used for estimating VOCs from 2000 and earlier vehicles (Section 2.1.2.1.1) and 2001 and later model year vehicles (Section 2.1.2.1.2), and data that applies to all model year vehicles (Section 2.1.2.1.3).

2.1.2.1.1 2000 and Earlier Model Year Vehicles

Major HAP emissions for 2000 and earlier model year vehicles operating on fuel blends containing 70-100 percent ethanol are estimated using toxic fractions of VOC. The toxic fractions were derived from data for four flexible-fuel vehicles running on E85 gasoline, collected during the EPAct program (Phase 3) and are displayed in Table 39. Since no measurements were obtained on an E70 blend (more typically used in winter) or blends above E85, the same toxic to VOC fractions are used for all ethanol-gasoline blends containing 70-100 percent ethanol. These ratios are applied to older technology (2000 and earlier vehicles), even though data were collected from Tier 2 vehicles The 2000 and earlier HAP emission rates are stored in the database table "ATRatioNonGas" (see Table 40).

Table 39. E70/E85 Major HAP VOC Fraction for 2000 and Earlier Model Year Vehicles

Pollutant (pollutantID)	Toxic Fraction
Benzene (20)	0.0170
Ethanol (21)	0.3724
1,3-butadiene (24)	0.0011
Formaldehyde (25)	0.0291
Acetaldehyde (26)	0.1644
Acrolein (27)	0.0010

Table 40. 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: "Running Exhaust" (processID = 1) "Start Exhaust" (processID = 2) "Extended Idle Exhaust" (processID = 90) "Auxiliary Power Exhaust" (processID = 91)
sourceTypeID	Identifies types of vehicles, classified by function	Motorcycle (11) Passenger Car (21) Passenger Truck (31) Light Commercial Truck (32)
fuelSubTypeID	Identifies specific fuel classes within the fuelTypeID	51 = "Ethanol (E85)" 52 = "Ethanol (E70)"
modelYearGroupID	Identifies a set of model years covered by a specific value of atRatio.	11,
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.	

2.1.2.1.2 2001 and Later Model Year Vehicles

For major HAPs in 2001 and later model year vehicles, we conducted a more comprehensive analysis than for the older model year vehicles. Instead of deriving toxic fractions of VOC, we developed adjustment factors that were compatible with the EPAct toxic ratios derived for gasoline 2001 and later model year vehicles discussed in the Section 2.1.1.2 The toxic 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 the 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. Numbers of vehicles in each program are summarized in Table 41.

Table 41. Number of Vehicles Included in the Analysis of Major HAPs

Test Program	Number of Vehicles
EPAct (phase 3)	4
NREL E40	9
CRC E-80	7
PM Speciation	2

Consistent emission trends were observed across datasets; 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 17. The adjustment factor was set to zero when the differences in emissions were not statistically different (i.e., acrolein).

$$E85\ adjustment\ factor = \frac{\frac{Toxics_{E85}}{VOC_{E85}}}{\frac{Toxics_{E10}}{VOC_{E10}}} \qquad \textbf{Equation 17}$$

The resulting adjustment factors are shown in Table 42, and are stored in the GeneralFuelRatioExpression table for fuelTypeID = 5. The E10 to E85 adjustments are used to estimate major HAP emissions for all 2001 model year vehicles and later.

Table 42. E70/E85 Adjustment Factors for Major HAPs for 2001 and Later Model Year Vehicles

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

2.1.2.1.3 Air Toxics Fractions that Apply to All Model Year Vehicles

Fractions for the remaining air toxic compounds modeled in MOVES were developed from the four flexible-fuel vehicles tested during the EPAct program (Phase 3) for all model year vehicles running on fuels containing 70-100 percent ethanol. A single emission test program was used for these pollutants, because they were not involved in the updated analysis discussed in the previous section (2.1.2.1.2). As stated earlier, the vehicles were tested on a single E85 gasoline fuel. These ratios are applied to older technology (2000 and earlier vehicles) as well as the modern technology vehicles in the test program; thus, there is more uncertainty in emission estimates for older technology vehicles running on high ethanol blends than for newer vehicles. The VOC fractions shown in Table 43 are stored in the minorHAPRatio table (see Table 14).

Table 43. Toxic Fractions of VOC for Vehicles Running on E70/E85 for All Model Year Vehicles

Pollutant (pollutantID)	Toxic Fraction of VOC
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

2.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Emissions of PAHs are estimated through the use of fractions in a manner similar to that used for VOCs as described in the previous section. However, for PAHs, the process is complicated by the fact that exhaust and crankcase emissions of 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 ≤ 2.5 μm ($OC_{2.5}$). We discuss the derivation of PAH fractions for vehicles operating on gasoline containing low ethanol percentages (Section 2.2.1) and high-ethanol percentages (Section 2.2.2).

2.2.1 Vehicles Operating on Fuel Blends Containing 0-20 percent Ethanol

The PAH emission fractions for gasoline vehicles are estimated from a set of 99 vehicles measured in the Kansas City Light-duty Vehicle Emissions Study (KCVES).[28] These vehicles were included in a subsample selected for chemical speciation. For each vehicle, emissions of THC and particulate matter 2.5 microns in diameter or less ($PM_{2.5}$) were measured. Fleet-average fractions of PAH/THC and PAH/$PM_{2.5}$ were calculated with each sample weighted by total emissions,[f] vehicle-miles traveled (VMT), and an equal weight between summer and winter. We used a VOC/THC fraction of 0.86 developed from the total organic-gas speciation profile developed from the Kansas City program (8750a) to estimate PAH/VOC fractions. We adjusted the PAH/$PM_{2.5}$ fraction by the fraction of OC measured in the start (42.6 percent) and running emission processes (55.7 percent) to produce PAH/$OC_{2.5}$ emission fractions. Because OC/PM fractions differ for start and running, we have separate PAH/OC toxic fractions for start and running.

The partitioning of PAH emissions between gaseous and particulate phases is assigned on the basis of average temperature and dilution conditions at the time of measurement, i.e., in the sample train and constant-volume sampler. Thus, the partitioning reflected in the emission fractions does not reflect cooling and dilution occurring in the "real world" after the exhaust leaves the tailpipe. The sampling conditions set forth in EPA regulations for particulate and hydrocarbon measurement differ for light-duty and heavy-duty vehicles, which affects the phase partitioning of PAH emissions obtained from both engine types. In preparing inputs for MOVES, we developed one set of phase allocation factors for gasoline sources and another for diesel sources in order to streamline data processing, and to be consistent with the measurement conditions reflected in the PAH measurements.

[f] Each sample contained emissions from one to five vehicles.

The allocations of PAHs into gaseous and particulate phases for gasoline vehicles 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 dilution temperatures.[29] 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 sampling line and dilution temperatures of 20°C and 47°C for four composite samples, with each composite sample containing one to three vehicles. Table 44 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 sample referred to as the 'medium-emitters.' This class contained a 1989 Camry and 1992 Voyager. In MOVES, we used the PAH phase-partitioning of this sample to estimate the relative gas and particle portioning of all gasoline-source emissions. Clearly, this sample may not adequately represent phase-partitioning of PAH emissions from the current in-use fleet; however, it was deemed the most representative of the breadth of gasoline vehicles sampled in the KCVES. Note that the PAH species partitioning was heavily dependent on molar mass (molecular weight); compounds with lighter molar masses (e.g., naphthalene) were measured almost entirely in the gaseous phase, whereas compounds with heavier molar masses were measured almost entirely in the particulate phase (e.g., dibenzo(a,h)anthracene).

Table 44. 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

The PAH/VOC and PAH/OC emission fractions used in MOVES2 are calculated by multiplying the PAH/VOC, and PAH/OC fractions calculated from KCVES by the gas/particle partitioning factors in Table 44. The calculation is displayed with Equation 18 and Equation 19 for each PAH, i= 1:16.

$$\frac{PAH_i}{VOC}(\text{Table 45}) = \frac{PAH_i}{VOC}(KCVES) \times Gaseous\ Fraction_i\ (\text{Table 44}) \quad \textbf{Equation 18}$$

$$\frac{PAH_i}{OC}(\text{Table 45}) = \frac{PAH_i}{OC}(KCVES) \times Particulate\ Fraction_i\ (\text{Table 44}) \quad \textbf{Equation 19}$$

Within MOVES, the PAH fractions in Table 45are applied to all gasoline fuels with ethanol content less than 20 percent. In the MOVES database, these fractions are stored in two tables. Fractions for the gaseous and particulate phases are stored in the tables pahGasRatio and pahParticleRatio, respectively. The two tables have the same structure, which is presented in Table 46.

Table 45. Toxic Fractions for PAH Compounds, in Gaseous and Particulate Phases for Gasoline Vehicles Fueled with Ethanol Content < 20 percent

Species	Gaseous Phase (PAH/VOC)	Particulate Phase (PAH/OC2.5)	
		Start	Running
Naphthalene	2.07×10^{-3}	1.68×10^{-4}	1.29×10^{-4}
Acenaphthylene	1.81×10^{-4}	5.01×10^{-5}	3.83×10^{-5}
Acenaphthene	3.99×10^{-5}	0.0	0.0
Fluorene	8.08×10^{-5}	0.0	0.0
Anthracene	3.35×10^{-5}	5.19×10^{-5}	3.97×10^{-5}
Phenanthrene	2.14×10^{-4}	1.81×10^{-4}	1.39×10^{-4}
Fluoranthene	5.60×10^{-5}	1.83×10^{-4}	1.40×10^{-4}
Pyrene	6.40×10^{-5}	1.98×10^{-4}	1.52×10^{-4}
Benz(a)anthracene	5.40×10^{-6}	4.76×10^{-4}	3.64×10^{-4}
Chrysene	6.05×10^{-6}	4.02×10^{-4}	3.08×10^{-4}
Benzo(a)pyrene	2.94×10^{-7}	1.19×10^{-3}	9.13×10^{-4}
Benzo(b)fluoranthene	4.01×10^{-6}	5.81×10^{-4}	4.45×10^{-4}
Benzo(k)fluoranthene	4.01×10^{-6}	5.81×10^{-4}	4.45×10^{-4}
Benzo(g,h,i)perylene	0.0	3.23×10^{-3}	2.47×10^{-3}
Indeno(1,2,3,c,d)pyrene	0.0	1.21×10^{-3}	9.28×10^{-4}
Dibenzo(a,h)anthracene	0.0	2.79×10^{-5}	2.13×10^{-5}

Table 46. Description of the Database Tables pahGasRatio and pahParticleRatio

Field	Description	Relevant Values
polProcessID	Identifies the pollutant (1st two digits and Emissions Process (last two digits).	Pollutants are identified in the table above; Relevant polprocesses include: 18501 = "Naphthalene gas, running exhaust" 18502 = "Naphthalene gas, start exhaust"
fuelTypeID	Identifies broad classes of fuels, e.g., "gasoline." "diesel."	1 = "Gasoline" 2 = "Diesel" 3 = "CNG" 5 = "Ethanol"
modelYearGroupID	Identifies a set of model years covered by a specific value of atRatio.	1960-1970 1971-1977 1978-1995 1996-2006 2007-2050
atRatio	Average PAH/VOC emission ratio 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.	

2.2.2 Vehicles Operating on Fuel Blends Containing 70-100 percent Ethanol

Hays et al. (2013)[30] reported speciated filter-collected semi-volatile organic compound (SVOC) measurements from three Tier 2 compliant vehicles tested using E0, E10 and E85 fuels. Reductions in total PAH between E0 and E85 in total measured filter-collected PAHs ranged between 22 percent and 93 percent depending on the temperature and phase of the LA-92 cycle. They found that E85 significantly reduced the lighter PAHs, including naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo(*a*)anthracene and chrysene. However, no significant effect was observed for the heavier PAHs, including benzo(*a*)pyrene, benzo(*k*)fluoranthene, benzo(*ghi*)perylene, and indeno(1,2,3-*cd*)pyrene.

Because Hays et al. (2013) reported only the filter-collected PAH emissions, and the results were conducted on a limited number of vehicles, we used the results to adjust the fleet-average PAH ratios derived from KCVES tested on E0 fuel. We reduced the VOC phase PAH ratios by 74 percent, assuming that (1) the annual average ethanol content of high ethanol fuels is 74 percent, and (2) the PAH in the gaseous phase are reduced proportionally to the gasoline content reductions. The 74 percent reduction is within the range of reductions observed by Hays et al. (2013)[30] for total PAHs. Because Hays et al. (2013)[30] observed no significant decrease of the heavier PAHs for which MOVES assumes exist primarily in the particle-phase (Table 44), we

assume the E85 particle PAH/OC fractions are the same as the E0-E20 fractions derived from KCVES. The resulting fractions are presented in Table 47.

Table 47. Toxic Fractions for PAH species for Vehicles Running on High-Ethanol Blends by Process

PAH species	PAH/VOC	PAH/$OC_{2.5}$	
		Start	Running
Naphthalene	5.38×10^{-4}	1.68×10^{-4}	1.29×10^{-4}
Acenaphthylene	4.71×10^{-5}	5.01×10^{-5}	3.83×10^{-5}
Acenaphthene	1.04×10^{-5}	0.0	0.0
Fluorene	2.10×10^{-5}	0.0	0.0
Anthracene	8.70×10^{-6}	5.19×10^{-5}	3.97×10^{-5}
Phenanthrene	5.57×10^{-5}	1.81×10^{-4}	1.39×10^{-4}
Fluoranthene	1.45×10^{-5}	1.83×10^{-4}	1.40×10^{-4}
Pyrene	1.66×10^{-5}	1.98×10^{-4}	1.52×10^{-4}
Benz(*a*)anthracene	1.41×10^{-6}	4.76×10^{-4}	3.64×10^{-4}
Chrysene	1.57×10^{-6}	4.02×10^{-4}	3.08×10^{-4}
Benzo(*a*)pyrene	7.65×10^{-8}	1.19×10^{-3}	9.13×10^{-4}
Benzo(*b*)fluoranthene	1.04×10^{-6}	5.81×10^{-4}	4.45×10^{-4}
Benzo(*k*)fluoranthene	1.04×10^{-6}	5.81×10^{-4}	4.45×10^{-4}
Benzo(*ghi*)perylene	0.0	3.23×10^{-3}	2.47×10^{-3}
Indeno(1,2,3,*cd*)pyrene	0.0	1.21×10^{-3}	9.28×10^{-4}
Dibenzo(*ah*)anthracene	0.0	2.79×10^{-5}	2.13×10^{-5}

2.3 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 models two groups of metal emissions, 1) metals that are used for air quality modeling, and 2) metals that are included due to their known toxicity. The metals that are included for air quality modeling, which include metals such as iron, aluminum and calcium are discussed in the MOVES201X Speciation report.[17] Emissions of these metals are estimated as fractions of $PM_{2.5}$ emission rates.

This report covers seven metal species included due to their known toxicity, including five metals and three forms of mercury, as listed in Table 4. The toxic metal emissions are estimated using distance-specific emission rates (g/mile). Manganese is the only metal that is required for both purposes, and is estimated using the g/mile approach. In the database, these rates are stored in the metalEmissionRate table, described in Table 49. Note that while the table contains a field for "fuel type," the emission rates listed in the table do not vary among fuel types.

Emission rates for magnesium and nickel were developed from the 99 vehicles sampled for chemical composition in the KCVES. The mean rates are calculated as weighted averages of metal measured on Bag 2 of the LA92, using weights designed to represent the onroad vehicle fleet.[31] The use of Bag 2 emissions in the averaging helps ensure that the emission rates for these

metals are consistent with the $PM_{2.5}$ emission profile for running emissions discussed in the MOVES201X Speciation Report.[17] These approaches were adopted because while $PM_{2.5}$ emissions are much lower during hot-stabilized running conditions, $PM_{2.5}$ emissions are 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 LA92; the difference in the Bag 2 emission rates from the average of the LA92 is 38 percent and -16 percent for manganese and nickel. Thus, in using Bag 2 emission rates for metal emission rates, the approach is both consistent with the $PM_{2.5}$ speciation running emission profile and provides a likely upper limit (in the case of manganese) when compared to the cycle average.

Hexavalent chromium was estimated using data collected at U.S. EPA's National Vehicle Emissions Laboratory and analyzed at the Wisconsin State Laboratory of Hygiene at the University of Wisconsin-Madison. These data were collected on a single vehicle, a 2008 Chevrolet Impala flexible-fuel vehicle. They are the only available data with direct measurement of hexavalent chromium from a highway vehicle. Development of a gasoline vehicle emission rate from these data is detailed in Appendix A. Eighteen percent of chromium was assumed to be hexavalent, based on combustion data from stationary combustion turbines burning diesel fuel.[32]

Emission factors for arsenic were developed from data reported for tunnel tests.[33] These data were collected in two Milwaukee tunnels in 2000/2001, using inductively-coupled plasma mass spectrometry (ICP-MS) and a chemical mass balance model was used to apportion concentrations to sources. Emission factors for mercury were obtained from a 2005 test program at EPA's National Exposure Research Laboratory (NERL). In this program mercury samples in raw exhaust were collected from 14 light-duty gasoline vehicles and two heavy-duty diesel vehicles. Documentation describing development of these emission factors can be found in Appendix B.

Table 48. Metal Emission Rates for Gasoline Motor Vehicles

Pollutant	Emission Rate (g/mi)
Chromium, hexavalent (6+)	1.20×10^{-8}
Manganese	1.33×10^{-6}
Nickel	1.50×10^{-6}
Mercury, Elemental (Gaseous Phase)	1.10×10^{-7}
Mercury, Reactive (Gaseous Phase)	9.90×10^{-9}
Mercury, Particulate Phase	4.00×10^{-10}
Arsenic	2.30×10^{-6}

Fleet-average metal emission rates were derived for vehicles running on gasoline and gasoline-ethanol blends. 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 conventional gasoline vehicles (see Table 48).

Table 49. 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: 1 = "Running Exhaust"
fuelTypeID	Identifies broad classes of fuels, e.g., "gasoline." "diesel."	1 = "Gasoline" 2 = "Diesel" 5 = "Ethanol"
sourceTypeID	Identifies vehicle types, classified by function	Motorcycles (11) Passenger Cars (21) Passenger Trucks (31) Light Commercial Trucks (32)
modelYearGroupID	Identifies a set of model years covered by a specific value of atRatio.	1960-1970 1971-1977 1978-1995 1996-2006 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.	

2.4 Dioxins and Furans

The MOVES model estimates mass and distance-based emission rates for 17 dioxin and furan congeners (gram/mile). We discuss the derivation of dioxin and furan emission rates for vehicles operating on gasoline containing low ethanol percentages (Section 2.4.1) and high-ethanol percentages (Section 2.4.2). .

2.4.1 Vehicles Operating on Fuel Blends Containing 0-20 percent Ethanol

The emission rates for dioxins and furans were obtained from the tunnel study used in EPA's dioxin assessment.[34,35] The emission rates from the tunnel study did not vary among fuel types, and we applied theses rates to gasoline vehicles in MOVES. The rates are stored in the dioxinEmissionRate table, which is described in Table 51.

Table 50.Dioxin Emission Rates for Motor Vehicles Running on Gasoline Fuel Blends with 0-20 Percent Ethanol

Pollutant	mg/mi
2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin (TCDD)	8.27×10^{-10}
1,2,3,7,8-Pentachlorodibenzo-*p*-Dioxin	3.70×10^{-10}
1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	3.87×10^{-10}
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	7.92×10^{-10}
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	4.93×10^{-10}
1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin	5.95×10^{-9}
Octachlorodibenzo-p-dioxin	4.70×10^{-8}
2,3,7,8-Tetrachlorodibenzofuran	2.76×10^{-9}
1,2,3,7,8-Pentachlorodibenzofuran	1.32×10^{-9}
2,3,4,7,8-Pentachlorodibenzofuran	9.68×10^{-10}
1,2,3,4,7,8-Hexachlorodibenzofuran	1.09×10^{-9}
1,2,3,6,7,8-Hexachlorodibenzofuran	1.16×10^{-9}
1,2,3,7,8,9-Hexachlorodibenzofuran	3.17×10^{-10}
2,3,4,6,7,8-Hexachlorodibenzofuran	1.36×10^{-9}
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1.21×10^{-8}
1,2,3,4,7,8,9-Heptachlorodibenzofuran	3.87×10^{-10}
Octachlorodibenzofuran	1.37×10^{-8}

Table 51. 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: 1 = "Running Exhaust"
fuelTypeID	Identifies broad classes of fuels, e.g., "gasoline." "diesel."	1 = "Gasoline" 2 = "Diesel" 5 = "Ethanol"
modelYearGroupID	Identifies a set of model years covered by a specific value of atRatio.	1960-2050 1960-2006 2007-2009 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.	

In the absence of additional data, the fractions for more recently-manufactured vehicles were assumed to be the same as those for vehicles employing older technologies (see page 48). Of course, this extrapolation from one set of technologies to another involves some degree of uncertainty.

2.4.2 Vehicles Operating on Fuel Blends containing 70-100 percent Ethanol

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 50) 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 52.

Table 52. Emission Factors for Dioxins and Furans, for Vehicles Operating on High-Ethanol Blends

Congener	Emission rate (mg/mile)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	2.15×10^{-10}
1,2,3,7,8-Pentachlorodibenzo-p-Dioxin	9.61×10^{-11}
1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	1.01×10^{-10}
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	2.06×10^{-10}
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	1.28×10^{-10}
1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin	1.55×10^{-9}
Octachlorodibenzo-p-dioxin	1.22×10^{-8}
2,3,7,8-Tetrachlorodibenzofuran	7.19×10^{-10}
1,2,3,7,8-Pentachlorodibenzofuran	3.43×10^{-10}
2,3,4,7,8-Pentachlorodibenzofuran	2.52×10^{-10}
1,2,3,4,7,8-Hexachlorodibenzofuran	2.84×10^{-10}
1,2,3,6,7,8-Hexachlorodibenzofuran	3.02×10^{-10}
1,2,3,7,8,9-Hexachlorodibenzofuran	8.24×10^{-11}
2,3,4,6,7,8-Hexachlorodibenzofuran	3.52×10^{-10}
1,2,3,4,6,7,8-Heptachlorodibenzofuran	3.16×10^{-9}
1,2,3,4,7,8,9-Heptachlorodibenzofuran	1.01×10^{-10}
Octachlorodibenzofuran	3.57×10^{-9}

3 Diesel Exhaust

Toxic fractions, dioxin and metal emission rates were developed for exhaust emissions from heavy-duty diesel vehicles and applied to all diesel vehicle categories. The pre-2007 diesel toxic fractions for VOCs and PAHs are applied to auxiliary power unit exhaust for all model year vehicles until 2024, because auxiliary power units are not subject to the same stringency of control as highway engines. There are no separate emission ratios or factors for diesel engines running on biodiesel fuels or synthetic diesel fuels, due to limited data. Biodiesel vehicles use the same toxic ratios and factors as regular diesel. The toxic emission data are based on heavy-duty testing but are applied to light-duty diesel with the same model year distinctions (pre-2007, 2007 to 2009, and 2010 and later).

3.1 Volatile Organic Compounds

The composition of VOC emissions for heavy-duty diesel engines lacking the advanced control technologies applied in more recently-manufactured vehicles differs substantially from earlier technologies. Thus, we developed one set of toxic fractions for pre-2007 diesel engines and another set for engines manufactured between 2007 to 2009, and 2010 and later.

3.1.1 Pre-2007 Diesel Engines

To estimate toxic fractions of VOC for vehicles in the pre-2007 model-year group, EPA relied on a database compiled for the Coordinating Research Council and the National Renewable Energy Laboratory (NREL) (CRC E-75).[36] 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, hexane, propionaldehyde, and toluene, toxic fractions of VOC were developed by Sierra Research. Their analysis of CRC E-75 data is described in detail in the technical report.[36] Data from tests using non-conventional diesel fuel (Fischer-Tropsch, bio-diesel, ethanol-Diesel blends, emulsified fuel, European blends, and other obvious research fuels) were excluded, as were data from light-duty engines. The fractions are provided in Table 53. Toxic fractions for other compounds in Table 53 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.

Table 53. Toxic Fractions of VOC 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

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 the APU VOC toxic emission rates for all model years until 2024.[37,] However, we anticipate that APU standards promulgated as part of the Phase 2 greenhouse gas regulation for medium and heavy-duty engines[38] will result in use of diesel particulate filters in 2024; thus we are using 2007-2009 diesel toxic emissions data for those units.

3.1.2 2007+ Diesel Engines

For heavy-duty diesel engines manufactured in 2007 and later, 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.[39, 40] ACES was conducted in two phases, with the first focusing on engines complying with 2009 standards and the second focusing on engines meeting 2010 standards. Engines tested in ACES that met the 2007 and 2010 standards had different emission control systems which had significant impact on composition of emissions. Whereas 2007-compliant engines added diesel particulate filters, 2010-compliant engines also had urea-based selective catalytic reduction (SCR) catalysts and ammonia oxidation catalysts. In ACES Phase 1, detailed

emissions measurements were performed on four engines, while in ACES Phase 2 measurements were performed on three engines. In both test programs, vehicles were operated on low-sulfur diesel fuel over several test cycles. We made use of data from the 16-hour transient cycle which is composed of FTP and CARB 5-Mode cycles, developed specifically to gain sufficient mass of toxics emitted at low concentrations, and to capture diesel particulate filter regeneration events. The ACES measurements for the selected VOC emissions in MOVES were background corrected using background dilution air.[39] Toxic fractions of VOC calculated from the ACES data are provided in Table 54. Because VOC emissions are so low in advanced technology diesels, there is considerable measurement uncertainty for gaseous air toxics.

Table 54. Toxic Fractions of VOC for 2007 and Later Diesel Vehicles

	Toxic Fraction	
Pollutant	2007-2009	2010 and later
1,3-Butadiene	0.00080	0.0
2,2,4-Trimethylpentane	0.0078	0.00411
Acetaldehyde	0.06934	0.03838
Acrolein	0.00999	0.00331
Benzene	0.01291	0.0
Ethyl Benzene	0.0063	0.01028
Formaldehyde	0.21744	0.02449
N-Hexane	0.0054	0.00081
Propionaldehyde	0.0031	0.00266
Styrene	0.0	0.0
Toluene	0.03	0.01687
Xylenes	0.038	0.07811

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[41] using estimates from EPA's SPECIATE 4.2 database[42] and information on compounds' physical and chemical properties. The allocations from SPECIATE were based on exhaust measured from two medium-duty diesel trucks tested in 1996 with low mileage.[43] The phase-partitioning factors are shown in Table 55. Compared to the partitioning for gasoline (Table 44), 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. However, it should be noted that the data used represent partitioning in the sampled diluted exhaust, which is not representative of partitioning in the atmosphere.

Emissions of PAH in the gaseous and particulate phases were estimated as fractions of total VOC and $OC_{2.5}$, respectively. We use the phase-partitioning factors in Table 55 for both pre-2007 and 2007+ diesel engines. However, we develop separate gaseous-phase PAH/VOC and particle-phase PAH/OC factors for pre-2007, 2007-2009 and 2010+ trucks as documented in the following subsections.

Table 55. Phase-Partition Fractions for Emissions of Polycyclic Aromatic Hydrocarbons from Diesel Engines

PAH species	Molar Mass (g/mol)	Phase Fraction	
		Gaseous	Particulate
Naphthalene	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(*ghi*)perylene	276	0.227	0.773
Indeno(1,2,3-*cd*)pyrene	276	0.0	1.0
Dibenzo(*ah*)anthracene	278	0.0	1.0

3.2.1 Pre-2007 Diesel Engines

PAH fractions for pre-2007 diesel engines 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 were 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(*ah*)anthracene. Table 56 shows fractions for PAH emissions relative to OC and VOC, by emissions process.

Table 56. Toxic Fractions for PAH Species, by Phase and Process, for Pre-2007 Diesel Vehicles

PAH	PAH/VOC	PAH/OC2.5		
		Start/Idle	Running	Extended Idle
Naphthalene	9.05×10^{-3}	0.0	0.0	0.0
Acenaphthylene	5.01×10^{-4}	0.0	0.0	0.0
Acenaphthene	2.98×10^{-4}	0.0	0.0	0.0
Fluorene	4.85×10^{-4}	2.80×10^{-4}	8.49×10^{-4}	2.54×10^{-4}
Anthracene	2.35×10^{-4}	1.63×10^{-4}	4.94×10^{-4}	1.48×10^{-4}
Phenanthrene	7.08×10^{-4}	6.44×10^{-4}	1.96×10^{-3}	5.86×10^{-4}
Fluoranthene	3.55×10^{-4}	6.24×10^{-4}	1.90×10^{-3}	5.68×10^{-4}
Pyrene	4.27×10^{-4}	9.02×10^{-4}	2.74×10^{-3}	8.21×10^{-4}
Benzo(*a*)anthracene	4.36×10^{-5}	3.23×10^{-4}	9.81×10^{-4}	2.94×10^{-4}
Chrysene	1.70×10^{-5}	2.04×10^{-4}	6.20×10^{-4}	1.86×10^{-4}
Benzo(*a*)pyrene	0.0	1.21×10^{-4}	3.69×10^{-4}	1.10×10^{-4}
Benzo(*b*)fluoranthene	0.0	3.60×10^{-5}	1.10×10^{-4}	3.28×10^{-5}
Benzo(*k*)fluoranthene	0.0	5.08×10^{-6}	1.54×10^{-5}	4.62×10^{-6}
Benzo(*ghi*)perylene	8.3×10^{-7}	5.78×10^{-6}	1.75×10^{-5}	5.26×10^{-6}
Indeno(1,2,3-*cd*)pyrene	0.0	9.24×10^{-6}	2.81×10^{-5}	8.41×10^{-6}
Dibenz(*ah*)anthracene	0.0	4.85×10^{-6}	1.47×10^{-5}	4.41×10^{-6}

The PAH Toxic fractions in Table 56 are applied to exhaust emission for 2006 and earlier model year diesel vehicles in MOVES. The extended idle toxic fractions are applied to auxiliary power unit (APUs) exhaust for all model year vehicles in MOVES prior to 2024, because the APUs are not subject to the same control as exhaust from the highway engines. However, as previously discussed, we are using 2007-2009 diesel toxic emissions data for 2024 and later units.

3.2.2 2007+ Diesel Engines

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. The PAH emissions measured in the ACES study were uncorrected for background concentrations.[39] Toxic fractions applicable to these engines are shown in Table 57, in which the fractions are differentiated by phase but not by emissions process. We used the same phase fractions presented in Table 55. 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 comprises multiple driving modes, as documented in the MOVES201X TOG and PM Speciation Report.[17]

Table 57. Toxic Fractions for Polycyclic Aromatic Compounds, by Phase, for 2007 and Later Diesel Vehicles

	2007-2009		2010 and later	
PAH	Gaseous Phase (PAH/VOC)	Particulate Phase (PAH/OC2.5)	Gaseous Phase (PAH/VOC)	Particulate Phase (PAH/OC2.5)
Naphthalene	1.63×10^{-2}	0.0	5.84×10^{-4}	1.35×10^{-5}
Acenaphthylene	8.53×10^{-5}	0.0	1.49×10^{-5}	1.29×10^{-6}
Acenaphthene	5.26×10^{-5}	0.0	1.56×10^{-5}	0
Fluorene	1.96×10^{-4}	2.41×10^{-4}	3.35×10^{-5}	0
Anthracene	3.04×10^{-5}	1.19×10^{-4}	6.47×10^{-6}	3.19×10^{-6}
Phenanthrene	8.51×10^{-4}	1.92×10^{-3}	9.62×10^{-5}	2.61×10^{-5}
Fluoranthene	4.57×10^{-5}	2.18×10^{-4}	6.41×10^{-6}	6.684×10^{-6}
Pyrene	3.79×10^{-5}	2.09×10^{-4}	4.72×10^{-6}	4.67×10^{-6}
Benzo(a)anthracene	3.00×10^{-7}	3.58×10^{-6}	6.92×10^{-7}	1.942×10^{-5}
Chrysene	5.00×10^{-7}	1.12×10^{-5}	2.51×10^{-7}	5.32×10^{-6}
Benzo(a)pyrene	0.0	1.48×10^{-5}	0.0	0.0
Benzo(b)fluoranthene	0.0	6.27×10^{-6}	0.0	0.0
Benzo(k)fluoranthene	0.0	6.27×10^{-6}	0.0	0.0
Benzo(ghi)perylene	2.00×10^{-7}	8.96×10^{-7}	0.0	0.0
Indeno(1,2,3-cd)pyrene	0.0	2.24×10^{-6}	0.0	0.0
Dibenz(a,h)anthracene	0.0	4.48×10^{-6}	0.0	0.0

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 hexavalent chromium, mercury and arsenic. The hexavalent chromium emission rate was obtained by multiplying the gasoline vehicle emission rate by the ratio of total chromium in diesel exhaust to that in gasoline exhaust. The total chromium estimates came from the previously cited CRC E-75 and KCVES programs, respectively. More details are provided in Appendix A. The pre-2007 diesel emission rate for arsenic is the same as for gasoline vehicles and obtained from the same study (see Table 48). It does not vary with emission control technology. The mercury emission rate for pre-2007 diesels is calculated from emission tests conducted on two heavy-duty diesel vehicles, as documented in Appendix B. Table 58 provides metal emission factors for all diesel vehicles.

Table 58. Emission Rates for Selected Metals for Diesel Vehicles

Pollutant	Emission Rate for 1960-2006 (g/mi)	Emission Rate for 2007-2009 (g/mi)	Emission Rate for 2010 and later (g/mi)
Chromium VI	$2.0x10^{-8}$	$5.8x10^{-9}$	$2.0x10^{-8}$
Manganese	8.0×10^{-6}	5.5×10^{-7}	$1.7x10^{-6}$
Nickel	1.4×10^{-5}	6.5×10^{-7}	$2.4x10^{-6}$
Mercury, Elemental Gaseous Phase	6.2×10^{-9}	6.2×10^{-9}	$6.2x10^{-9}$
Mercury, Reactive Gaseous Phase	3.2×10^{-9}	3.2×10^{-9}	$3.2x10^{-9}$
Mercury, Particulate Phase	1.6×10^{-9}	1.6×10^{-9}	$1.6x10^{-9}$
Arsenic	2.3×10^{-6}	2.3×10^{-6}	$2.3x10^{-6}$

Emissions rates for manganese and nickel representing diesel engines manufactured in 2007 and later were developed using data from the ACES program. The ACES metal emission rates were uncorrected for background concentrations.[39] The emission rate for arsenic is identical to the emission rate used for gasoline vehicles and pre-2007 diesels (Table 48). The emission rates for mercury are the same as those derived for pre-2007 diesel engines, as discussed in Appendix B. The hexavalent chromium emission rates for pre-2007, 2007 to 2009, and 2010 and later diesel engines, were obtained by multiplying the gasoline vehicle emission rate by the ratio of total chromium from diesel and gasoline engines. The total chromium estimates came from the previously cited KCVES and ACES test programs, respectively. More details are provided in Appendix A.

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.[44] In this study, dioxin emissions from three heavy-duty engines manufactured prior to 1994 were measured. These engines included a 1985 GM 6.2 L, a 1987 Detroit Diesel 6V92 and 1993 Cummins L10. The emission factors in mg/mi are shown in Table 59. Since these engines are older than most of the pre-2007 fleet, dioxin emissions for pre-2007 engines may be overestimated.

Table 59. Emission Rates for Dioxin/Furan Congeners for Diesel Vehicles (mg/mi)

Congener	1970-2006	2007 - 2009	2010 and later
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	2.23×10^{-10}	0.0	0.0
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	0.0	0.0	0.0
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	0.0	0.0	0.0
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	1.03×10^{-10}	0.0	0.0
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	4.78×10^{-10}	4.11×10^{-11}	0.0
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	4.18×10^{-9}	2.58×10^{-10}	1.05×10^{-9}
Octachlorodibenzo-*p*-dioxin	1.61×10^{-8}	9.30×10^{-10}	6.98×10^{-9}
2,3,7,8-Tetrachlorodibenzofuran	6.50×10^{-9}	0.0	5.09×10^{-11}
1,2,3,7,8-Pentachlorodibenzofuran	1.39×10^{-9}	0.0	1.07×10^{-10}
2,3,4,7,8-Pentachlorodibenzofuran	2.23×10^{-9}	6.30×10^{-11}	3.24×10^{-10}
1,2,3,4,7,8-Hexachlorodibenzofuran	8.02×10^{-10}	0.0	2.20×10^{-10}
1,2,3,6,7,8-Hexachlorodibenzofuran	4.24×10^{-10}	0.0	2.43×10^{-10}
1,2,3,7,8,9-Hexachlorodibenzofuran	0.0	0.0	0
2,3,4,6,7,8-Hexachlorodibenzofuran	3.03×10^{-10}	0.0	1.80×10^{-10}
1,2,3,4,6,7,8-Heptachlorodibenzofuran	2.16×10^{-9}	3.00×10^{-10}	9.94×10^{-10}
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.0	0.0	5.81×10^{-11}
Octachlorodibenzofuran	1.85×10^{-9}	7.06×10^{-10}	1.74×10^{-9}

The data used to calculate the emission rates for engines manufactured between 2007 and 2009 were obtained from the EPA diesel dioxin study of 2007 and later engines.[45] The results represent measurements of transient tests conducted on a MY2008 Cummins ISB engine over 48 replicates 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. The 2007-2009 and 2010 and later emission rates are presented in Table 59.

4 Compressed Natural Gas (CNG) Exhaust

MOVES201X estimates emissions of toxics from heavy-duty vehicles fueled by compressed natural gas. This section describes the development of toxic emission inputs for this class of vehicles.

4.1 Volatile Organic Compounds

We used speciated hydrocarbon measurements from work sponsored by the California Air Resources Board.[46] These measurements were taken on a 2000 MY Detroit Diesel Series 50G engine with and without an oxidation catalyst, measured on the Central Business District (CBD) cycle. As discussed in the MOVES201X Speciation report[17], we used the uncontrolled results to represent speciation from pre-2002 CNG transit buses, and the results with oxidation-catalyst to represent 2002 and later buses. The use of the CBD cycle is also consistent with the results used for criteria-pollutant emissions.

The toxic fractions of VOC derived from this set of measurements are displayed in Table 60. The total VOC emission rates are reduced by 70 percent from pre-2002 levels. As shown in the table, formaldehyde emissions are preferentially reduced by the oxidation catalyst. Formaldehyde contributes over 50 percent of the VOC emissions for the uncontrolled CNG bus, but only 16.2 percent 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 60. Toxic Fractions of VOC for CNG Transit Buses

	No control (pre-2002)	With oxidation catalyst (2002+)
1,3 Butadiene	0.000234	0.0
Benzene	0.00135	0.00253
Toluene	0.000691	0.00786
Ethylbenzene	0.0000841	0.00131
Xylenes	0.000823	0.00634
Formaldehyde	0.517	0.162
Acetaldehyde	0.0305	0.138
Acrolein	0.00235	0.0
Propionaldehyde	0.0153	0.0

4.2 Polycyclic Aromatic Hydrocarbons

The PAH toxic fractions for compressed natural gas are derived from tests on a model year 2000 DDC Series 50G engine on a New Flyer CNG transit bus tested by the California Air Resources Board (CARB).[47] This engine had no catalyst, but the emission fractions are used to represent both catalyst and non-catalyst engines. 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 61.

Table 61. PAH Fractions of Volatile Organic Carbon (Volatile PAHs), and of Organic Carbon (Particle-Phase for CNG Transit Buses

Compound	VOC fraction	OC fraction
Naphthalene	9.554×10^{-6}	2.114×10^{-5}
Acenaphthylene	4.230×10^{-6}	ND
Acenaphthene	1.243×10^{-6}	1.886×10^{-5}
Fluorene	2.986×10^{-6}	3.301×10^{-5}
Anthracene	1.164×10^{-6}	1.644×10^{-6}
Phenanthrene	8.356×10^{-6}	2.043×10^{-5}
Fluoranthene	1.936×10^{-6}	2.874×10^{-5}
Pyrene	3.743×10^{-6}	5.350×10^{-5}
Benz(*a*)anthracene	1.682×10^{-7}	9.390×10^{-6}
Chrysene/triphenylene	2.441×10^{-7}	1.911×10^{-5}
Benzo(*a*)pyrene	ND	ND
Benzo(*b*)fluoranthene	ND	ND
Benzo(*k*)fluoranthene	ND	ND
Indeno(1,2,3-*cd*)pyrene	ND	ND
Benzo(*ghi*)perylene	ND	5.502×10^{-6}
Dibenz(*ah*)anthracene	ND	ND

Note:
ND = not detected, fractions set to 0.

4.3 Metals

We used the nickel emission rates reported from an uncontrolled 2000 MY DDC Series 50G.[48] We used the uncontrolled bus to be consistent with the $PM_{2.5}$ speciation profile. The hexavalent chromium emission rate was obtained by multiplying the gasoline emission rate by the ratio of total chromium from the DDC Series 50G CNG engine and total chromium from gasoline engines in the previously cited KCVES program. More details are provided in Appendix A.

Results for the other metals predicted by MOVES were not available in the published literature. Thus, we used the same emission rates as for gasoline vehicles. The rates are presented in Table 62.

Table 62. Metal Emission Rates and Sources used for CNG Transit Buses

Pollutant	Emission Rate (g/mi)	Source
Chromium 6+	2.1×10^{-10}	University of Wisconsin (Appendix A) and Okamoto et al. (2006)
Manganese	1.33×10^{-6}	Same as gasoline
Nickel	1.00×10^{-8}	Okamoto et al. (2006)
Elemental Gas Phase Hg	1.10×10^{-7}	Same as gasoline
Reactive Gas Phase Hg	9.90×10^{-9}	Same as gasoline
Particulate Hg	4.00×10^{-10}	Same as gasoline
Arsenic	2.30×10^{-6}	Same as gasoline

4.4 Dioxins and Furans

No published dioxin and furan emission rates for CNG vehicles were available. Thus, we are using the dioxin emission rates for gasoline reported in Table 50.

5 Evaporative Emissions

Emissions of toxics emitted through evaporation of unburned fuel are estimated as fractions of total evaporative VOC. MOVES estimates toxic emission ratios for each evaporative processes from gasoline vehicles (including gasoline-ethanol blends) and for refueling emissions from diesel vehicles. Currently, MOVES does not estimate evaporative emissions (e.g., refueling natural gas leaks) from CNG vehicles as discussed in the evaporative emission report.[49] This section documents the source of the toxic ratios used for evaporative emissions from gasoline and diesel vehicles.

5.1.1 Gasoline Vehicles

The derivation of the toxic fractions for vapor venting, fuel leaks and refueling emission processes are documented in Section 5.1.2 and for permeation in Section 5.1.3.

5.1.2 Vapor Venting, Fuel Leaks, and Refueling Emission Processes

MOVES estimates evaporative emissions from gasoline vehicles using toxic fractions that pertain to evaporative emission processes. The toxic 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 63.

Expressions used to generate complex fractions were adapted from those used in MOBILE6.2.[50] These equations were adapted to compensate for a lack of data from newer vehicles collected in the context of appropriate experimental designs. 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, equations for hot soak in MOBILE6.2 are used for vapor venting and refueling vapor loss, and equations for running loss are used for fuel leaks and refueling spillage loss. The equations are applied for fuels containing up to 20 percent ethanol, and are presented in Table 64. MOVES has fields for evaporative naphthalene, but all values in the model are zero. E0 data used for MOBILE6.2 had very low but detectable naphthalene, and it is often measured at very low levels in gasoline. However, we do not include naphthalene emissions from evaporative processes in MOVES since it is inconsistently measured in detectable quantities in evaporative emission testing.

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.[51] The fractions for these compounds are the same for all pollutant processes (except permeation) and are presented in Table 65.

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

For vehicles operating on fuels containing 15 percent 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.[11] Resulting toxic fractions are provided in Table 65.

For vehicles containing 20 percent ethanol, toxic fractions were developed for fuel speciation profiles created 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 65.

For vehicles operating on fuels containing high levels of ethanol, ranging from 70 to 100 percent, the toxic fractions were developed using results of two-day diurnal tests on four 2007 model year flex-fuel vehicles from CRC E-80 program.[26] Following typical speciation procedures, the fraction of each compound in a test was first calculated by dividing its emission rates for each compound by the sum of all rates for that test. The percentages for each compound were then averaged across all tests to form the composite profile. The resulting fractions are presented in Table 65.

Table 63. Data Sources and Estimation Methods Used in Estimation of Toxic Fractions for Evaporative VOCs

Compound	Process	Fraction Type	Basis for Estimation	MOVES Table
Benzene	Vapor venting/refueling (vapor)	complex	Adapted from MOBILE6.2	GeneralFuelRatioExpression for E0 to E20; atRatioNonGas for E70-E100
	Fuel leaks/spillage	complex	Adapted from MOBILE6.2	GeneralFuelRatioExpression for E0 to E20; atRatioNonGas for E70-E100
2,2,4-trimethylpentane	All (except permeation)	simple	Speciation profile	minorHAPratio
Ethylbenzene	All (except permeation)	simple	Speciation profile	minorHAPratio
N-Hexane	All (except permeation)	simple	Speciation profile	minorHAPratio
Toluene	All (except permeation)	simple	Speciation profile	minorHAPratio
Xylenes	All (except permeation)	simple	Speciation profile	minorHAPratio
Ethanol	All (except permeation)	simple	Speciation profile	GeneralFuelRatioExpression for E0 to E20; atRatioNonGas for E70-E100

Note:
[1]For E70 through E100 fuels, the toxic ratios for benzene and ethanol are simple fractions stored in the atRatioNonGas table

Table 64. Complex Fractions of VOC for Evaporative Emissions of Benzene Applied to Vehicles Running on Gasoline (E0 to E20)

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

Table 65. Toxic Fractions for Evaporative VOC Emissions, for Vapor-venting and Refueling-Spillage Processes

Pollutant	Ethanol Level				
	0.0% (E0)	10% (E10)	15% (E15)	20% (E20)	70-100% (E85)
Ethanol[1]	0.00000	0.11896	0.1935	0.2227	0.61042[2]
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	0.07999	0.06423	0.05735	0.0711	0.00733
Benzene	Table 64				0.00664[2]

Notes:
[1]Note: Ethanol toxic fraction is estimated 0.01189ETOH (The ethanol % volume in the fuel) using the GeneralFuelRatioTable for E0 to E20 fuels,
[2]The toxic ratios for Ethanol and Benzene for E70-E100% fuel are simple ratios stored in the atRatioNonGas table

5.1.3 Permeation

The composition of VOCs 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 in the CRC E-77-2b and E-77-2c test programs.[52,53] 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 E0, E10 and E20 fuels by averaging data from fuel formulations with varying vapor pressures. Fractions are presented in Table 66 for all compounds except benzene. To estimate toxic fractions for vehicles operating on fuels containing 15 percent ethanol, the fractions for E10 and E20 fuels were linearly interpolated for ethanol levels of 15 percent. Toxic fractions are shown in Table 66, for all compounds except benzene. To estimate toxic fractions for vehicles operating on fuels containing 15 percent ethanol, the fractions for E10 and E20 fuels were linearly interpolated for ethanol levels of 15 percent.

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 20.[54] 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.[55] Thus the diurnal emissions algorithm was multiplied by 1.77.

$$f_{benz,permeation} = 1.77[(-0.02895\ OXY - 0.080274\ \ RVP + 1.3758)benz/100] \quad \textbf{Equation 20}$$

In MOVES, the permeation values are stored in the same location as the toxic values for other evaporative processes. Ethanol and Benzene are stored in the GeneralFuelRatioExpression Table for E0 through E20 fuels, and the atRatioNonGas Table for E70-E100 fuels. The other toxics (2,2,4-Trimethylpentane, Ethylbenzene, Hexane, Toluene and Xylene) are stored in the minorHAPratio table.

Table 66. Toxic Fractions Representing Permeation Emissions as Components of Total VOC Emissions, by Ethanol Level (Source: CRC E-77-2b and CRC E-77-2c)

Pollutant	Ethanol Level				
	0.0% (E0)	10% (E10)	15% (E15)	20% (E20)	70-100% (E85)
Ethanol	0.000	0.202	0.2694	0.3296	0. 61042[1]
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]
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]
Benzene	Equation 20				0. 00664[1]

Note:
[1] Identical to fractions for the vapor-venting process, based on CRC E-80 program (Table 65).

For ethanol levels of 70-100 percent, no permeation data were available. Thus, the toxic fraction for non-permeation evaporative emissions was also applied to permeation.

5.2 Diesel Vehicles

For diesel-fueled vehicles, evaporative emissions are estimated for the refueling-spillage process only. As there were no data characterizing 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.[42] The fractions are shown in Table 67. The values are stored in the minorHAPratio table, except for benzene which is stored in the atRatioNonGas table.

Table 67. 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

6 Crankcase Emissions

Crankcase emissions are modeled as a ratio of the exhaust emissions. Discussion of the ratios used to estimate THC, CO, NOx, and PM crankcase emissions can be found in the light-duty[56] and heavy-duty[57] emission rate reports. In general, toxic crankcase emissions that are calculated as a ratio from VOC or from PM are computing as a fraction of the toxic exhaust emissions. The details on crankcase emissions are discussed in the following sections.

6.1 Volatile Organic Compounds

Table 1 lists the VOC toxics modeled in MOVES, which are also modeled from crankcase emission processes. MOVES models the crankcase emissions from these toxics by multiplying the exhaust emissions of these species by the THC crankcase emission fraction listed in the light-duty and heavy-duty emissions reports. For example, the THC crankcase/exhaust fraction for light-duty gasoline (1969 and later model year) is 0.013. Thus, crankcase emissions for 1,3-butadiene are calculated as 1.3 percent of the exhaust emissions of 1,3-butadiene. Similar calculations are applied to all VOC toxic emissions. The crankcase emission ratios are stored in the MOVES table crankcaseEmissionratio, which differentiates the factors according to pollutant, process, model year range, source type and fuel type.

6.2 Polycyclic Aromatic Hydrocarbons

The PAH fractions for exhaust emissions are also applied to crankcase emissions. The gaseous PAHs are modeled in a similar fashion as the VOC toxic emissions. The PAH crankcase emissions are modeled as a fraction of the tailpipe exhaust gaseous PAH emissions, with factors stored in the crankcaseEmissionRatio table. The PAH crankcase emission factors are the same as the THC crankcase emission factors (e.g. 0.013 for 1969 and later gasoline vehicles).

To estimate crankcase particulate PAH emissions, MOVES applies the PAH/OC fractions developed for exhaust emissions to the crankcase OC emissions. The PAH/OC ratios are stored in the pahParticleRatio table for the crankcase emission processes (15, 16, and 17). The OC/PM speciation can be substantially different between crankcase emissions and exhaust emissions. For example, because conventional diesel crankcase emissions have a higher OC/PM composition than the tailpipe exhaust emissions, MOVES models elevated particulate PAH emissions in crankcase emissions compared to tailpipe PAH emissions. Research on conventional diesel vehicles validates that PM emissions from the crankcase are more enriched with PAHs than emissions from the exhaust.[58]

6.3 Metal and Dioxin Emissions

MOVES models crankcase metal emissions for the metal species included in the $PM_{2.5}$ speciation profiles, such as iron and aluminum. Details on speciation of crankcase emissions are included in the speciation report.[59] MOVES does not produce crankcase emission rates for metals that are not included in the speciation profiles such as arsenic, mercury and other metals listed in Table 4. Similarly, MOVES does not estimate dioxin and furan emissions from crankcase emissions, assuming that the emissions from crankcase are negligible compared to exhaust emissions.

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Appendix A Development of Motor Vehicle Emission Factors for Chromium

The emission rate for gasoline vehicles and trucks in MOVES for hexavalent chromium, or chromium 6+ (Cr(VI)) is 8.9×10^{-7} grams/mile.[1] This gasoline emission factor (EF) remained unchanged from the value used in NMIM (National Mobile Inventory Model) and was obtained from a paper by Ball, 1997.[2] The Ball (1997) test program and other testing from motor vehicles included only total chromium measurements, therefore Cr(VI) concentrations were estimated based on combustion data from stationary combustion turbines that burn diesel fuel which showed eighteen percent of chromium was hexavalent. [3]

An updated total chromium emission rate for gasoline vehicles and trucks was recently developed for MOVES based on data from the KCVES program.[4] The KCVES program sampled 99 vehicles for chemical composition from which a total chromium emission factor of 4.07×10^{-6} grams/mile was developed.[5] This average grams/mile rate was calculated by averaging the metal measured in Bag 2 of the LA92 driving schedule test (described below), with a weighted-average computed using vehicle miles traveled (VMT).

In 2010, the EPA's National Vehicle and Fuel Emissions Laboratory (NVFEL) collected particulate matter (PM) and volatile organic compound (VOC) exhaust samples, as well as CO, NO_x, CO_2, and CH_4 samples from a 2008 3.5L V6 Chevrolet Impala flex fuel light-duty gasoline vehicle. This testing also included direct Cr(VI) measurements.

The Impala had a beginning odometer reading of 38,934 miles and was tested using E10 gasoline. The vehicle test procedure used four sample bags and the LA92 "unified" dynamometer driving schedule.[6] The bags in this study represent the following conditions:

> Bag 1 – concentrated cold start compared to FTP (Federal Test Procedure); short distance, low speeds.
> Bag 2 – hot and running; longer distance and higher speeds than FTP (represents realistic real world driving).
> Bag 3 – hot start; short distance, low speeds.
> Bag 4 – hot and running; long distance.

PM was collected on four (labeled A-D) pre-cleaned and prepared filter media per bag. The PM filter samples labeled D were sent to the Wisconsin State Laboratory of Hygiene at the University of Wisconsin-Madison for chromium metal speciation. Total and hexavalent chromium was measured in extracts of filter-collected PM sent from NVFEL. Detection limits were in the <0.2 ng/filter range. A comparison of 47mm filter collection substrates was performed using Polyvinyl Chloride (PVC) and bicarbonate-impregnated Mixed Cellulose Ester (MCE) filters. Total chromium was analyzed by SF-ICPMS (Sector Field Inductively Coupled Plasma Mass Spectrometry) and Cr(VI)was analyzed by Inductively Coupled (IC)-post-column derivation. The Cr(VI) results obtained using PVC collection substrates were below the detection limit, with the exception of the tunnel blanks, and thus not listed in this memo. The extractable total chromium levels in the filters and bicarbonate were at such a level that swamp any signal from the PM, making the ICPMS data useless. However, the Cr(VI) data from the MCE filters analyzed by IC could be used to develop new emission rates as described below.

Spike and blank studies were performed. Spike studies had a recovery between 93-104 percent, indicating the matrix did not interfere with the chromium results. The Cr(VI) MCE filter results were blank corrected by subtracting the mean background value of 0.298 ng/filter (standard deviation±0.098 ng/filter; 95 percent confidence interval±0.157). The 95 percent confidence interval was calculated from student's *t*-distribution as a function of the probability and degrees of freedom and multiplied by the standard deviation over the square root of the number of blanks.

Cr(VI) speciation results and emission rates are reported in Table A-1 along with the corresponding distance driven per sample. The emission rates were calculated by dividing the blank-corrected Cr(VI) MCE mass/filter by the distance driven per sample and multiplying by a factor representing the CVS (constant volume sampler) volume over the individual filter sample volume (NVFEL filter sample D was used for each bag). This factor was used because all exhaust was not passed through the collection filter during the test.

$$Emission\ Rate = \frac{blankcorrected\ Cr(VI)MCE\ mass/filter}{distance} \times \frac{CVS\ volume}{Sample\ volume}$$

The overall emission rate in Table A-1 is a composite average of the total Cr(VI) measured divided by the total distance of the test and then multiplied by the sum of CVS volumes/sum of filter sample volumes.

Table A-1. Cr(VI) Emission Rates from an Onroad Gasoline Engine

Sample/bag number	Cr(VI) (ng/filter)	Mean IC Blank± Std Deviation (ng/filter)	Blank-corrected Cr(VI) (ng/filter)	CVS Volume (scf at 68ºF)	Sample Volume (scf at 68ºF)	Distance (miles)	Emission Rate (g/mile)
1	0.792	0.298±0.098	0.49	1666.87	7.675	1.194	$8.9x10^{-8}$
2	0.493	0.298±0.098	0.20	6280.73	28.815	8.612	$5.1x10^{-9}$
3	0.488	0.298±0.098	0.19	1682.74	7.711	1.186	$3.5x10^{-8}$
4	0.508	0.298±0.098	0.21	6281.82	28.894	8.620	$5.3x10^{-9}$
Overall			1.1	15912.2	73.10	19.61	**$1.2x10^{-8}$**

Direct Cr(VI) emission factors were not measured from a diesel engine. To develop on-road diesel emission factors, the overall gasoline emission factor from Table A-1 is multiplied by the ratio of total chromium from diesel engines verses gasoline engines. Emission factors are calculated for diesel engines based on the most recent estimates from engines before[7] and after[8,9] implementation of EPA's 2007 heavy-duty highway rule which reduced PM emissions from heavy-duty diesel vehicles. The total chromium emission factor for gasoline comes from the Kansas City Particulate Matter Characterization Study ($4.07x10^{-6}$ g/mi).[10]

Cr(VI) Pre-2007 On-road Diesel Emission Factor

$$EF = Gasoline\ Cr(VI)EF \times \frac{Total\ Cr\ EF_{diesel}}{Total\ Cr\ EF_{gasoline}} = 1.2x10^{-8}\frac{g}{mi} \times \frac{6.8x10^{-6}\frac{g}{mi}}{4.07x10^{-6}\frac{g}{mi}} = \mathbf{2.0x10^{-8}\frac{g}{mi}}$$

Cr(VI) 2007 to 2009 On-road Diesel Emission Factor

$$EF = Gasoline\ Cr(VI)EF \times \frac{Total\ Cr\ EF_{diesel}}{Total\ Cr\ EF_{gasoline}} = 1.2x10^{-8}\frac{g}{mi} \times \frac{1.94x10^{-6}\frac{g}{mi}}{4.07x10^{-6}\frac{g}{mi}} = \mathbf{5.8x10^{-9}\frac{g}{mi}}$$

Cr(VI) 2010 and Later On-road Diesel Emission Factor

$$EF = Gasoline\ Cr(VI)EF \times \frac{Total\ Cr\ EF_{diesel}}{Total\ Cr\ EF_{gasoline}} = 1.2x10^{-8}\frac{g}{mi} \times \frac{6.92x10^{-6}\frac{g}{mi}}{4.07x10^{-6}\frac{g}{mi}} = \mathbf{2.0x10^{-8}\frac{g}{mi}}$$

A Cr(VI) emission factor for transit buses using compressed natural gas is calculated by multiplying the overall Cr(VI) emission factor from Table A-1 by the ratio of total chromium from CNG transit buses[11] verses gasoline light-duty vehicle engines (from KCVES study).

Cr(VI) Transit Bus Compressed Natural Gas (CNG) Emission Factor

$$EF = Gasoline\ Cr(VI)EF \times \frac{Total\ Cr\ EF_{CNG}}{Total\ Cr\ EF_{gasoline}} = 1.2x10^{-8}\frac{g}{mi} \times \frac{7.0x10^{-8}\frac{g}{mi}}{4.07x10^{-6}\frac{g}{mi}} = \mathbf{2.1x10^{-10}\frac{g}{mi}}$$

A summary of the results for Cr(VI) emission factors is presented in Table A-2. While these results are based on measured Cr(VI), the results are limited by the following:

- Emissions from only one vehicle were measured, so the data do not provide information regarding variability among vehicles.
- No measurements have been made for diesel and CNG vehicles or engines.

Table A-2. Summary: Cr(VI) Emission Factors

	Emission Factor	Units
Onroad gasoline (MY2008)	$1.2x10^{-8}$	grams/mile
Onroad diesel (pre-2007)	$2.0x10^{-8}$	grams/mile
Onroad diesel (2007 and later)	$5.8x10^{-9}$	grams/mile
CNG Transit Buses	$2.1x10^{-10}$	grams/mile

Ibid.[1] http://www.epa.gov/otaq/models/moves/documents/420b12029a.pdf

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Table 1. MCE filter, Test# 20100024028

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Appendix B Development of Motor Vehicle Emission Factors for Mercury

Appendix B-1 Calculation of Mercury Emission Factors from Vehicle Tests

In 2005, the USEPA National Exposure Research Laboratory (NERL) collected mercury (Hg) 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 the 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 B-1. The data collected from these vehicles in diluted exhaust in the constant volume sampler (CVS) included 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 B-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 and used to correct exhaust measured values that are reported at higher frequencies. The particulate matter measurements were filter-based, test-level measurements and were corrected in that manner.

Appendix B-2 Calculation of Emission Rates

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:

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

$$\text{Exhaust flow} = (\text{CVS flow} / \text{dilution factor})$$

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.

Appendix B-3 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.

Appendix B-4 Calculating Weighted Emission Test Results

Highway vehicles were tested on the LA92 cycle; a more aggressive chassis-dynamometer test similar in concept to the 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. We considered it appropriate to calculate 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.

The equation used to calculate test-level emission rates is as follows:

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

Where:
E_{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 composite 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 B-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 they appeared nominal during the first LA92 cycle. We decided that only using measurements collected before 715 seconds in both tests provided the most reliable data.

Nonroad grams per gallon emission factors in Table B-2 were calculated from the onroad factors using a fuel economy estimate of 17 miles per gallon for the gasoline vehicle and 19 for the diesel vehicle.

Table B-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