Air Toxic Emissions from On-road Vehicles in MOVES2014

EPA United States Environmental Protection Agency

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Assessment and Standards Division
Office of Transportation and Air Quality
U.S. Environmental Protection Agency

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1 Introduction: Air Toxics

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 to estimate emissions of toxic compounds emitted from highway vehicles in the MOVES2014 database and model. The current release of the MOVES database (MOVES2014) includes substantial updates to inputs and structures used to estimate emissions of air toxics, incorporating data from recent programs conducted on new vehicles employing current technologies. It also includes the capability to estimate emissions for ethanol blends containing more than 10% ethanol, including E15, E20, and E85 (70-100% 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 table "Pollutant") is identical to the CAS number (minus the dashes).

Table 1. Hydrocarbons and Volatile Organic Compounds included in MOVES2014.

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
Methyl-Tertiary-Butyl Ether (MTBE)	22	1634-04-4
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

[1] This species represents the sum of emissions from three isomers of xylene, i.e., *ortho*-, *meta*-, and *para*-xylene.

Table 2. Polycyclic Aromatic Hydrocarbons included in MOVES2014.

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 MOVES2014

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 MOVES2014.

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

1.1 Methods

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. While MOVES attempts to estimate emissions from vehicles representing relevant combinations of technology and fuel, the availability and quality of data acquired and used varied widely. Consequently, the methods and approaches used to develop model inputs also varied as necessary.

During model 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 are themselves 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 so as to distinguish "permeation" and "non-permeation" processes. Finally, fractions vary with level of emission control (e.g. pre-Tier 2 versus Tier 2), and for old 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 are expressed on a distance-specific basis (g/mile). The rates for dioxins/furans are also distance-specific, but are not expressed in terms of mass directly. Rather, dioxins and furans are expressed in terms of "toxic equivalents" (TEQ), which effectively resolves the emissions of all dioxin and furan congeners into a single "species," represented by the two most carcinogenic congeners, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin. That is, the emissions of the other congeners are expressed as equivalent masses of these two congeners.

It should be noted that metals and dioxin emission rates are only produced from the 'running' exhaust emission process with the g/mile rates. We do not estimate their emissions explicitly from other exhaust emission processes such as start, extended idle, auxiliary power unit usage, and crankcase processes. In fact, for extended idle, auxiliary power unit usage, and crankcase emissions we do not have data on these emissions. However, in some cases the start emissions for these pollutants are included in the driving cycle used to derived distance-based emision factors as discussed in the report.

Finally, a uniform approach was used to develop single sets of inputs to estimate emissions of toxics from gasoline fuels containing ethanol at levels of 70-100 volume percent (vol.%). The data used for this purpose were typically measured on "E85" blends, containing 70-85 vol.% 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, 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.

1.2 Overview of the Report

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 two technologies groups are used to distinguish 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, 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 Sections 3 and 4. The development of inputs for diesel vehicles are defined as "pre-2007" and "model year 2007 and later" based on technology and emissions standards for heavy-duty vehicles. This distinction is made because emission controls on 2007 and later engines 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 also used to represent light-duty diesel vehicles, as well as diesel engines used as auxiliary power units, as noted in Section 3

Section 5 contains the derivation of the toxic emission rates for CNG-powered transit buses in MOVES. At present, MOVES only models CNG fuel usage within transit buses. Toxic emissions from evaporative emission processes and crankcase emission processes are addressed in Section 6 and 7.

2 Gasoline Exhaust

2.1 Volatile Organic Compounds

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

2.1.1.1 2000 and Earlier Model Year Vehicles

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

Table 5. Calculation Methods for 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
Methyl-tert-butyl ether	complex	Derived from Complex Model Database
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 2.1.1.1.4

2.1.1.1.1 Use of Equations Developed for 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.[3] 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 only "normal–emitting" vehicles. The tenth group represents all "high emitters," regardless of technology. In application, the 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.

[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 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). While MOBILE6 applied separate equations for older technologies not included in the Complex Model, such as vehicles without catalysts or vehicles equipped only with oxidation catalysts, these equations were not included in MOVES since these vehicles now comprise an extremely small and ever shrinking portion of the fleet. For 1974 and earlier model years, 1975 weightings are used. In addition, while MOBILE6.2 relied on very limited data from heavy-duty gasoline vehicles, MOVES applies Complex Model effects to both light-duty and heavy-duty gasoline vehicles. This step was taken because the very limited data specific to heavy-duty gasoline vehicles are not adequate to account for effects of fuel properties

2.1.1.1.2 Overview of the Complex Model

The Complex Model is so called because it was designed to model the "complex" behavior of selected emissions in relation to changes in a set of selected fuel properties.

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

In fitting the Complex 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, the model is fit as shown in Equation 1, using terms for oxygenate (wt.%), aromatics (vol.%) 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, 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

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

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

Property	Units	Mean Value
Aromatics	Vol. %	28.26110
Olefins	Vol. %	7.318716
Methyl-tertiary-butyl-ether (MTBE)[1]	Wt.%	0.947240
Ethyl-tertiary-butyl-ether (ETBE)[1]	Wt.%	0.023203
Ethanol (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

[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	MTBE	ETBE	EtOH	TAME	RVP	E200	E300
1	-0.05548	-	-0.03646	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	-	-0.05598	0.316467	0.249326	-	-	-	-0.01216

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

Technology Group	Fuel Property								
	Aromatics	Olefins	MTBE	ETBE	EtOH	TAME	RVP	E200	E300
1	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
2	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
3	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
4	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
5	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
6	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
7	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
8	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
9	-0.00717	-	0.046213	-	-	-	-	-	-0.01023
10	-0.00717	-0.03135	0.046213	-	-	-	-	-	-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	Oxygenate	Olefins	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	-0.06077	0.043696	-0.00731	-0.00806

For each compound, the model equations as shown in Equation 1, are evaluated for a "base" and a "target" fuel. 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.[19] The "target" fuels are represented by specific sets of 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 30 ages listed in the table gives a set of 30 adjustments, with each 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 for 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.

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

As of calendar year 2008, MTBE (pollutantID = 22) has been almost completely phased-out of the fuel supply in the United States due to concerns related to contamination of ground water. Thus, its inventory levels as predicted by MOVES based on default inputs should be very small if not zero in future years. It is presently in the MOVES model as a legacy pollutant for calendar

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

years 1990 and 1999 – 2005[c]. However, the MTBE fuel volume is a user input, and MOVES has the capability to calculate MTBE emissions for any calendar year.

For MTBE, a fuel-effects model based on the Complex Model database and applied in MOBILE6.2 was used.[4,5] This model is based on equations fit to data representing nearly 900 observations. However, instead of using model equations directly, MOBILE6.2 was run at different fuel MTBE volumes (V_{MTBE}). Using the results of the MOBILE6.2 runs, the MTBE fractions of VOC were calculated and related to MTBE fuel levels using a simple least-squares regression. A quadratic equation fixed at the origin was selected, and gives results consistent with the original parameterization in MOBILE6.2. The parameters are shown in Table 13. The same equation is used for both start and running processes and is shown in Equation 7.

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

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

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

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

Data were not available to develop emission effects for ETBE and TAME blends; thus, the equations for ethanol-oxygenated gasoline were used for ETBE blends, and those for MTBE-oxygenated gasoline were used for TAME blends.

2.1.1.1.4 Simple Fractions of VOC

Table 14 lists toxic fractions of VOC for a set of additional compounds designed to represent toxic emissions for several fuel blends containing different oxygenates. With the exception of ethanol, for gasoline fuels containing 0 and 10% ethanol (E0 and E10), fractions were developed by Sierra Research using speciation profiles estimated from EPA's SPECIATE 4.2 database.[6] The fractions for E10 are also used to represent blends in which the oxygenate is ethyl-tertiary-butyl-ether (ETBE) at levels of 5 vol.% or greater.

For blends containing methyl-tertiary-butyl ether (MTBE), however, fractions were adopted from the National County Database for the National Mobile Inventory Model (NMIM). The fractions used in NMIM were derived for the 1999 National Emission Inventory (NEI) for hazardous air pollutants (HAPS), version 3, and summarized in Volume 1, Appendix D, Table 1 of the documentation. These fractions were based on older speciation profiles than the E0 and E10 data. One set of fractions represents winter fuels containing MTBE at 12 vol. % or greater, or tertiary-amyl-methyl-ester (TAME) at levels of 13% or more (winter). A second set represents reformulated gasoline fuels containing MTBE at levels between 5.0 and 13.0 vol.% or TAME at levels between 5.0 and 13.0 vol.% (RFG). These fractions are provided in Table 15.

c MOVES does not currently explicitly model calendar years 1991-1998

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

No data exist for 2000 and earlier vehicles running on E15 or E20. 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%[11], and flex-fuel vehicles were manufactured in only the 1999 and 2000 model years. For pollutantIDs 40 – 46, we used toxics ratios for 2001 and later vehicles, found in Table 41. For acrolein and ethanol, we simply extended the E10 toxic fractions as shown in Table 14.

Table 14. 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	0.0239	0.0239	0.0239
Acrolein	27	0.000628	0.000628	0.000628	0.000628
2,2,4-Trimethylpentane	40	0.01823	0.01849	Table 41	
Ethyl Benzene	41	0.02147	0.01932		
Hexane	42	0.01570	0.01593		
Propionaldehyde	43	0.00086	0.00086		
Styrene	44	0.00108	0.00097		
Toluene	45	0.09619	0.08657		
Xylene	46	0.07814	0.07032		

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

Compound	pollutantID	MTBE	
		Winter	RFG
Acrolein	27	0.0006	0.0006
2,2,4-Trimethylpentane	40	0.04327	0.04327
Ethyl Benzene	41	0.01398	0.01484
n-Hexane	42	0.00861	0.00888
Propionaldehyde	43	0.00073	0.00073
Styrene	44	0.00328	0.00340
Toluene	45	0.09873	0.10494
Xylene	46	0.05557	0.05910

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

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

Field	Description	RelevantValues
polProcessID	Identifies the pollutant (1st two digits and Emissions Process (last two digits).	Pollutants are identified in the table above; Relevant processes include: "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 MY2001 and later, and certified to NLEV or Tier 2 standards, 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 17.

Table 17. 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)

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

2.1.1.2.1 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 MOVES 2010b 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), with the three components of the label denoting the designation given to the study by the EPA, DOE and CRC, respectively.

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

Initiated in March 2009, the Phase 3 program involved measurement of exhaust emissions from fifteen high-sales-volume Tier-2 certified vehicles. 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 18.

Table 18. 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 19. 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 19. 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 19, plus two-way interactions of ethanol and the other five properties, as shown in Equation 8, in which β represents a linear coefficient for each effect.

$$Y = \beta_0 + \beta_1 \text{etOH} + \beta_2 \text{Arom} + \beta_3 \text{RVP} + \beta_4 \text{T50} + \beta_5 \text{T90} + \beta_6 \text{T50}^2 + \beta_{11} \text{etOH}^2 \beta_7 \text{etOH} \times \text{Arom} + \beta_8 \text{etOH} \times \text{RVP} + \beta_9 \text{etOH} \times \text{T50} + \beta_{10} \text{etOH} \times \text{T90} + \varepsilon \quad \textbf{Equation 8}$$

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 20.

Emissions measured include carbon dioxide (CO_2), carbon monoxide (CO), THC, methane (CH4), 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 21.

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 20 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[12]" and "EPAct Analysis Report.[13]"

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

Table 20. 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

[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 21. 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 9. Note that the means and standard deviations are calculated from the fuel set used for the program (see Table 20). The result is a "Z score," representing a "standard normal distribution" with a mean of 0.0 and a standard deviation of 1.0.

$$Z_i = \frac{x_i - \bar{x}}{s} \qquad \textbf{Equation 9}$$

For the linear effects in the model, standardization is performed using the values of each fuel property, each in their respective scales (vol. %, psi, °F.). Using aromatics as an example, the standardization of the linear term is shown in Equation 10.

$$Z_{\text{arom}} = \frac{x_{\text{arom}} - \bar{x}_{\text{arom}}}{s_{\text{arom}}} \qquad \textbf{Equation 10}$$

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 11, 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.

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

Standardized terms for interaction effects are constructed similarly. For example, Equation 12 shows the standardization of an interaction term between ethanol and aromatics.

$$ZZ_{\text{etOH}\times\text{eArom}} = \frac{Z_{\text{etOH}} Z_{\text{Arom}} - m_{Z_{\text{etOH}} Z_{\text{Arom}}}}{s_{Z_{\text{etOH}} Z_{\text{Arom}}}} \qquad \textbf{Equation 12}$$

Means and standard deviations for relevant model terms are shown in Table 22. 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 23. 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.[14]

Table 22. 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		

[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 23. 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 10)											
	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						0.9630	0.9630	-0.0367	-0.0992	-0.5413	0.1633
Std. Dev.						0.8028	0.7398	0.9785	0.9996	0.7692	0.9728
Two-Stage Standardized Values (ZZ) (Equation 11, Equation 12)											
						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

[1] Mean and Standard Deviations of fuel properties for the entire fuel set. See Table 22.
[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 23. Thus, the model to be fit includes some subset of the 11 candidate terms shown in Equation 13.

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

Equation 13

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.

When the available data were sufficient, "mixed models" were fit, in which the terms listed in Table 22 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.[15]

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.[16]

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).[17] 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 24 through Table 27. 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.

During MOVES runs, 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.[d] 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 determine NMHC.[18] 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 28. This model was fit using the same methods as that for total hydrocarbons (THC), as described in the Fuel Effects Report.[19]

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

Table 24. 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				

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

Table 25. 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				

[1] See 9.2.2 and Appendix L.3 in the Project Report.[13]

Table 26. 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				

[1] See 9.2.2 and 8.7.4 in the Project Report
[2] Not fit by the Tobit model, manually recalculated from intercepts for individual vehicles.

Table 27. 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				

[1] See 9.2.2 in the Project Report.[13]
[2] Not fit by the Tobit model, manually recalculated from intercepts for individual vehicles.

Table 28. 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				

[1] See 9.1.2 in the Project Report[13]

2.1.1.2.4 Model development under the Reduced Design

Recall that, 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 21, 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 2.1.1.2.3 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 29 through Table 32. 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 33 through Table 37. 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.

Table 29. 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				

[1] See 9.2.2 and Appendix O.3 to the Project Report.[13]

Table 30. 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				

[1]See 9.2.2 in the Project Report.[13]

Table 31. 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				

[1]See 9.2.2 in the Project Report.[13]

Table 32. 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				

[1] See 9.2.2 in the Project Report.[13]

Table 33. 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				

[1] See 9.2.2 and Appendix K.3 to the Project Report.[13]

Table 34. 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				

[1] See 9.2.2 and Appendix L.4 to the Project Report.[13]

Table 35. 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				

[1] See 9.2.2 and Appendix N.4 to the Project Report.[13]

Table 36. 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				

[1] See 9.2.2 in the Project Report.[13]

Table 37. 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				

[1] See 9.2.2 and Appendix Q.4 to the Project Report.[13]

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. So, to model the behavior of the fraction with respect to changes in fuel properties, it was necessary to develop models for NMOG and ethane, as well as the toxics, because VOC is estimated as NMOG minus ethane.[e]

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.%), aromatics content (vol.%), RVP (psi), T50 (°F) and T90 (°F), as well as selected interaction terms among these five parameters.

The statistical models generated from the EPAct data follow the general structure shown in Equation 14 below, which uses the model for acetaldehyde as an example (see Table 24). 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.

$$\text{Emissions (g/mi)} = e^{\mathbf{X\beta}}$$

$$= \exp\begin{pmatrix} \beta_0 + \beta_e Z_e + \beta_a Z_a + \beta_r Z_r + \beta_5 Z_5 + \beta_9 Z_9 + \\ \beta_{ee} ZZ_{ee} + \beta_{55} ZZ_{55} + \\ \beta_{ea} ZZ_{ea} + \beta_{er} ZZ_{er} + 0.5(s^2_{veh} + s^2_{\varepsilon}) \end{pmatrix} \qquad \textbf{Equation 14}$$

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

When 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

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

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 14 to each compound for a specified fuel. The toxic emissions as a fraction of VOC emissions (f_{toxic}) are given by

$$\text{Toxic Fraction} = f_{\text{toxic}} = \frac{e^{\mathbf{X\beta}_{\text{toxic}}}}{e^{\mathbf{X\alpha}_{\text{NMOG}}} - e^{\mathbf{X\theta}_{\text{ethane}}}} \qquad \textbf{Equation 15}$$

For all compounds, the calculation shown in Equation 15 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. That is to say, if the toxic model was fit with the reduced design, we combined it with the NMOG and ethane models also fit with the reduced design. We followed this approach to prevent the calculation and propagation of artifacts in the estimated fractions resulting from differing levels of information and complexity in the numerator and denominator in Equation 15. In this context we considered it important to apply "information parity" to the toxic model in the numerator and the NMOG model in the denominator, as the vast majority of VOC mass is represented by NMOG, with ethane comprising only a small fraction. Table 38 summarizes the combinations of models used to calculate toxic fractions for start and running emissions.

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 or higher than levels ostensibly measurable in vehicle exhaust. Estimation of "simple" toxic fractions for these compounds is covered in the following sub-section.

Table 38. References to Tables containing Coefficients for Models used to Calculate Toxic Fractions of VOC (see Table 17, page 18)

Compound	Start Emissions (Bag 1)			Running Emissions (Bag 2)		
	Toxic	NMOG	Ethane	Toxic	NMOG	Ethane
Acetaldehyde	Table 24	Table 28	Table 32	Table 33	Table 36	Table 37
Formaldehyde	Table 25	Table 28	Table 32	Table 34	Table 36	Table 37
Acrolein	Table 26	Table 28	Table 32	NO MODEL		
Ethanol	Table 27	Table 28	Table 32	Table 35	Table 36	Table 37
Benzene	Table 29	Table 31	Table 32	NO MODEL		
1,3-butadiene	Table 30	Table 31	Table 32	NO MODEL		

2.1.1.2.6 Estimating Simple Fractions of VOC for Running Emissions

As noted in Table 21, 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[20].

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 39. 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 39. Benzene (Running): Derivation of a Ratio-of-Means Estimator for Benzene as a Fraction of VOC.

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

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

The VOC fraction for acrolein was derived similarly (Table 40). 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 40. 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

[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.[21,22] With benzene represented as a fraction of VOC (as in Equation 15) denoted as $f_{benzene}$, a value modified to account for benzene levels in different fuels ($f^*_{benzene}$) is calculated as shown in Equation 16 where $x_{benzene}$ is the benzene level for the fuel modeled (weight percent), A is the mean benzene level in the EPAct exhaust program fuel set (0.66 weight percent), and B is an empirical coefficient, taking a value of 0.24.

$$f^*_{benzene} = \left[\left(x_{benzene} - A\right) \cdot B \cdot f_{benzene}\right] + f_{benzene} \qquad \textbf{Equation 16}$$

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.[23] Starting with an unadjusted toxic fraction for 1,3-butadiene (f_{buta}), the modified fraction f^*_{buta} is calculated using Equation 17, 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.

$$f^*_{buta} = f_{buta}\left(\frac{Ax^2_{olefin} + Bx_{olefin} + C}{D}\right) \qquad \textbf{Equation 17}$$

2.1.1.2.8 Additional Air Toxics Estimated from EPAct Speciation Profiles

For fuel blends with 0%, 10% and 15% ethanol, composite speciation profiles developed from the results of EPAct (Phase 1) were used to develop toxic fractions of VOC for the hazardous air toxics listed in Table 41.[f] These profiles were based on averaging results of tests from 3 vehicles.[24,25] Toxic fractions for E10 are used for all gasolines containing ethanol levels of 5 vol.% or greater. For fuel blends containing 20% ethanol, fractions were developed using a composite speciation profile developed using results from the EPAct (Phase 3) program. The fractions are also presented in Table 41. The values shown in Table 41 are stored in the database table minorHAPRatio (see Table 16). For blends containing MTBE, no data were available for Tier 2 vehicles; thus the toxic to VOC ratios for Tier 1 and earlier vehicles were used (See Table 15).

[f] 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 41. 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)**	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

[1] For fuels containing 0-20% ethanol, fractions for ethanol, benzene, acetaldehyde, formaldehyde, 1,3-butadiene, and acrolein were estimated using methods described in 2.1.1.2.1.

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

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

2.1.2.1 2000 and Earlier Model Year Vehicles

Major HAP emissions for 2000 and earlier model year vehicles operating on fuel blends containing 70-100% 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 42. 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% ethanol. These ratios are applied to older technology (2000 and earlier vehicles), even though data were collected from Tier 2 vehicles[g]. The 2000 and earlier HAP emission rates are stored in the database table "ATRatioNonGas" (see Table 43).

Table 42. 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

[g] Because the data used to derive the E85 emission rates are based on Tier 2 vehicles, there is more uncertainty in the emission rates from 2000 and older technology vehicles running on high ethanol blends in MOVES. However, pre-2001 flex-fuel vehicles are minor portion of the light-duty gasoline fleet. For example, the default MOVES2014 population indicates that less than 1-3% of the 1998-2000 model year light-duty gasoline vehicles are flex-fuel vehicles, and MOVES2014 doesn't include any flex-fuel vehicles earlier than 1998. Additionally, the number of flex-fuel vehicles that use high ethanol blends is limited; making pre-2001, high-ethanol blend fueled vehicles a small portion of the vehicle emissions inventory.

Table 43. 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.	
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.	

2.1.2.2 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[26], Coordinating Research Council (CRC) E-80[27], and the PM Speciation Program[28]. 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 44.

Table 44. 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 18. The adjustment factor was set to zero when the differences in emissions were not statistically different (i.e., acrolein).

$$E85\ adjustment\ factor = \frac{\frac{Toxics_{E85}}{VOC_{E85}}}{\frac{Toxics_{E10}}{VOC_{E10}}} \qquad \textbf{Equation 18}$$

The resulting adjustment factors are shown inTable 45, and are stored in the database table, "GeneralFuelRatioExpression" for fuelTypeID = 5. The E10 to E85 adjustments are used to estimate major HAP emissions for all 2001 model year vehicles and later.

Table 45. 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

2.1.2.3 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% 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 (2.1.2.2). 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.[g] The VOC fractions shown in Table 46 are stored in the database table "minorHAPRatio" (see Table 16).

Table 46. 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)

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

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 ($OC_{2.5}$).

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).[29] 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[h], vehicle-miles traveled (VMT), and an equal weight between summer and winter.[32] We used a VOC/THC fraction of 0.86 developed from the total organic-gas speciation profile developed from the Kansas City program (8750a), in estimation of PAH/VOC fractions. We adjusted the PAH/$PM_{2.5}$ fraction by the fraction of OC measured in the start (42.6%) and running emission processes (55.7%) to produce PAH/$OC_{2.5}$ emission fractions.[32] 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.

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.[30] 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 47 reports the TIGF/XAD phase allocation factors measured at 47°C (which was the measurement temperature for the Kansas

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

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 MOVES2014, 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 47. 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 MOVES2014, are calculated by multiplying the PAH/VOC, and PAH/OC fractions calculated from the Kansas City Vehicle Emission Study (KCVES) by the gas/particle partitioning factors in Table 19. The calculation is displayed with Equation 19 and Equation 20 for each PAH, i= 1:16.

$$\frac{PAH_i}{VOC}(\text{Table 48}) = \frac{PAH_i}{VOC}(KCVES) \times Gaseous\ Fraction_i\ (\text{Table 47}) \qquad \textbf{Equation 19}$$

$$\frac{PAH_i}{OC}(\text{Table 48}) = \frac{PAH_i}{OC}(KCVES) \times Particulate\ Fraction_i\ (\text{Table 47}) \qquad \textbf{Equation 20}$$

Within MOVES, the PAH fractions in Table 20 are applied to all gasoline fuels with ethanol content less than 20%. In the MOVES database, these fractions are stored in two tables. Fractions for the gaseous and particulate phases are stored in the tables "pahgasratio" and "pahparticleratio," respectively. The two tables have the same structure, which is presented in Table 49.

Table 48. Toxic Fractions for PAH Compounds, in Gaseous and Particulate Phases for Gasoline Vehicles Fueled with Ethanol Content < 20%

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 49. Description of the Database Table "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% Ethanol

Hays et al. (2013)[31] 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% and 93% 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 the Kansas City Vehicle Study tested on E0 fuel. We reduced the VOC phase PAH ratios by 74%, assuming that (1) the annual average ethanol content of high ethanol fuels is 74%, and (2) the PAH in the gaseous phase are reduced proportionally to the gasoline content reductions. The 74% reduction is within the range of reductions observed by Hays et al. (2013)[31] for total PAHs. Because Hays et al. (2013)[31] observed no significant decrease of the heavier PAHs for which MOVES assumes exist primarily in the particle-phase (Table 47), we assume

the E85 particle PAH/OC fractions are the same as the E0-E20 fractions derived from the Kansas City Light-duty Vehicle Emissions Study. The resulting fractions are presented in Table 50.

Table 50. 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. MOVES2014 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 MOVES2014 Speciation report.[32] 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 table *metalEmissionRate*, described in Table 52. 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 on-road vehicle fleet.[32]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 MOVES2014 TOG and PM Speciation Report.[32] 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% and -16% 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.[33]

Emission factors for arsenic were developed from data reported for tunnel tests.[34] 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 51. 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 51, page 46).

Table 52. 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

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

The MOVES model estimates emissions for 17 dioxin and furan congeners. The emissions are estimated using distance-specific emission rates multiplied by World Health Organization 2005 toxic-equivalency factors (TEFs;Table 53).[35] Thus, emission rates for the various congeners are expressed as TEQs of the most toxic congener (2,3,7,8 TCDD) (Table 54). These emission rates were obtained from a tunnel study and used in EPA's dioxin assessment.[36,37] They do not vary among fuel types. The rates are stored in the database table "dioxinEmissionRate," which is described in Table 55.

Table 53. Dioxin/Furan Toxic Equivalency Factors (World Health Organization)

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

Table 54. Dioxin Emission Rates for Motor Vehicles Running on Gasoline Fuel Blends with 0-20% Ethanol.

Pollutant	TEQ (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^{-11}
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	7.92×10^{-11}
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	4.93×10^{-11}
1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin	5.95×10^{-11}
Octachlorodibenzo-p-dioxin	1.41×10^{-11}
2,3,7,8-Tetrachlorodibenzofuran	2.76×10^{-10}
1,2,3,7,8-Pentachlorodibenzofuran	3.96×10^{-11}
2,3,4,7,8-Pentachlorodibenzofuran	2.90×10^{-10}
1,2,3,4,7,8-Hexachlorodibenzofuran	1.09×10^{-10}
1,2,3,6,7,8-Hexachlorodibenzofuran	1.16×10^{-10}
1,2,3,7,8,9-Hexachlorodibenzofuran	3.17×10^{-11}
2,3,4,6,7,8-Hexachlorodibenzofuran	1.36×10^{-10}
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1.21×10^{-10}
1,2,3,4,7,8,9-Heptachlorodibenzofuran	3.87×10^{-12}
Octachlorodibenzofuran	4.11×10^{-12}

Table 55. 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 Table 54, 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% 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 54) 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 56.

Table 56. 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^{-11}
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	2.06×10^{-11}
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	1.28×10^{-11}
1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin	1.55×10^{-11}
Octachlorodibenzo-p-dioxin	3.67×10^{-12}
2,3,7,8-Tetrachlorodibenzofuran	7.19×10^{-11}
1,2,3,7,8-Pentachlorodibenzofuran	1.03×10^{-11}
2,3,4,7,8-Pentachlorodibenzofuran	7.55×10^{-11}
1,2,3,4,7,8-Hexachlorodibenzofuran	2.84×10^{-11}
1,2,3,6,7,8-Hexachlorodibenzofuran	3.02×10^{-11}
1,2,3,7,8,9-Hexachlorodibenzofuran	8.24×10^{-12}
2,3,4,6,7,8-Hexachlorodibenzofuran	3.52×10^{-11}
1,2,3,4,6,7,8-Heptachlorodibenzofuran	3.16×10^{-11}
1,2,3,4,7,8,9-Heptachlorodibenzofuran	1.01×10^{-12}
Octachlorodibenzofuran	1.07×10^{-12}

3 Diesel Exhaust: Pre-2007

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, 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 and post-2007).

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 in 2007 and later.

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).[38] 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.[38] 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 57. Toxic fractions for other compounds in Table 57 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 57. 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.[39]

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[40] using estimates from EPA's SPECIATE 4.2 database[41] and information on compounds' physical and chemical properties. The allocations from SPECIATE were based on medium-duty diesel engine data.[42] The phase-partitioning factors are shown in Table 58. Compared to the partitioning for gasoline (Table 47), 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.

Table 58. 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

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

In estimating fractions, we relied on data collected in the United States on heavy-duty diesel engines running on conventional diesel fuels, measured on test-cycles representative of real world operation. It should be noted that for some compounds, substantially more data 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 59 shows fractions for PAH emissions relative to OC and VOC, by emissions process.

Table 59. 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 59 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 (1960-2050), because the APUs are not subject to the same control as exhaust from the highway engines.

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 Kansas City test 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 51). It does not vary with emission control technology. The mercury emission rates for pre-2007 diesels is calculated from emission tests conducted on two heavy-duty diesel vehicles, as documented in Appendix B. Table 60 provides metal emission factors for pre-2007 diesel vehicles.

Table 60. Emission Rates for Selected Metals for Pre-2007 Diesel Vehicles

Pollutant	Emission Rate (g/mi)
Chromium VI	$2.0x10^{-8}$
Manganese	8.0×10^{-6}
Nickel	1.4×10^{-5}
Mercury, Elemental Gaseous Phase	6.2×10^{-9}
Mercury, Reactive Gaseous Phase	3.2×10^{-9}
Mercury, Particulate Phase	1.6×10^{-9}
Arsenic	2.3×10^{-6}

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.[43] 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 TEQ are shown in Table 61. Since these engines are older than most of the pre-2007 fleet, dioxin emissions for pre-2007 engines may be overestimated.

Table 61. Emission Rates for Dioxin/Furan Congeners for Pre-2007 Diesel Vehicles

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

4 Diesel Exhaust: MY 2007 and later

4.1 Volatile Organic Compounds

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.[44] In this study detailed emissions measurements were performed on four engines operated on low-sulfur diesel fuel over several test cycles. We made use of data from 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[44]. Toxic fractions of VOC calculated from the ACES data are provided in Table 62.

Table 62. Toxic Fractions of VOC for 2007 and later Diesel Vehicles.

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

4.2 Polycyclic Aromatic Hydrocarbons

For heavy-duty diesels manufactured in 2007 and later, advanced emission controls reduce the total mass of PAH emitted and change the composition of these compounds. For these engines, we relied on speciated emissions data from the ACES study. The PAH emissions measured in the ACES study were uncorrected for background concentrations.[44] Toxic fractions applicable to these engines are shown in Table 63, in which the fractions are differentiated by phase but not by emissions process. We used the same phase fractions presented in Table 58. 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 MOVES2014 TOG and PM Speciation Report.[18]

Table 63. Toxic Fractions for Polycyclic Aromatic Compounds, by Phase, for 2007 and later Diesel Vehicles

PAH	Gaseous Phase (PAH/VOC)	Particulate Phase (PAH/OC2.5)
Naphthalene	1.63×10^{-2}	0.0
Acenaphthylene	8.53×10^{-5}	0.0
Acenaphthene	5.26×10^{-5}	0.0
Fluorene	1.96×10^{-4}	2.41×10^{-4}
Anthracene	3.04×10^{-5}	1.19×10^{-4}
Phenanthrene	8.51×10^{-4}	1.92×10^{-3}
Fluoranthene	4.57×10^{-5}	2.18×10^{-4}
Pyrene	3.79×10^{-5}	2.09×10^{-4}
Benzo(a)anthracene	3.00×10^{-7}	3.58×10^{-6}
Chrysene	5.00×10^{-7}	1.12×10^{-5}
Benzo(a)pyrene	0.0	1.48×10^{-5}
Benzo(b)fluoranthene	0.0	6.27×10^{-6}
Benzo(k)fluoranthene	0.0	6.27×10^{-6}
Benzo(ghi)perylene	2.00×10^{-7}	8.96×10^{-7}
Indeno(1,2,3-cd)pyrene	0.0	2.24×10^{-6}
Dibenz(a,h)anthracene	0.0	4.48×10^{-6}

4.3 Metals

Emissions rates for manganese and nickel representing diesel engines manufactured since 2007 were developed using data from the ACES program. The ACES metal emission rates were uncorrected for background concentrations.[44] The emission rate for arsenic is identical to the emission rate used for gasoline vehicles and pre-2007 diesels (Table 51, page 46). 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 rate was 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 Kansas City and ACES test programs, respectively. More details are provided in Appendix A. Metal emission rates are presented in Table 64.

Table 64. Emission Rates for Metals, for 2007 and Later Diesel Vehicles

Pollutant	Emission Rate (g/mi)
Chromium VI	$5.8\text{x}10^{-9}$
Manganese	5.5×10^{-7}
Nickel	6.5×10^{-7}
Mercury, Elemental Gaseous Phase	6.2×10^{-9}
Mercury, Reactive Gaseous Phase	3.2×10^{-9}
Mercury, Particulate Phase	1.6×10^{-9}
Arsenic	2.3×10^{-6}

4.4 Dioxins and Furans

The data used to calculate the emission rates for engines manufactured in 2007 and later were obtained from the EPA diesel dioxin study of 2007 and later engines.[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. Rates are presented in Table 65.

Table 65. Emission Rates for Dioxins and Furans, for 2007 and Later Diesel Vehicles (mg/mi TEQ)

Congener	2007 - 2009	2010 and later
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	0.0	0.0
1,2,3,7,8-Pentachlorodibenzo-*p*-Dioxin	0.0	0.0
1,2,3,4,7,8-Hexachlorodibenzo-*p*-Dioxin	0.0	0.0
1,2,3,6,7,8-Hexachlorodibenzo-*p*-Dioxin	0.0	0.0
1,2,3,7,8,9-Hexachlorodibenzo-*p*-Dioxin	4.11×10^{-12}	0.0
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-Dioxin	2.58×10^{-12}	1.05×10^{-11}
Octachlorodibenzo-*p*-dioxin	2.79×10^{-13}	2.09×10^{-12}
2,3,7,8-Tetrachlorodibenzofuran	0.0	5.09×10^{-12}
1,2,3,7,8-Pentachlorodibenzofuran	0.0	3.21×10^{-12}
2,3,4,7,8-Pentachlorodibenzofuran	1.89×10^{-11}	9.73×10^{-11}
1,2,3,4,7,8-Hexachlorodibenzofuran	0.0	2.20×10^{-11}
1,2,3,6,7,8-Hexachlorodibenzofuran	0.0	2.43×10^{-11}
1,2,3,7,8,9-Hexachlorodibenzofuran	0.0	0
2,3,4,6,7,8-Hexachlorodibenzofuran	0.0	1.80×10^{-11}
1,2,3,4,6,7,8-Heptachlorodibenzofuran	3.00×10^{-12}	9.94×10^{-12}
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.0	5.81×10^{-13}
Octachlorodibenzofuran	2.12×10^{-16}	5.21×10^{-16}

5 Compressed Natural Gas (CNG) Transit Bus Exhaust

MOVES2014 estimates emissions of toxics from transit buses fueled by compressed natural gas. This section describes the development of toxic emission inputs for this class of vehicles.

5.1 Volatile Organic Compounds

We used speciated hydrocarbon measurements 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 MOVES2014 heavy-duty emission rates report[58], 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 66. The total VOC emission rates are reduced by 70% from pre-2002 levels. As shown in the table, formaldehyde emissions are preferentially reduced by the oxidation catalyst. Formaldehyde contributes over 50% of the VOC emissions for the uncontrolled CNG bus, but only 16.2% of the VOC emissions for the CNG bus equipped with an oxidation catalyst. The MOVES toxics not measured in this study are assumed to be negligible, and are modeled as 0.

Table 66. 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

5.2 Polycyclic Aromatic Hydrocarbons

The PAH toxic fractions for compressed natural gas are derived from tests on a MY2000 DDC Series 50G engine on a New Flyer CNG transit bus tested by the California Air Resources Board (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 67.

Table 67. 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

ND = not detected, fractions set to 0.

5.3 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 Kansas City test 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 68.

Table 68. 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 (2010)
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

5.4 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 54.

6 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.

6.1 Gasoline Vehicles

6.1.1 Vapor Venting, Fuel Leaks, and Refueling Emission Processes

MOVES estimates evaporative emissions from gasoline vehicles using toxic fractions that pertain to the evaporative emission processes. In addition, 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 69.

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% ethanol, and are presented in Table 70. 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 decided to 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 71.

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

For vehicles operating on fuels containing 15% ethanol (E15), no data describing evaporative emissions are available. For the vapor-venting and spillage emission processes, emission rates calculated from E15 and E10 fuel speciation data from the EPAct Program were used to adjust the E10 evaporative emissions speciation.[52] Resulting toxic fractions are provided in Table 71.

For vehicles containing 20% 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 71.

For vehicles operating on fuels containing high levels of ethanol, ranging from 70 to 100%, 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.[27] 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 71.

Table 69. Data Sources and Estimation Methods Used in Estimation of Toxic Fractions for Evaporative VOCs

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

Table 70. Complex Fractions of VOC for Evaporative Emissions of Two Compounds Applied for Fuels Containing up to 10% Ethanol.

Pollutant	Process	Equation for Toxic Fraction
Benzene	Vapor venting/Refueling (vapor)	(-0.03420*OXY - 0.080274*RVP + 1.4448)*BNZ/100
	Fuel Leaks/Spillage	(-0.03420*OXY - 0.080274*RVP + 1.4448)*BNZ/100
MTBE	Vapor Venting/Refueling (vapor)	(24.205 - 1.746*RVP)*MTBE/1000
	Fuel Leaks/Spillage	(17.8538 - 1.6622*RVP)*MTBE/1000
OXY = oxygen content (wt%) RVP = Reid Vapor Pressure (psi) BNZ = benzene content (vol.%) MTBE = methyl-tertiary-butyl ether content (vol.%).		

Table 71. 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	0.00000	0.11896	0.1935	0.2227	0.61042
2,2,4-Trimethylpentane	0.01984	0.03354	0.05313	0.0430	0.00830
Ethyl Benzene	0.02521	0.01721	0.01662	0.0155	0.00124
N-Hexane	0.02217	0.02536	0.007478	0.0186	0.01276
Toluene	0.09643	0.14336	0.1406	0.0874	0.01608
Xylene [a]	0.07999	0.06423	0.05735	0.0711	0.00733
Benzene	Table 70		0.02758	0.0073	0.00664

6.1.2 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.[53,54] 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 72, for all compounds except benzene. To estimate toxic fractions for vehicles operating on fuels containing 15% ethanol, the fractions for E10 and E20 fuels were linearly interpolated for ethanol levels of 15%. Toxic fractions are shown in Table 72.

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 21.[55] 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.[56] Thus the diurnal emissions algorithm was multiplied by 1.77.

$$f_{benz,permeation} = 1.77\left[\left(-0.02895\,OXY - 0.080274\,RVP + 1.3758\right)benz/100\right] \quad \textbf{Equation 21}$$

In the absence of data on permeation emissions for MTBE, a complex fraction $f_{MTBE,permeation}$ is calculated using the resting-loss algorithm from MOBILE6.2 (Equation 22).

$$f_{MTBE,permeation} = \left(22.198 - 1.746\,RVP\right)MTBE/1{,}000 \quad \textbf{Equation 22}$$

Table 72. 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 21		0.0236	0.0244	0. 00664[1]

[1] Identical to fractions for the vapor-venting process, based on CRC E-80 program (Table 71).

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

6.2 Diesel Vehicles

For diesel-fueled vehicles, evaporative emissions are estimated for the refueling-spillage process only. As no results describing the speciation of spilled diesel fuel, we developed toxic fractions of total VOC based on a diesel "headspace" profile, in which the "headspace" is the empty space above the liquid fuel in a tank. The profile used was No. 4547 from the SPECIATE database.[41] The fractions are shown in Table 73.

Table 73. 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

7 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[57] and heavy-duty[58] 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.

7.1 Volatile Organic Compounds

Table 1 lists the VOC toxics modeled in MOVES2014, which are also modeled from crankcase emission processes. MOVES2014 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% 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.

7.2 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 has 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.[59]

7.3 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.[32] 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. We are 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 2010b (EPA's Motor Vehicle Estimation Simulator) 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 Kansas City test program.[4] The Kansas City test 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%, 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% confidence interval±0.157). The 95% 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.

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

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 On-road 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	8.9×10^{-8}
2	0.493	0.298±0.098	0.20	6280.73	28.815	8.612	5.1×10^{-9}
3	0.488	0.298±0.098	0.19	1682.74	7.711	1.186	3.5×10^{-8}
4	0.508	0.298±0.098	0.21	6281.82	28.894	8.620	5.3×10^{-9}
Overall			1.1	15912.2	73.10	19.61	**1.2×10^{-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] 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).[9]

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 and Later On-road Diesel Emission Factor

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

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[10] verses gasoline light-duty vehicle engines (from the Kansas City study).

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

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

Non-road emission factors for gasoline engines are presented in grams per gallon and calculated from the 2008 Chevrolet Impala based on a city fuel economy of 18 miles per gallon.[11]

Cr(VI) Non-road Gasoline Emission Factor

$$EF = 1.2x10^{-8}\frac{g}{mi} \times 18\frac{mi}{gal} = \mathbf{2.2x10^{-7}\frac{g}{gal}}$$

Non-road pre-2007 and 2007 and later diesel emission factors are calculated from the overall gasoline emission factor from Table A-1. The above gram per gallon gasoline emission factor is multiplied by the ratio of total chromium emission factors from diesel engines (before and after 2007) verses gasoline engines (from the Kansas City study) to obtain the nonroad diesel engine gram per gallon emission factor.

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

$$EF = 2.2x10^{-7}\frac{g}{gal} \times \frac{6.8x10^{-6}\frac{g}{mi}}{4.07x10^{-6}\frac{g}{mi}} = \mathbf{3.7x10^{-7}\frac{g}{gal}}$$

Cr(VI) 2007 and Later Non-road Diesel Emission Factor

$$EF = 2.2x10^{-7}\frac{g}{gal} \times \frac{1.94x10^{-6}\frac{g}{mi}}{4.07x10^{-6}\frac{g}{mi}} = \mathbf{1.0x10^{-7}}\frac{\boldsymbol{g}}{\boldsymbol{gal}}$$

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
On-road gasoline (MY2008)	$1.2x10^{-8}$	grams/mile
On-road diesel (pre-2007)	$2.0x10^{-8}$	grams/mile
On-road diesel (2007 and later)	$5.8x10^{-9}$	grams/mile
CNG Transit Buses	$2.1x10^{-10}$	grams/mile
Non-road gasoline (MY2008)	$2.2x10^{-7}$	grams/gallon
Non-road diesel (pre-2007)	$3.7x10^{-7}$	grams/gallon
Non-road diesel (2007 and later)	$1.0x10^{-7}$	grams/gallon

[a] calculated by dividing bags 2 and 4 blank corrected Cr(VI) MCE mass/filter by the distance driven for bags 2 and 4, then multiplied by the bag 2+4 sum of CVS volumes/sum of sample volumes

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

[2] Ball, James C. Emission Rates and Elemental Composition of Particles Collected From 1995 Ford Vehicles Using the Urban Dynamometer Driving Schedule, the Highway Fuel Economy Test, and the USO6 Driving Cycle. 97FL-376. Society of Automotive Engineers, Inc. 1997.

Table 1. MCE filter, Test# 20100024028

[3] Taylor, M. Memorandum: Revised HAP Emission Factors for Stationary Combustion Turbines, Prepared by Alpha-Gamma Technologies, Inc for Sims Roy, EPA OAQPS ESD Combustion Group. August, 2003.Docket ID: OAR-2002-0060-0649. Access via http://www.regulations.gov

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[5] Sonntag, D. B., R. W. Baldauf, C. A. Yanca and C. R. Fulper (2013). Particulate matter speciation profiles for light-duty gasoline vehicles in the United States. *Journal of the Air & Waste Management Association* 64(5): 529-545.

[6] http://www.epa.gov/otaq/standards/light-duty/la92.htm

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[10] Okamoto et al. 2006. Unregulated Emissions from Compressed Natural Gas (CNG) Transit Buses Configured with and without Oxidation Catalyst. Environ. Sci. Technol. Vol. 40, 332-341 (value obtained from page 338, Table 6)

[11] http://www.fueleconomy.gov/feg/Find.do?action=sbs&id=24696

Appendix B Development of Motor Vehicle Emission Factors for Mercury

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.

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.

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.

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 on-road 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

Appendix C Responses to Peer-Review Comments

C.1 Adequacy of Selected Data Sources

Does the presentation give a description of selected data sources sufficient to allow the reader to form a general view of the quantity, quality and representativeness of data used in the development of emission rates? Are you able to recommend alternate data sources might better allow the model to estimate national or regional default values?

C.1.1 Dr. Tom Durbin

No comments specific to the Toxics Report.

C.1.2 Dr. Allen Robinson

I thought that the report did not do a good job of providing in text citations to the data sources. Often when the report referred to a data source there was not an in text citation. For example, on page 14 -- they were taken directly from the Complex Model Spreadsheet "*CM Final.xls*". Need a reference for this spreadsheet. This is just one example.

> *RESPONSE: We removed the reference to the Complex Model Spreadsheet in the text, which referenced Equation 4, and the value used are presented within the Report in Table 8,Table 9,Table 10, and Table 11. We also added text citations for data sources (The number of cited references increased from 49 to 59 in the main report) .*

Pre2000 vehicles (Section 2.1) This model is based on old Tier 0 data, which is applied to a large fraction of Tier1 vehicles. There is a lot of speciated data for Tier 1 vehicles from the KCVES. Why was a model not developed based on that data? The proposed model should be tested against the KCVES Tier 1 data to demonstrate that it is applicable to those vehicles. At a minimum this needs to be discussed.

> *RESPONSE: We added footnote "[a]" on page 8, which states: "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".*

C.2 Clarity of Analytical Methods and Procedures

Is the description of analytic methods and procedures clear and detailed enough to allow the reader to develop an adequate understanding of the steps taken and assumptions made by EPA to develop the model inputs? Are examples selected for tables and figures well chosen and designed to assist the reader in understanding approaches and methods?

C.2.1 Dr. Tom Durbin

p. 6 – 2nd paragraph discusses pre-2001 vehicles and 2004+ vehicles, but does not address 2001-2004 vehicles. 4th paragraph – what two fuel properties are used for evaporative emissions.

RESPONSE: Vehicles in MY 2001-2004 are represented by inputs for Tier 2 vehicles. We have modified the text to clarify this point in Section 1.2. We moved the discussion regarding fuel properties accounted for in modeling evaporative emission processes to Section 6.

p. 15 – its not clear what is meant by the phrase that "relations of air toxic emissions to changes in fuel properties has remained stable from Tier 0 to Tier 1"

RESPONSE: We added a sentence and edited the sentence on page 14 to state: "The equations and parameters presented are used to estimate the fuel effect 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."

p. 17 – There is a reference to modeling 2000 and earlier vehicles on E15-E20, but not discussion on factors that would be used for such fuels. It would be useful to at least reference the section where this will be discussed.

RESPONSE: We added columns to Table 14 to include or reference the toxic fractions used for E15 and E20. We also added text on page 16 discussing the source of the data.

For section 2.2.1 see suggestions for the report "Gasoline Fuel Effects for Vehicles Certified to Tier-2 Standards". Then on page 32, it talks about the "full" vs. "reduced" design. The fact that the reduced design represents 5 vehicles and 11 fuels (as opposed to 5 vehicles by 27 fuels) should be discussed in the 1st paragraph, rather than the 2nd. Then the 2nd paragraph talks about Table 30 and 31 before these tables are introduced in the 3rd paragraph, so the 2nd paragraph seems out of place. It should at least be mentioned here that acrolein, benzene, and 1,3 butadiene are not modeled for hot running emissions in this section (even though it is discussed in the next section). The approach using "information parity" appears to the reasonable for NMOG and ethane.

*RESPONSE: We added background on the EPAct program and our analysis of the results in Section 2.1.1.2, including descriptions of the data used to fit models for each combination of pollutant and test phase (bag) (*Table 17*). In addition, we amplified the explanation of the full and reduced designs (Section 2.1.1.2.1).*

Section 2.1.3 – It should be mentioned at the start of the paragraph that metals are represented both with these metals and the metals presented in the PM2.5 emission profile. Also, "conservative" is probably too weak a term to describe using the bag 2 emission rates, since its actually more of an upper limit estimate (although this only appears to be the case for manganese).

RESPONSE: We have added the text in the beginning of Section 2.3 that mentions the two ways MOVES models metals (using speciation profiles, and gram/mile emissions). We also removed the term "conservative" and mentioned that using bag-2 is a likely upper limit estimate.

p. 42 – A recent study by CARB/UC Riverside/UC Davis should provide some information related to biodiesel emission factors.

RESPONSE: We will consider these studies in future updates of the model.

p. 42/43 seems like final paragraph on 42 and 1st paragraph on 43 could be combined, since the three different references to Table 39 in these paragraphs is a little confusing.

RESPONSE: The change was made so that all the references to Table 57 (old Table 39) are contained in one paragraph.

p. 46 – section 2.3.4 – It seems like dioxin emissions might be overestimated using a data set with such older vehicles. This might be worth mentioning in the text.

RESPONSE: We have added text to mention this point in Section 3.4.

p. 47 – section 2.4.2 – It's not clear what the basis of the particulate to gaseous phase split is for the PAHs. If it is discussed previously, it should be reiterated here.

RESPONSE: we have added text in Section 4.2 to reference the source of the apportionment (Table 58).

p. 53 – 3rd paragraph on 20% ethanol. It is unclear what fuel speciation data was used here. Was this from in-use fuels? Since the test fuels were not necessary representative of average fuels, but rather represent the extremes of in-use fuels. Table 51 (now Table 69) is useful.

RESPONSE: The text has been modified to clarify that we used data for blends containing 20 vol.% ethanol from the EPAct program. These data are not representative of in-use fuels, but are the best available information.

C.2.2 Dr. Allen Robinson

The report commonly uses the word "fraction" or "toxic fraction". You need to define fraction of what – VOC, NMOG, THC, etc (presumably each of these is defined using standard EPA definitions). For tables actually defining in header as was done for Table 20 (now Table 48) is useful. Also is this a mass or a mole fraction?

RESPONSE: Section 1.1 defines the term toxic fraction (as a function of VOC) and OC for particulate compounds, and that all fractions are mass-based. We have reviewed the report to make sure we are clear about the definition of the fraction we are discussing in each section.

Please make sure that all variables are defined – a nomenclature table with units should be added to the report.

RESPONSE: We have carefully reviewed the document to ensure that all variables were properly defined in the text, prior to first use. We have ensured that the units for the emission rates for metals, and dioxin/furans are defined in each table the results are presented (e.g. Table 61*), and that the definition of the toxic ratios are clear (see previous comment).*

Centering data (page 10) (now page 9) – It appears that you are using a different centering approach for older data than for the new model (e.g. eqn 8) (now Equation 9). Why were different approaches used?

RESPONSE: The Complex Model and the EPAct models were developed in separate research efforts by different authors at different times. Not surprisingly, the approaches used are similar to some degree but not identical. The EPAct study reflects improvements in computer-optimized study design and analytic methods developed and introduced between 1993 (Complex Model) and 2008 (EPAct). The approach used in the Complex Model ("centering") effectively shifts the means of all fuel properties to the origin, but leaves each property in its native units, i.e., each property is scaled differently. The approach used in EPAct ("standardization") centers the fuel properties, and goes one step further to express all properties in the same scale, i.e., each property is expressed in units of its own standard deviation.

What is meant by model year specific weightings (page 10)? [Table 12]. What do these weights represent? Fraction of vehicles for a given year?

RESPONSE: We added text on page 13 clarifying that the weights represent the sales mix of technologies within a given model year.

Equation 1 – what are the units of the different variables?

RESPONSE: The primary purpose for including the equation was to illustrate the "centering" approach used in the analysis. Nonetheless, we have specified units in the text for the terms shown in the equation. In addition, units for all terms are specified in Table 7.

Table 8 – Complex Model coefficients – these are beta's in equation (1).

RESPONSE: Yes. The β are regression coefficients for the centered fuel-property terms. We have added text after Equation 1 to make this point explicit.

Page 13 "For each compound, the model equations as shown in Equation 1, are evaluated for a "base" and a "target" fuel." This base fuel resides in MOVES? Is this the same as the average fuel listed in Table 7?

RESPONSE: Table 7 does not describe an "average fuel." Rather, this table lists the set of properties included in the Complex Model, and lists the mean value of each property for the fuel set used in the analysis. The mean values are used in Equation 1.

The "base fuel" is stored in the MOVES database. Several base fuels are used by MOVES, with each applied to a different set of model years. Base fuels are applied to represent the fuel implicitly reflected in the base emission rates. Thus, because "in-use" fuels applying to model runs for specific locations differ from the base fuels, MOVES calculates and applies fuel adjustments, relative to the base fuel, to represent corresponding fuel effects.We reference the MOVES2014 Fuel Effects report in this section which provides more detail on the use of base fuels in MOVES. Page 14 – equation 3. It was not clear how the weights are being applied. You are trying to derive one adjustment factor for all pre2000 vehicles? Are you driving a separate factor for the 10 different technology classes? This needs to be clarified.

RESPONSE: We have added text to clarify the meaning of the weights:"The weights represent the sales fractions for the ten vehicle technologies defined in Table 6. 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 30 ages listed in the table gives a set of 30 adjustments, with each applied to a single model year, which represents a specific age with respect to the calendar year simulated."

Table 12 (page 14) -- According to the text these weights represent prevalence for a given technology year. Prevalence means what? Fraction of vehicles based on number, VMT? I am confused that Table 12 lists weights based on "age" as opposed to model years? Is this age relative to 2000? It would be clear to define a base year to calculate age.

RESPONSE: Prevalence indicates the fraction of new vehicle sales in a given model year. We added text clarifying that vehicle age 0 represents the simulation year for which an inventory is calculated. The other ages represent older model years relative to the simulation year.

Equation 6 -- What is I_{VOC}? Where does the value come from? The standard moves code.

RESPONSE: These two terms are defined in the paragraph immediately preceding their use in Equation 6.

Post2000 organic emissions are based on models derived from the EPAct data. It was not clear if these models are the same as those in the EPAct report. I assumed that they were. If so, the Toxic report needs to specifically acknowledge that. In addition, it should provide specific references to which models are being used as the EPAct report describes a whole bunch of models. Please provide in text citations for the EPAct report.

RESPONSE: We have substantially revised this section (Section 2.1.1.2.1) of the report, adding material and tables to better describe the origins of the EPAct models and provide appropriate references to the project report.

Table 1 – Are all these hydrocarbons? There are compounds that contain elements other H and C, which I don't consider to be hydrocarbons.

RESPONSE: We have altered the text to note that the list includes volatile organic compounds, which is inclusive of the organic gases in the toxics report.

When you use the term "start" please define it as either cold (e.g. bag 1 of LA92 with appropriate preconditioning) or hot start (bag 3 of LA92).

RESPONSE: In this context, "start" is synonymous with "cold start," or Bag 1 of the LA92. We have added text to make this usage explicit on page 20.

Page 6 "algorithms" –are these really curve fits as opposed to algorithms?

RESPONSE: We have removed the terms algorithms from the report and substituted with terms such as "statistical models fit to these data"

Page 8 "Toxics inputs for MOVES are not explicitly designed to vary by temperature." Not sure what this means? The outputs do not vary with temperature? What does temperature refer to? Ambient? Cold versus hot start?

RESPONSE: Text was added in Section 1.1 to clarify that the coefficients and other inputs used to estimate emissions of toxics do not vary by temperature, but that resulting emissions estimates may, because they are modeled as a function of VOC and $OC_{2.5}$, for which estimated emissions are adjusted for temperature.

"In addition, while MOBILE6.2 relied on very limited data from heavy-duty gasoline vehicles, MOVES applies Complex Model algorithms to both light-duty and heavy-duty gasoline vehicles" Is there a basis for this extensions. Have additional heavy duty gasoline vehicle data been obtained? If not why is MOVES being extended to heavy duty gas while MOBILE did not?

RESPONSE: The approach taken in MOVES differs from that in MOBILE because the data from heavy-duty gasoline vehicles used in MOBILE was so limited that it did not allow for estimation of differences in emissions attributable to changes in fuel properties. We included this rationale within the text in Section 2.1.1.1.1.

Page 16 (last sentence of first paragraph) Does MOVES have representative fuel data for different regions and simulations year? Given the focus of fuel dependence of emissions providing the user with a robust set of default fuel values (year and region) would be helpful.

RESPONSE: The MOVES database does provide a set of fuels designed to represent typical commercially available fuels throughout the nation. This set of inputs is designated as the "fuel supply" and is described in a separate MOVES2014 report[19].

Equation 7 – what is V and what are its units? Equation 7 and associated parameters in Table 13 were derived by fitting MOBILE output. Why not fit directly the original data or use the original parameterization in MOBILE? You claim this equation provides the best fit. What are statistics of fit?

RESPONSE: The variable V is defined in the paragraph immediately preceding its use in Equation 7. The equation used is consistent with the best fit parameterization originally developed for MOBILE and has the same two terms. We have simplified coding in MOVES by developing a quadratic regression that gives results consistent with the original model used in MOBILE6.2.

Table 12 -- What do these weight represent? The distribution of different classes of vehicles in different model years? It seems like the minimum age of 2000 vehicle is 13 years (if running a present day simulation).

RESPONSE: The weights represent the sales fractions of each technology group in vehicle sales for a given model year. The table lists sets of weights for ages 0-30 within a broad model-year group, "1960-2000." Thus, each age represents a single model year within the broader group. The models described in this section are applied to vehicles in model year 2000 and earlier, so in a present-day simulation, it is correct that vehicles in MY2000 would be 12-14 years old.

[Equation 7] "It should be noted that the sulfur effects terms in the equations were not included; rather, sulfur effects on toxic emissions were assumed to be proportional to the sulfur impacts on total VOC estimated by MOVES." Sulfur effects in what equations? There is no sulfur in equation 7 (which is the equation that this sentence seems to refer to).

RESPONSE: The reviewer is correct that this sentence is not relevant to Equation 7. It has accordingly been moved to Section 2.1.1.1.2 and revised to clarify that the sulfur terms in the original Complex Model were not included when the model was adapted for application in MOVES. Rather, sulfur effects on toxic emissions are assumed to be proportional to the effect of sulfur on total VOC, as estimated by MOVES.

Table 16 exists in Pre-2000 section (Section 2.1.1.1.4) but appears to apply more generally. Move into a more general section of the report?

RESPONSE: This table does also apply to vehicles manufactured after 2000, but we thought it sufficient to describe the table in its current location in the report and then reference it as appropriate in later sections, (e.g. Section 2.1.1.2.8).

Do you really want to call ethanol blends gasohol? When I hear gasohol I think of Brazil.

RESPONSE: We agree that this term seems out of date. However, as it is currently used in the MOVES database, in the table "FuelSubType", we have retained it for the present in Table 16. However, it is a good candidate for replacement with a more current term, such as "ethanol blend", which is used consistently throughout the text of the report.

Page 31: "one set representing start emissions and a second set representing hot-running" start emissions is hot start (LA92 bag 3) or cold start (LA92 bag 1, with appropriate conditioning)?

RESPONSE: In revising Section 2.1.1.2.1, we have added text to clarify that "start" refers to "cold-start," as represented by LA92 Bag 1, and that "running" represents LA92 Bag 2.

There are table reference problems (e.g. see page 32, 35, 38, 40, …). There are other instances of this.

RESPONSE: We have modified and updated table references as needed.

Table 27, 28, etc. Are these parameters from the EPAct report. If so provide citation. Please cite the specific model from the EPAct report, not just the general report.

Page 40: What is OC2.5 VOC?

RESPONSE: This combination of terms was simply a typographical error that we have corrected.

Page 41—dioxins and furans – "to be similar" You are assuming them to be the same not just similar. Seems like these estimates are very uncertain since they are based on very old vehicles.

RESPONSE: We have combined the previous two sections discussing gasoline dioxin and furan emission rates into a single section (Section 2.4) of the revised report, to help the reader understand that we are using fleet-average emission rates for dioxins and furans. We modified the language in Section 2.4 to be more precise regarding the use of the data for newer vehicles and have noted the uncertainty involved in this extrapolation.

Diesel PAH data [Section 3.2]– Similar problems with the partitioning estimates. Partitioning in Schauer study is biased compared to atmosphere. This needs to be explicitly noted in the report.

There is a "higher concentration of particles in diesel exhaust" compared to gasoline exhaust in the CVS or plume, but not in the atmosphere. Concentrations in the atmosphere not exhaust is what matters for partitioning.

RESPONSE: Please see our response to the similar question in C.3.2, pages 92-93.

Table 49 – Particle phase naphthalene? That must be a measurement artifact.

RESPONSE: As mentioned in the response C.3.2 pages 92-93, the gas-particle partitioning is meant to be representative of the sampling conditions from which the emissions are measured, not atmospheric conditions. We left the gas-phase partitioning in Table 47 as reported by Fujita et al. (2013), and assume that 99.96% of the naphthalene is from the gas phase, and 0.04% is in the particle-phase. Whether we used 100% or 99.96% as the gas-phase fraction will have a trivial impact on the total naphthalene estimated by MOVES.

C.3 Appropriateness of Technical Approach

Are the methods and procedures employed technically appropriate and reasonable, with respect to the relevant disciplines, including physics, chemistry, engineering, mathematics and statistics? Are you able to suggest or recommend alternate approaches that might better achieve the goal of developing accurate and representative model inputs? In making recommendations please distinguish between cases involving reasonable disagreement in adoption of methods as opposed to cases where you conclude that current methods involve specific technical errors.

C.3.1 Dr. Tom Durbin

Overall, the Complex Model provides a robust framework for modeling acetaldehyde, formaldehyde, benzene, and 1-3 butadiene, especially with its recent updates.

Table 7 – the mean value for centering the sulfur at 204 ppmw is relatively high compared to current sulfur levels. Will this potentially be modified going into the future?

RESPONSE: The sulfur terms in the Complex Model were not retained when the equations were adapted for use in MOVES, as sulfur effects were modeled using a different approach. For this reason, the mean value for sulfur in Table 7 *is irrelevant in MOVES and has been removed from the table.*

Tables 8 to 11 – What do the dashes in the table represent? Is that where the data show no effect or are insufficient? For example, there is no sulfur effect on formaldehyde.

RESPONSE: We added text on page 10 stating that the dash means the data show no effect for a given term. Stated differently, the term for the fuel property was not significant or did not contribute to fit.

For MTBE, the model applied previously in MOBILE6.2 should be adequate, especially since MTBE use is essentially historical. Similarly, in section 2.2.2.1.1,[now Section 2.1.1.2.8] the use of Tier 1 and earlier vehicles for Tier 2 vehicles appears reasonable.

Section 2.1.2[now Section 2.2]: Its not clear what samples are being used to estimate the PAHs. It talks about a set of 99 samples being used for the fractions in the second paragraph and how the fractions are determined in terms of PAH/THC and PAH/OC2.5. Then it talks about the partitioning into gaseous and particulate phases in the 3rd and 4th paragraph that appears to be based on 2 vehicles in the medium emitter category, which was selected from 4 samples collected at two temperatures. Why was the "medium emitter" sample selected? How significant were the differences between the samples collected at 20°C and 47°C? If there were big differences wouldn't that make a big difference in the partitioning for the PAH/THC and PAH/OC2.5 for the other 99 samples? Then its unclear what Table 20 [now Table 48] represents, since it is multiplying fractions (PAH/THC and PAH/OC2.5) by fractions (Table 19)[Table 47] in a seemingly strange was. Where do the absolute emission rates for the individual species play in here?

RESPONSE: We added a paragraph, Equation 19 and Equation 20 to demonstrate how we are using the KCVES emission rates, with the phase-partitioning values in Table 48 from the follow-on KCVES study, to derive the PAH ratios used in MOVES.

We also added text in Section 2.2.1 to emphasize that the gas-particle partitioning is not indented to be representative of atmospheric conditions, but of the measurement conditions from which VOC and PM emission factors are calculated.

We recognize that using the 'medium emitter' for phase-partitioning may not be representative of all the vehicles measured in the Kansas City study or for Tier 2 vehicles, but it was deemed the most representative for phase-partitioning the PAH measurements made in KCVES. We added text in Section 2.2.1 to explain our rationale. "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."

Fujita et al. (2006) did find that the dilution tunnel had an impact on the PAH speciation, and PM emissions. However, the impact was not always intuitive (e.g. They observed higher OC emission rates at the higher dilution temperature). We used the phase-partitioning at 47°C because the dilution tunnel was operated at that temperature during the main study (from which the PAH, THC, and PM measurements were made).

We also added Table 49 to provide information on the structure of the database that contains the PAH/VOC and PAH/OC ratios.

Page 37 - Although benzene can be a function of fuel benzene, it can also be a function of other low weight aromatics, especially toluene. In the EPA study on benzene, how did toluene levels vary between the fuels?

RESPONSE: We added a footnote in Section 2.1.1.2.7 stating that the toluene levels were constant. The only difference between the fuels was the benzene level.

Section 2.3 – Developing the air toxics factors from the E-75 database appears to be a reasonable approach. Its unclear how these factors might account for states with low levels of aromatics, such as California. Also, its unclear why the partitioning for the PAHs was made based on a medium-duty diesel engine. Maybe just one sentence to clarify this.

RESPONSE: Since data were not adequate to develop a fuel-effects model for diesel, results will not account for impacts of low aromatics diesel fuel on toxic emissions. We added text to Section 3.2 stating that the PAH partitioning was done using data from a medium-duty diesel engine, because it was the best available data for the purpose at the time of analysis.

The ACES study provides a good data set for the development of the air toxics factors for the 2007 and new engines. p. 49 section 2.4.4 – Would be interested to see how backgrounds were dealt with in this study. At such levels backgrounds would be important in terms of not overestimating emissions.

RESPONSE: We added information regarding background corrections in Sections 4.1 ,4.2, and 4.3. The ACES program background corrected the VOC measurements, but not the PAH or metal measurements. Details on the background correction are available at the cited ACES Phase I report[44].

Section 2.6 – CNG emissions – For the PAHs, is there any consideration given to how the oxidation catalyst would reduce PAHs?. It appears that the estimates were based on measurements without an oxidation catalyst, but that these are applied to both technology categories. p. 51–

RESPONSE: In Section 5.2 we only used the PAH emissions from the CNG transit bus without an oxidation catalyst (Okamoto et al. 2006) to simplify modeling of this relatively small source. We decided to use the non-catalyst equipped PAH emission rates as a way to be environmentally conservative.

Section 2.6.3 – By using the only the data where chromium and nickel were detected, this would presumably overestimate emissions. Were the metal rates from heavy-duty engines also considered before deciding to use the gasoline emission rates[?].

RESPONSE: In Section 5.3, the heavy-duty diesel emission rates were also considered as a surrogate for the CNG emission rates. We chose to use gasoline rates, because both fuel types employ spark-ignition engines, and gasoline is a lighter fuel than diesel.

Section 3 – Some more details should be provided for why the hot soak and running loss algorithms from MOBILE6.2 are applied to MOVES for the non-permeation factors. The methodologies for the permeation factors appear reasonable.

RESPONSE: We added text in section 6.1.1 stating that these algorithms were adopted due to a lack of relevant data from vehicles with more recent technologies measured over a fuel set with an applicable range of properties.

Appendix A [now Appendix B]– the fleet of vehicles used for this study appears to be too heavily weighted towards older vehicles. Were the results for the different vehicles [used] to provide a profile that was more representative of the modern fleet?

RESPONSE: The data did not suggest that mercury concentrations varied by vehicle age, mileage, displacement or other factors.

Using an average exhaust flow might tend to underestimate emissions, since often periods of higher emissions also can be periods with higher exhaust flow.

RESPONSE: Proportional sampling was not used and the Hg sample was extracted from raw exhaust. The sample flow rate was held constant, although the total exhaust flow is varies during the emision test. Thus, the sampler under sampled at high exhaust flow rates and over sampled at low exhaust flow rates. We did not have a way to correct for this, and it is a source of Hg measurement uncertainty (that we acknowledged in the report) in the test program.

Last paragraph [in Appendix B.4] – by using only the first 715 seconds, would this over represent cold start emissions?.

RESPONSE: Yes, however the data from the diesel tested represents the best available information. We mention the uncertainty regarding using the only the first 715 seconds in Appendix B.4.

C.3.2 Dr. Allen Robinson

It is not clear why the demarcation for the gasoline vehicles is MY2000 – it seems like the years in which tier 1 or tier 2 vehicles were introduced would make alot more sense. In contrast, the MY2007 distinction for diesel vehicles makes alot more sense than the apparently arbitrary split for gasoline vehicles.

RESPONSE: In calendar year 2001, the national low emission vehicle program (NLEV) went into effect, and fuel effects are better represented by Tier 2 vehicles tested in the EPAct program.

Page 19 section 2.1.1.2 It seems very problematic to be using emissions data from EPAct for a new Tier 2 vehicle to apply to these older vehicles to simulate emissions from high ethanol fuel operations from a pre2000 vehicle. The uncertainty must be very large. Can you run older vehicles on E85? There seems to be little basis for this extrapolation – it seems like you are simply trying to be comprehensive. Ideally a quantitative estimate of uncertainty should be provided for this estimate. At a minimum MOVES should flag the value as massively uncertain.

*RESPONSE: We have added a footnote (*g*) in Section 2.1.2.1 and Section 2.1.2.3 pointing out the uncertainty inherent in the emission rates, while also understanding that this is a minor contribution to the uncertainty of the total inventory due to the small number of pre-2001 vehicles operating on high-ethanol blended gasoline.*

Phase partitioning of PAH (page 21). This applies to all vehicles (pre2000 and post2000). However it is in the pre2000 section. I found this confusing. Why not have one section that says PAH emissions of all gasoline vehicles estimated using this approach.

RESPONSE: We revised the outline of the report to have one section (Section 2.2,2.3 and 2.4) for gasoline PAH, dioxin, and metal emissions, respectively, which do not have separate inputs for pre- and post-2001 vehicles. Additionally, we added text to clarify that we used a fleet-average PAH emission rates from a sample of vehicles with model years ranging from 1968 to 2004.

More PAH: There is a paragraph that provides the caveat that "gas-particle partitioning of PAHs emission in the atmosphere depends on particle and gas concentrations, exhaust temperature and other factors." It is good to state this. However, presumably the relevant temperature for

atmosphere partitioning is atmospheric temperature (not exhaust). This paragraph implies, but does not specifically state, that the gas particle partitioning measured in source test is not representative of atmospheric conditions (or at least not all atmospheric conditions). I think that this caveat needs to be explicitly stated. "The gas particle partitioning of PAHs measured in source tests and implemented in MOVES is likely not representative of atmospheric partitioning."

RESPONSE: We also added text in Section 2.2 to emphasize that the gas-particle partitioning is not intended to be representative of atmospheric conditions, but of the measurement conditions from which VOC and PM emission factors are calculated.

More PAH: The model use results for composite class, "medium emitters," to estimate gas particle partitioning of all PAHs. Why was a medium-emitters class used? I also suspect that the conditions inside the CVS during the test of these old vehicles (esp. PAH concentrations, PM concentrations, BC concentrations) are not representative of atmospheric conditions (or the newer Tier 2 vehicles). This likely biases phase partitioning towards particle phase. EPA should choose a test in which the conditions concentration and temperature inside the CVS were within the envelope of conditions that likely occur in the atmosphere. This likely would be a test for a cleaner vehicles. An even better approach would be to review the literature of ambient gas-particle partitioning measurements of these compounds and use those values (as opposed to values from a source test). Finally, if the phase partitioning of PAHs is an important output for some of MOVES uses then it is not difficult to implement a gas-particle partitioning model.

RESPONSE: We added/edited the text in Section 2.2.1to address that the MOVES emission rates are developed to be consistent with average measurement test conditions, rather than atmospheric conditions.

We also added text in Section 2.2.1 explaining the use of the phase-partitioning from the medium emitter. "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."

Lastly, the phase partitioning of PAHs is not viewed as an important output of PAH emissions. In the National Emission Inventory, the gas-phase and particle-phase PAH valued are summed for each PAH species.

MOVES reports emissions as measured in emission test programs. Substantial work and research is needed if MOVES is changed to estimate the gas-particle partitioning of emissions as emitted into the atmosphere. We agree that this is an important area of further research.

Table 20 –The same PAH emissions ratios appear to be applied to all vehicles, which are based on some sort of fleet average from the entire KCVES (or just the pre-2001 vehicles)? It is not clear why this approach was adopted. With this approach you are locking in the emissions based on a fleet that was 10 years old today. How constant were these ratios across the fleet? If they are not constant, why not stratified the emissions into classes (at least Tier1, Tier2) which will allow the model to better forecast future emissions?

RESPONSE: The PAH emissions are based on a fleet-average of emissions that contain measurements of vehicles with model years ranging from 1968 to 2004. They measurements are fleet-weighted, so the newer vehicles contribute according to their expected contribution to VMT in the KC metropolitan area. No Tier 2 vehicles were tested as part of the KCVES. A single-fleet average PAH emission factor was derived to be consistent with the fleet-average PM speciation profile developed from the Kansas City study, and for the reasons given in the Speciation report[32]. These include: 1) avoiding over-fitting data to model year groups, and 2) underestimation of high-emitters within the newer model year groups. We added text referencing the Kansas City profile to the text, which references the TOG and PM Speciation Profiles.

C.4 Appropriateness of Assumptions

In areas where EPA has concluded that applicable data is meager or unavailable, and consequently has made assumptions to frame approaches and arrive at solutions, do you agree that the assumptions made are appropriate and reasonable? If not, and you are so able, please suggest alternative sets of assumptions that might lead to more reasonable or accurate model inputs while allowing a reasonable margin of environmental protection.

C.4.1 Dr. Tom Durbin

p. 9 at the top The EPA assumption that metals should be independent of temperature appears reasonable. It might be useful to examine metal emissions as a function of operation mode, however, for example, comparing more vs. less aggressive driving, although perhaps not for the metals included in Table 4.

RESPONSE: We agree that such an analysis would be useful, but data are too limited for this type of analysis.

Page 16 developing regressions for ETBE and TAME from algorithms for ethanol and MTBE appears to be a reasonable assumption, especially as these fuels are not at all prevalent.

p. 37 – When modeling 1,3 butadiene as 0.0 for hot-running operation, the impact of olefins should be considered. Later on the page – CRC E-83 can be considered for olefins, although these values were near background levels as well.

RESPONSE: EPA will consider data from CRC E-83 for future updates of the inputs for 1,3-butadiene.

Section 2.2.2.2 – Overall, the assumptions used in this section appear to be reasonable, as E85 data are not available for some of the toxics being measured. The section does use a range of different descriptions of higher ethanol levels from E70 to E85 to 74% ethanol without clearly describing when all of these different conditions are applied. For example is the same factor used for E70 and E85? Also, on page 40, the approach that ethanol contributes no PAHs should be verified. A UC Riverside/CEC/SCAQMD study will be completed next year that will provide some data in that area.

RESPONSE: We added text to clarify that the PAH fractions developed in Table 50 apply to all high-ethanol blends (E70-E100).

In response to this comment, we examined PAH emissions data collected on E85 vehicles tested by Hays et al. (2013). We found there was insufficient evidence to model a reduction in the heavier PAHs with the use of E85. We did find sufficient evidence to model reductions in the lighter PAHs, that exist primarily in the gaseous phase in measurement testing. For modeling in MOVES we updated the PAH particle ratios to reflect no difference to the E0-E20 PAH particle ratios in MOVES. The text is included in Section 2.2.2.

Section 3 – For section 3.1.1, when using the fuel speciation from the EPAct study to make estimates for E15 and E20, was the volatility of the species considered? This would not necessarily be an essential change.

RESPONSE: We did not account for volatility of the species.

C.4.2 Dr. Allen Robinson

In this chapter/report there is wider range of data quality compared to other reports and chapters. Some of the models are based on pretty robust data sources (e.g. basic gaseous organic air toxics), but others are based on data that, at best, are loosely related to the source (Why should fraction of hexavalent chromium emissions from a stationary turbine be representative of onroad vehicles? Or why should emissions from a tier 2 E85 vehicle be representative of emissions from much older vehicle operating on high ethanol blends). I understand the desire for the model to be comprehensive as possible, but the uncertainty of the predictions will vary widely. It does not seem like the model user will have any idea about the quality of the predictions. Ideally each MOVES prediction would provide a quantitative estimate for every prediction. At a minimum the model should provide a grade (e.g. similar to AP42) for each pollutant. For pollutants with robust models, the grade will be high (e.g. A). For less robust models (e.g. hexavalent chromium), the grade would be poor (e.g. F).

RESPONSE: We agree in concept that it would be desirable to provide uncertainty estimates with MOVES predictions. In fact, MOVES was originally designed to include a Monte Carlo simulation feature to estimate uncertainty in model runs by repeating scenarios with random variations. However, given the scope and complexity of the model, applying the uncertainty feature has become infeasible for most users, and not relevant to their goals. Notwithstanding these points, development and application of quality levels to at least some inputs could be considered.

In some cases there are important sources of data that have not been utilized (e.g. KCVES to estimate pre2000 vehicle air toxics emissions or PAH emissions for post2000 vehicles).

*RESPONSE: For all toxics except the four included in the Complex Model for Reformulated Gasoline, the data used to develop toxic emission estimates were in fact obtained from the Kansas City Test Program (KCVES) which contains measurements from vehicles ranging from 1968-2004 model years. However, for benzene, 1,3-butadiene, formaldehyde and acetaldehyde, we relied on the Complex Model because data were collected on a matrix of different fuels which enabled modeling impacts of changes in fuel properties.*CNG buses – It seems like there is more data available. WVU has done a bunch of testing on transit buses. Aerodyne research also did a bunch of chase studies of CNG powered transit buses in which they measured high formaldehyde emissions.

RESPONSE: As shown in Table 66, the formaldehyde emission fraction composes a large percentage of the VOC emissions. We are aware of additional studies being conducted on CNG-fueled vehicles equipped with three-way catalysts, including those from WVU, but unfortunately, these were not available to us at the time we were developing inputs for the current MOVES update. We plan to continue to update these rates in future versions of MOVES.

Section 2.1.3 Metals –You assume constant emission rates across fleet (which seems plausible, much more so than for PAHs). However, if there were systematic variations in metals emission rates across the fleet why not stratify the model to capture them. What is the quality of the metal emissions? Presumably metal emissions will be sensitive to lube oil therefore it is not clear how widely applicable the data are.

RESPONSE: The metal emission rates were developed as fleet averages to be consistent with the fleet-based PM speciation profile cited in Section 2.3.

Hexavalent chromium – The speciation is based on stationary combustion turbine testing. Is there any reason to think that is applicable to on-road vehicles? If not, why even report it. At best the results will be highly uncertain. I think this an example of where the model predictions are not supported by robust data.

RESPONSE: We have replaced the emission factors for hexavalent chromium with test data from a motor vehicle, as discussed Sections 2.3, 0, 4.3, 5.3, and Appendix A

Page 25 – Why are dioxins and furans expressed as TEQs as opposed to not mass. I am not familiar with dioxins but it struck me as strange. The quality of the dioxins data seemed low.

RESPONSE: This convention is commonly used with dioxins and furans, to resolve the multiple congeners into a single "species," by expressing all compounds as equivalents of the most toxic congener, e.g., the "2,3,7,8" congener for the dioxins.

C.5 Consistency with Existing Body of Data and Literature

Are the resulting model inputs appropriate, and to the best of your knowledge and experience, reasonably consistent with physical and chemical processes involved in emissions formation and control? Are the resulting model inputs empirically consistent with the body of data and literature that has come to your attention?

C.5.1 Dr. Tom Durbin

Overall, the methodologies selected and applied for this report appear to be providing reasonable input to the MOVES model. As additional data sets become available, they should also be considered for incorporation into the model, as discussed above.

C.5.2 Dr. Allen Robinson

The report does not provide sufficient information to assess this.

C.6 General/Catch-All Reviewer Comments

Please provide any additional thoughts or review of the material you feel important to note that is not captured by the preceding questions.

C.6.1 Dr. Tom Durbin

- page 5 extra page
- p. 6 2nd paragraph used to calculate~~d~~ toxic..; final sentence "persistent" is not a well defined word here.
- p. 9 1st sentence – make it two sentences ~~As~~ Metals… emission rates. T~~t~~hese rates ; 2nd paragraph look at indentation; final paragraph look at indentation
- page 10 1st paragraph don't capitalize Air injection; last sentence goes to next page
- page 11 1st sentence Table 8 to Table 11.
- page 13 last sentence 1st paragraph – last sentence signpost?
- page 16 2nd paragraph MTBE levels using a simple regression; 3rd to last paragraph MTBE …used for TAME blends; 2nd to last paragraph end of 1st sentence; last paragraph from the National County Database;
- page 17 3rd line 12 vol. % or more or tert.. extra space
- page 19 3rd sentence winter, or~~and~~ blends
- page 21 PAH seems like it should be PAHs throughout page and in title; 2nd paragraph end of 1st sentence; 3rd paragraph last sentence particulates and hydrocarbons also differ… and heavy-duty vehicles**,** ; last sentence small~~est~~er high~~est~~er e.g.**,** dibenzo..
- page 22 – 1st sentence table error; last sentence structure**,** which
- page 23– last paragraph 1st sentence end of sentence; page 24 include reference to 2005 EPA study; 1st paragraph 2nd to last sentence … differences … are
- page 25– end of 3rd sentence
- page 31– last sentence VOC emissions are~~is~~
- page 32– several table reference errors; 3rd paragraph reverse order of second sentence; 4th paragraph 1st sentence VOCs; last sentence in this context**,**
- page 38– 20% ethanol**,** fractions; also switch the order of the last two sentences in the final paragraph. Also, eliminate "the" before Table 34 in the last sentence.
- page 40– Table error under 2.2.3.1; last sentence …fractions are …add period at end of sentence.
- page 41— The word "data" is plural. E.g. Data were not data was
- page 42– section title should be pre-2007 or MY 2006 and earlier.
- page 43– table reference error in last paragraph
- page 50– 2nd sentence gasoline ~~of~~or diesel

- page 51– 1st paragraph under section 2.6.3, end of last sentence in paragraph has extra space?
- page 52– 1st paragraph after 3.1 (evaporative?); later <source>
- page 55– under eq. 18 linearlyinterpolated
- Appendix A – p. 61 2nd paragraph 1st sentence "in the raw exhaust"; p. 62 last paragraph the end of the 1st sentence is no clear, and should have a comma after power, "; p. 63 last sentence "The ~~E~~equation.."

RESPONSE: These clarifications and grammatical errors have been addressed.

C.6.2 Dr. Allen Robinson

Compared to the other reports there were more typos, broken links, placeholders like "???" in the text, and many typos (e.g. superscripts for references and on numbers, e.g. see Table 47) in this report.

RESPONSE: These clarifications and grammatical errors have been addressed.