# MOVES2010b: Additional Toxics Added to MOVES



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



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Appendix A

### 1. Introduction

The previous version of MOVES, MOVES 2010a, estimated emissions for only a limited number of air toxics from highway vehicles, including benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, naphthalene, and ethanol. Furthermore, estimation of air toxic emissions was done largely by relying on algorithms carried over from MOBILE6.2 and the National Mobile Inventory Model (NMIM). Exceptions included addition of toxic to hydrocarbon ratios for ethanol.

For benzene, 1,3-butadiene, formaldehyde and acetaldehyde from light duty gasoline vehicles and trucks, algorithms calculated toxic to VOC ratios using fuel parameters. These algorithms were derived from U. S. EPA's Complex Model for Reformulated Gasoline, developed in the early 1990's for the Federal Reformulated Gasoline Rule. MOVES 2010b continues to rely on these algorithms for exhaust and non-permeation evaporative emissions. Acrolein, naphthalene and ethanol were estimated using simple toxic to VOC ratios. Ratios for ethanol and non-permeation evaporative emissions of naphthalene are the same for gasoline vehicles in this version of the model, but ratios for exhaust naphthalene have been updated. Acrolein ratios are the same for light-duty gasoline vehicles in both versions of the model; however, acrolein ratios for heavy-duty gasoline vehicles differed from light-duty gasoline vehicles in MOVES210a, while in MOVES2010b, the ratios for heavy-duty gasoline vehicles are the same as light-duty gasoline ratios. Algorithms for diesel vehicles have all been updated.

None of the other toxics estimated using EPA's National Mobile Inventory Model (NMIM) were included in draft MOVES2010a. However, these HAPs have all been added to MOVES2010b. In NMIM, for other light duty gasoline toxics, and for all toxics from other vehicle and engine types, the algorithms took one of three forms: toxic to VOC ratios (for gaseous HAPs), toxic to PM ratios (PAHs), and basic emission rates (metals). In MOVES2010b, the same approach is used, except for PAHs. PAH mass emissions are apportioned into the gas and particle phase, and gas phase PAHs are estimated using toxic/VOC ratios and particle phase PAHs were estimated using toxic to OC<sub>2.5</sub> (organic carbon less than 2.5 microns) ratios.

The algorithms in NMIM were developed over 10 years ago. More recent data are now available, representing more modern vehicles and engines, and fuels more representative of what is currently being sold. For many vehicle types, data used to develop algorithms were also very limited, and quality of estimates can be enhanced by addition of more data. U. S. EPA has analyzed more recent data, reflecting advanced emission control technology and modern fuels, and added more data for older technology vehicles to enhance the quality of emission rate estimates.

MOVES2010b includes all air toxic pollutants in the National Emission Inventory (NEI) and National Air Toxics Assessment (NATA) that are emitted by mobile sources. This list of pollutants is provided in Table 1.1. These pollutants are organized into four categories:

### 1) Gaseous hydrocarbons

- 2) Polycyclic aromatic hydrocarbons (PAHs) These hydrocarbons which contain fused aromatic rings can be found in the gas phase, particle phase, or both, depending on properties of the compound, particle characteristics, and atmospheric condtions
- 3) Dioxins and furans polychlorinated organic compounds which are persistent and bioaccumulative
- 4) Metals

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

**Table 1.** Air toxics included in MOVES 2011, along with MOVES PollutantID numbers and NEI pollutant codes.

	MOVES	
Pollutant	Pollutant ID	<b>CAS Number</b>
Gaseous Hydrocarbons		
1,3-Butadiene	24	106990
2,2,4-Trimethylpentane	40	540841
Acetaldehyde	26	75070
Acrolein	27	107028
Benzene	20	71432
Ethanol	21	64175
Ethyl Benzene	41	100414
Formaldehyde	25	50000
Hexane	42	110543
Methyl Tert Butyl Ether (MTBE)	22	1634044
Propionaldehyde	43	123386
Styrene	44	100425
Toluene	45	108883
Xylenes	46	1330207
PAHs		
Acenaphthene particle	70	83329
Acenaphthylene particle	71	208968
Anthracene particle	72	120127
Benz(a)anthracene particle	73	56553
Benzo(a)pyrene particle	74	50328
Benzo(b)fluoranthene particle	75	205992
Benzo(g,h,i)perylene particle	76	191242
Benzo(k)fluoranthene particle	77	207089
Chrysene particle	78	218019
Dibenzo(a,h)anthracene particle	68	53703
Fluoranthene particle	69	206440

	MOVES	
Pollutant	Pollutant ID	<b>CAS Number</b>
Fluorene particle	81	86737
Indeno(1,2,3,c,d)pyrene particle	82	193395
Naphthalene particle	23	91203
Phenanthrene particle	83	85018
Pyrene particle	84	129000
Acenaphthene gas	170	83329
Acenaphthylene gas	171	208968
Anthracene gas	172	120127
Benz(a)anthracene gas	173	56553
Benzo(a)pyrene gas	174	50328
Benzo(b)fluoranthene gas	175	205992
Benzo(g,h,i)perylene gas	176	191242
Benzo(k)fluoranthene gas	177	207089
Chrysene gas	178	218019
Dibenzo(a,h)anthracene gas	168	53703
Fluoranthene gas	169	206440
Fluorene gas	181	86737
Indeno(1,2,3,c,d)pyrene gas	182	193395
Naphthalene gas	185	91203
Phenanthrene gas	183	85018
Pyrene gas	184	129000
Dioxins and Furans		
2,3,7,8-Tetrachlorodibenzo-p-Dioxin	142	17466016
1,2,3,7,8-Pentachlorodibenzo-p-		
Dioxin	135	40321764
1,2,3,4,7,8-Hexachlorodibenzo-p-		
Dioxin	134	39227286
1,2,3,6,7,8-Hexachlorodibenzo-p-		
Dioxin	141	57653857
1,2,3,7,8,9-Hexachlorodibenzo-p-		
Dioxin	130	19408743
1,2,3,4,6,7,8-Heptachlorodibenzo-p-		
Dioxin	144	35822469
Octachlorodibenzo-p-dioxin	131	3268879
2,3,7,8-Tetrachlorodibenzofuran	136	51207319
1,2,3,4,6,7,8-		
Heptachlorodibenzofuran	144	67562394
1,2,3,4,7,8,9-		
Heptachlorodibenzofuran	137	55673897
1,2,3,4,7,8-Hexachlorodibenzofuran	145	70648269
1,2,3,6,7,8-Hexachlorodibenzofuran	144	57117449
1,2,3,7,8,9-Hexachlorodibenzofuran	146	72918219

	MOVES	
Pollutant	<b>Pollutant ID</b>	<b>CAS Number</b>
1,2,3,7,8-Pentachlorodibenzofuran	135	57117416
2,3,4,6,7,8-Hexachlorodibenzofuran	143	60851345
2,3,4,7,8-Pentachlorodibenzofuran	138	57117314
Octachlorodibenzofuran	133	39001020
Metals		
Mercury (elemental gaseous)	60	200
Mercury (divalent gaseous)	61	201
Mercury (particulate)	62	202
Arsenic compounds	63	93
Chromium (Cr3+)	64	16065831
Chromium (Cr6+)	65	18540299
Manganese Compounds	66	7439965
Nickel Compounds	67	7440020

This document provides data methodologies and sources for gasoline vehicles and trucks running on E0, E10 and MTBE blends, and diesel vehicles and trucks. Toxics inputs for MOVES do not vary by temperature or operating mode. Ambient temperature also affects these ratios, but we assumed toxic emission of gaseous toxics and PAHs change proportionally with VOC and PM as temperature varies. In general, data are inadequate to account for temperature effects on toxic to VOC and toxic to PM ratios. Emission rates for metals are assumed to be independent of operating mode and temperature; very little data exist to account for impacts of these parameters.

### 2. Gasoline Vehicles and Trucks

### 2.1. Exhaust

### 2.1.1. Gaseous Hydrocarbons

MOVES 2010b provides the capability to model toxic emissions from vehicles running on gasoline, E10, and MTBE blends. E10 is defined as fuel containing ethanol which is greater than or equal to 5% by volume. For additional HAPs, the same toxic to VOC ratios are used for MTBE blends and E0. For 2003 and earlier vehicles, toxic to VOC ratios for E0 an E10 were developed by Sierra Research<sup>6</sup> using estimates from EPA's SPECIATE 4.2 database (Table 2). Ratios for LDG vehicles were used for all gasoline vehicle classes.

**Table 2.** Toxic to VOC ratios for selected air toxics from Tier 1 and earlier gasoline vehicles and trucks.

pollutant		=10
Name	E0	E10
2,2,4-Trimethylpentane	0.01823	0.01849
Ethyl Benzene	0.02147	0.01932
Hexane	0.01570	0.01593
Propionaldehyde	0.00086	0.00086
Styrene	0.00108	0.00097
Toluene	0.09619	0.08657
Xylene	0.07814	0.07032

For 2004 and later vehicles running on E0 and E10, ratios for additional gaseous HAPs for E0 and E10 were obtained from Phase 1 of the EPAct test program. These profiles were based on tests from 3 vehicles.<sup>7</sup> Toxic to VOC ratios for E10 are used in MOVES for all gasoline above 5% ethanol by volume. Ratios are provided in Table 3.

Table 3. Toxic to VOC ratios for selected air toxics from Tier 2 gasoline vehicles and trucks

pollutant Name	E0	E10
2,2,4-Trimethylpentane	0.03188	0.01227
Ethyl Benzene	0.01683	0.01660
Hexane	0.00279	0.02911
Propionaldehyde	0.00122	0.00054
Styrene	0.00085	0.00083
Toluene	0.07542	0.07440
Xylene	0.06127	0.06047

### 2.1.2. Polycyclic Aromatic Hydrocarbons

As mentioned previously, in the NMIM model<sup>8</sup>, PAH emissions were estimated as ratios to PM. This approach was used, even though PAHs are found in the gas, semi-volatile and particle phase, because there is generally reasonable correlation between PAH and PM emissions.<sup>9, 10</sup> However, for MOVES 2010b, PAH mass emissions are apportioned into the gas and particle phase, and gas phase PAHs are estimated using toxic/VOC ratios and particle phase PAHs were estimated using toxic to OC<sub>2.5</sub> (organic carbon less than 2.5 microns) ratios. Although partitioning of PAHs into the gas and particle phases depends on concentration, temperature and other factors, MOVES applies one set of allocation factors under all conditions in order to streamline data processing. These allocation factors were developed by Sierra Research<sup>11</sup> using estimates from EPA's SPECIATE 4.2 database<sup>12</sup> and information on

compounds' physical and chemical properties. Table 4 provides molecular weights and allocation factors. The allocations from SPECIATE were based on medium duty diesel engine data. Using PAH and VOC emissions data from Norbeck et al.  $(1998)^{14}$  and the allocation factors in Table 4, the toxic/VOC ratios in Table 5 were developed. Norbeck et al. data were also used to develop toxic/PM<sub>10</sub> ratios. These ratios were then converted to toxic/OC<sub>2.5</sub> ratios for start and running operation. These conversions were made using assumptions that 90% of PM<sub>10</sub> is PM<sub>2.5</sub><sup>15</sup>, 87.3% of running PM<sub>2.5</sub> is OC, and 66.6% of start PM<sub>2.5</sub> is OC. OC percentages of PM2.5 were obtained from MOVES runs. PAH to VOC and PAH to OC<sub>2.5</sub> ratios do not vary between E0 and E10 fuels.

### 2.1.3. Metals

Metals emissions can result from trace level contamination of fuel and engine oil, as well attrition from exhaust emission components. MOVES estimates metal emissions using gram per mile emission factors. Emission factors for metals remain unchanged from the values used in NMIM (Table 6). Emission factors for chromium, magnesium and nickel are obtained from a paper by Ball, 1997. Eighteen percent of chromium was assumed to be hexavalent, based on combustion data from stationary combustion turbines that burn diesel fuel. Emission factors for mercury were obtained from a 2005 EPA test program. Documentation describing development of these emission factors can be found in Appendix A. Emission factors for arsenic were developed from data reported for tunnel tests. Metal emission rates do not vary among fuel types.

Table 4. PAH gas/particle phase allocation factors

	Molecular	Allocation Fraction	
PAH Species	Weight	PM Phase	Gaseous Phase
Acenapthene	154	0	1
Acenaphthylene	152	0	1
Anthracene	178	0.466	0.534
Benz(a)anthracene	228	0.723	0.277
Benzo(a)pyrene	252	1	0
Benzo(b)fluoranthene	252	1	0
Benzo(g,h,i)perylene	276	0.773	0.227
Benzo(k)fluoranthene	252	1	0
Chrysene	228	0.823	0.177
Dibenzo(a,h)anthracene	278	1	0
Fluoranthene	202	0.516	0.484
Fluorene	166	0.215	0.785
Indeno(1,2,3-cd)pyrene	276	1	0
Phenanthrene	178	0.335	0.665
Pyrene	202	0.552	0.448

**Table 5.** PAH/VOC and PAH/PM ratios for gasoline vehicles and trucks.

	Start	Running	
	Fraction of	Fraction of	Fraction of
<u>PAH</u>	$OC_{2.5}$	$OC_{2.5}$	VOC
Benzo(a)anthracene	0.0001237	0.0000944	0.0000007
Benzo(a)pyrene	0.0001711	0.0001306	0.0000000
Benzo(b)fluoranthene	0.0002032	0.0001551	0.0000000
Benzo(k)fluoranthene	0.0002032	0.0001551	0.0000000
Chrysene	0.0001408	0.0001075	0.0000005
Dibenz(a,h)anthracene	0.0000000	0.0000000	0.0000000
Indeno(1,2,3-			
cd)pyrene	0.0001283	0.0000979	0.0000000
Acenaphthene	0.0000000	0.0000000	0.0000185
Acenaphthalene	0.0000000	0.0000000	0.0001040
Anthracene	0.0006577	0.0005020	0.0000114
Benzo(ghi)perylene	0.0003306	0.0002524	0.0000015
Fluoranthene	0.0007834	0.0005980	0.0000111
Fluorene	0.0005425	0.0004141	0.0000300
Naphthalene	0.0000000	0.0000000	0.0022928
Phenanthrene	0.0014184	0.0010827	0.0000427
Pyrene	0.0011450	0.0008740	0.0000141

**Table 6.** Metal emission factors for gasoline vehicles and trucks.

Pollutant	Emission Rate (g/mi)
Chromium 6+	$8.9 \times 10^{-7}$
Chromium 3+	$4.1 \times 10^{-6}$
Manganese	$1.7 \times 10^{-6}$
Nickel	$3.6 \times 10^{-6}$
Elemental Gas Phase Hg	1.1x10 <sup>-7</sup>
Reactive Gas Phase Hg	9.9x10 <sup>-9</sup>
Particulate Hg	$4.0 \times 10^{-10}$
Arsenic	$2.3 \times 10^{-6}$

# 2.1.4. Dioxins and Furans

MOVES estimates emissions for 17 dioxin and furan congeners (Table 7). The emissions are estimated using mg/mile emission factors. These emission factors were obtained from EPA's dioxin assessment.<sup>19</sup> They do not vary among fuel types.

**Table 7.** Dioxin emission factors for gasoline vehicles.

Pollutant	Mg/mi
2,3,7,8-TCDD TEQ	8.27E-10
1,2,3,7,8-Pentachlorodibenzo-p-Dioxin	3.70E-10
1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	3.87E-10
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	7.92E-10
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	4.93E-10
1,2,3,4,6,7,8-Heptachlorodibenzo-p-	
Dioxin	5.95E-09
Octachlorodibenzo-p-dioxin	4.70E-08
2,3,7,8-Tetrachlorodibenzofuran	2.76E-09
1,2,3,7,8-Pentachlorodibenzofuran	1.32E-09
2,3,4,7,8-Pentachlorodibenzofuran	9.68E-10
1,2,3,4,7,8-Hexachlorodibenzofuran	1.09E-09
1,2,3,6,7,8-Hexachlorodibenzofuran	1.16E-09
1,2,3,7,8,9-Hexachlorodibenzofuran	3.17E-10
2,3,4,6,7,8-Hexachlorodibenzofuran	1.36E-09
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1.21E-08
1,2,3,4,7,8,9-Heptachlorodibenzofuran	3.87E-10
Octachlorodibenzofuran	1.37E-08

### 2.2. Evaporative and Permeation

Toxic to VOC ratios for evaporative non-permeation emissions of benzene, MTBE, ethanol and naphthalene remain unchanged from those in MOVES2010a. In summary, benzene and MTBE ratios are estimated using algorithms originally developed for MOBILE 6.2. However, evaporative emissions processes for MOVES differ from those in MOBILE6.2. Thus, algorithms for hot soak in MOBILE6.2 are used for vapor venting and refueling vapor loss in MOVES, and algorithms for running loss are used for fuel leaks and refueling spillage loss (Table 8). Ratios for naphthalene and ethanol are given in Table 9.

Ratios for the additional air toxics found in evaporative non-permeation emissions (2,2,4-trimethylpentane, ethyl benzene, hexane, propionaldehyde, toluene and xylenes) were obtained from profiles developed for EPA by Environ Corporation, using data from the Auto/Oil test program conducted in the early 1990's. These ratios are also given in Table 9. For all pollutants except benzene, ratios are the same for all types of non-permeation evaporative emissions. The ratios for 10% ethanol are used for all fuels with greater than or equal to 5% ethanol and less than 12%.

**Table 8.** Toxic/VOC algorithms for benzene and MTBE gasoline vehicle evaporative emissions.

Polluta nt	Process	Toxic Fraction Equation (Toxic/VOC)
Benzene	Vapor Venting/Refueling Vapor Fuel Leaks/Spillage	(-0.03420*OXY - 0.080274*RVP + 1.4448)*BNZ/100 (-0.03420*OXY - 0.080274*RVP + 1.4448)*BNZ/100
MTBE	Vapor Venting/Refueling Vapor Fuel Leaks/Spillage	(24.205 - 1.746*RVP)*MTBE/1000 (17.8538 - 1.6622*RVP)*MTBE/1000

Note: OXY = wt% oxygen RVP = Reid vapor pressure in psi

BNZ = vol% benzene MTBE = vol% MTBE

**Table 9.** Evaporative Toxic/VOC ratios for other toxics from gasoline vehicles (Auto/Oil).

Pollutant	<b>E</b> 0	E10
Ethanol	0.00000	0.11896
Naphthalene	0.00040	0.00040
2,2,4-Trimethylpentane	0.01984	0.03354
Ethyl Benzene	0.02521	0.01721
Hexane	0.02217	0.02536
Toluene	0.09643	0.14336
Xylene	0.07999	0.06423

The composition of permeation emissions differs significantly from other types of evaporative emissions. Work to better characterize these permeation emissions was recently conducted for the Coordinating Research Council. These data were used to develop the toxic to VOC ratios in Table 10. Data from the CRC E-65 study were used for ethanol, while data from the CRC E-77-2b study were used for the rest of the air toxics in Table 10. For the CRC E-77-2b study, data from 3-day diurnal tests on vehicles meeting Tier 1 and near zero evaporative emission standards were used. Toxic to VOC ratios for E0 and E10 were estimated by averaging data from gasolines of different RVPs.

Toxic to VOC ratios for benzene, MTBE, and naphthalene are not found in Table 10. For benzene, the diurnal emissions algorithm from MOBILE6.2 was used instead, since this algorithm accounts for impacts of changing oxygenate, RVP and fuel benzene levels. However, the CRC E-65 study suggests that the ratio of benzene from permeation to total VOC is about 1.77 times higher than the ratio associated with evaporation.<sup>23</sup> Thus the diurnal emissions algorithm was multiplied by 1.77. This algorithm is:

$$1.77[(-0.02895*OXY - 0.080274*RVP + 1.3758)*BNZ/100]$$

In the absence of data on permeation emissions for MTBE, the resting loss algorithm from MOBILE6.2 was used:

For naphthalene, the toxic to VOC ratio for non-permeation evaporative emissions was also applied to permeation.

**Table 10.** Gasoline vehicle permeation toxic/VOC ratios for air toxics except benzene, naphthalene and MTBE (CRC E-65 and E-77-2b).

Pollutant	E0	E10
2,2,4-Trimethylpentane	0.036	0.024
Ethyl Benzene	0.003	0.001
Hexane	0.050	0.065
Toluene	0.110	0.101
Xylene	0.016	0.011
Ethanol		0.333

### 3. Diesel Vehicles and Trucks

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

### 3.1. Exhaust

### 3.1.1. Gaseous Hydrocarbons

The composition of VOCs for heavy-duty diesel engines without model year 2007 and later emission controls versus those engines with such controls vary significantly. Thus, we developed one set of toxic to VOC ratios for pre-2007 diesel engines and another set for 2007 and later engines. Since extended idle emissions associated with auxiliary power units (APUs) are not subject to 2007 standards, toxic to VOC ratios for pre-2007 diesel engines were used for them. Since light-duty diesels comprise a very small portion of the fleet, the same ratios were applied to all diesel vehicle classes to streamline modeling.

EPA relied on a database compiled for the Coordinating Research Council (CRC E-75) and National Renewable Energy Laboratory (NREL) to develop toxic to VOC ratios for pre-2007 engines. This database was developed from a literature survey and included data from 13 different studies. The studies included in this database 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 to VOC ratios developed by Sierra Research from CRC E-75 data were used. The methodology they used to develop ratios is described in detail in their technical report. Data from tests using non-conventional diesel fuel (Fischer-Tropsch, bioDiesel, ethanol-Diesel blends, emulsified fuel, European blends, and other obvious research fuels) were excluded, as were data from non-heavy duty engines. The ratios are provided in Table 11.

Toxic to VOC ratios for benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, naphthalene, ethylbenzene, styrene and xylenes were developed by EPA from the E-75 database.

We relied on United States data from heavy-duty diesel engines running on conventional diesel fuels, collected on test-cycles representative of real world operation. Some studies measured emissions over distance, while other studies measure emissions relative to brake horsepower. For studies which measured emissions relative to distance, we calculated mean emissions per mile for toxics and VOC, then calculated a ratio of toxics to VOC. For studies which measured emissions relative to brake horsepower hour, we calculated mean emissions per brake horsepower hour for toxics and VOC, then calculated a second ratio of toxics to VOC. We then calculated a composite ratio using sample size to weight the two ratios. The resulting ratios are provided in Table 11.

For 2007 and later heavy-duty diesels, and 2004 and later light-duty diesels which meet Tier 2 vehicle standards, advanced emission controls change the composition of VOCs. For these engines, we relied on speciated emissions data from the Advanced Collaborative Emissions Study (ACES), directed by the Health Effects Institute and Coordinating Research Council, with participation from a range of government and private sector sponsors. Detailed emissions data from the study were provided to EPA at the request of the Coordinating Research Council. The data were collected on four engines on several test cycles with low sulfur diesel fuel. EPA used data from a 16-hour transient cycle. Toxic to VOC ratios obtained from the ACES data are provided in Table 12.

**Table 11.** Toxic to VOC Ratios for pre-2007 diesel engines (CRC E-75).

Pollutant	Toxic/VOC
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
Hexane	0.00197
Propionaldehyde	0.00468
Styrene	0.001312
Toluene	0.00433
Xylenes	0.003784

**Table 12.** Toxic to VOC Ratios for 2007 and later diesel engines.

Pollutant	Toxic/VOC
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
Hexane	0.00541
Propionaldehyde	0.00314
Styrene	0.00000
Toluene	0.02999
Xylenes	0.03800

### 3.1.2. Polycyclic Aromatic Hydrocarbons

As with gasoline vehicles, PAH mass emissions from diesel engines were apportioned into the gas and particle phase, using a single set of allocation factors for all conditions. Gas phase PAHs were estimated using toxic/VOC ratios and particle phase PAHs were estimated using toxic to OC<sub>2.5</sub> ratios. Toxic to VOC and toxic to PM<sub>2.5</sub> ratios for pre-2007 diesel engines were developed by EPA from the E-75 database. Toxic to PM<sub>2.5</sub> ratios were converted to toxic to OC<sub>2.5</sub> ratios using OC<sub>2.5</sub> to PM<sub>2.5</sub> percentages from MOVES. We relied on United States data from heavy-duty diesel engines running on conventional diesel fuels, collected on test-cycles representative of real world operation. It should be noted that for some PAHs, there were substantially more data than for others; thus the level of confidence in emission factors varies among individual compounds. For instance, while data from 66 tests were available for acenaphthene, data from only two tests were available for dibenz(a,h)anthracene. Table 13 provides VOC and PM ratios for PAHs from these older technology engines.

For 2007 and later diesels, advanced emission controls change the composition and reduce the total mass of PAHs. For these engines, we relied on speciated emissions data from the ACES study. Table 14 provides VOC and  $OC_{2.5}$  ratios for PAHs from these newer technology engines.

**Table 13.** PAH/VOC and PAH/ OC2.5 ratios for pre-2007 diesel engines.

	Start Fraction of	Running Fraction of	Fraction of
PAH	OC <sub>2.5</sub>	OC <sub>2.5</sub>	HC
Benzo(a)anthracene	0.0002100	0.0005806	0.0000445
Benzo(a)pyrene	0.0000789	0.0002180	0.0000000
Benzo(b)fluoranthene	0.0000234	0.0000648	0.0000000
Benzo(k)fluoranthene	0.0000033	0.0000091	0.0000000
Chrysene	0.0001327	0.0003667	0.0000235
Dibenz(a,h)anthracene	0.0000032	0.0000087	0.0000000
Indeno(1,2,3-	0.0000060	0.0000166	
cd)pyrene			0.0000000
Acenaphthene	0.0000000	0.0000000	0.0003210
Acenaphthalene	0.0000000	0.0000000	0.0005009
Anthracene	0.0001058	0.0002924	0.0002353
Benzo(ghi)perylene	0.0000038	0.0000104	0.0000276
Fluoranthene	0.0004058	0.0011217	0.0006108
Fluorene	0.0001818	0.0005025	0.0005914
Naphthalene	0.0000000	0.0000000	0.0090464
Phenanthrene	0.0004187	0.0011574	0.0019446
Pyrene	0.0005865	0.0016213	0.0007577

**Table 14.** PAH/VOC and PAH/PM ratios for 2007 and later diesel engines.

	Start	Running	
	Fraction of	Fraction of	Fraction of
<u>PAH</u>	$OC_{2.5}$	$OC_{2.5}$	HC
Benzo(a)anthracene	0.0000015	0.0000010	0.0000003
Benzo(a)pyrene	0.0000061	0.0000042	0.0000000
Benzo(b)fluoranthene	0.0000026	0.0000018	0.0000000
Benzo(k)fluoranthene	0.0000026	0.0000018	0.0000000
Chrysene	0.0000046	0.0000031	0.0000005
Dibenz(a,h)anthracene	0.0000018	0.0000013	0.0000000
Indeno(1,2,3-cd)pyrene	0.0000009	0.0000006	0.0000000
Acenaphthene	0.0000000	0.0000000	0.0000526
Acenaphthalene	0.0000000	0.0000000	0.0000853
Anthracene	0.0000488	0.0000334	0.0000304
Benzo(ghi)perylene	0.0000004	0.0000003	0.0000002
Fluoranthene	0.0000896	0.0000613	0.0000457
Fluorene	0.0000990	0.0000677	0.0001963
Naphthalene	0.0000000	0.0000000	0.0163278
Phenanthrene	0.0007886	0.0005395	0.0008507
Pyrene	0.0000859	0.0000588	0.0000379

### 3.1.3. Metals

Emissions factors for chromium, magnesium, and nickel from pre-2007 diesels were based on data from the CRC E-75 test program. Emission factors for 2007 and later diesels are from the ACES test program. Emission factors for mercury and arsenic were obtained from the same 2005 EPA test program and tunnel study as the gasoline vehicle emission factors. They do not vary with emission control technology. Table 15 provides metal emission factors for heavy duty engines.

**Table 15.** Metal emission factors for diesel vehicles and trucks.

Pollutant	Pre-2007 Emission Rate (g/mi)	2007 and Later Emission Rate (g/mi)
Chromium 3+	5.6x10-6	1.6x10 <sup>-6</sup>
Chromium 6+	$1.2x10^{-6}$	$3.4 \times 10^{-7}$
Manganese	$8.0 \times 10^{-6}$	$5.5 \times 10^{-7}$
Nickel	$1.4 \times 10^{-5}$	$6.5 \times 10^{-7}$
Elemental Gas Phase Hg	$6.2 \times 10^{-9}$	$6.2 \times 10^{-9}$
Reactive Gas Phase Hg	$3.2 \times 10^{-9}$	$3.2 \times 10^{-9}$
Particulate Hg	1.6x10 <sup>-9</sup>	1.6x10 <sup>-9</sup>
Arsenic	$2.3 \times 10^{-6}$	$2.3 \times 10^{-6}$

### **3.1.4.** Dioxins

MOVES estimates emissions for 17 dioxin and furan congeners (Table 16). The emissions are estimated using mg/mile emission factors. These emission factors were obtained from EPA's dioxin assessment.<sup>26</sup>

**Table 16.** Dioxin/furan emission factors for diesel vehicles and trucks.

Pollutant	Mg/mi
2,3,7,8-TCDD TEQ	5.52E-08
1,2,3,7,8-Pentachlorodibenzo-p-Dioxin	4.67E-08
1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	6.57E-08
1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin	1.29E-08
1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin	2.37E-07
1,2,3,4,6,7,8-Heptachlorodibenzo-p-	
Dioxin	1.55E-06
Octachlorodibenzo-p-dioxin	7.14E-06
2,3,7,8-Tetrachlorodibenzofuran	1.39E-07
1,2,3,7,8-Pentachlorodibenzofuran	5.55E-08
2,3,4,7,8-Pentachlorodibenzofuran	1.23E-07
1,2,3,4,7,8-Hexachlorodibenzofuran	2.08E-07
1,2,3,6,7,8-Hexachlorodibenzofuran	9.47E-08
1,2,3,7,8,9-Hexachlorodibenzofuran	5.51E-08
2,3,4,6,7,8-Hexachlorodibenzofuran	1.37E-07
1,2,3,4,6,7,8-Heptachlorodibenzofuran	4.30E-07
1,2,3,4,7,8,9-Heptachlorodibenzofuran	4.89E-08
Octachlorodibenzofuran	4.91E-07

# 3.2. Evaporative

MOVES estimates evaporative emissions associated with spillage for diesel vehicles. Since there are no speciated emissions of diesel spillage emissions, we developed toxic to VOC ratios based on a diesel headspace profile, profile number 4547 from the SPECIATE database. These ratios are provided in Table 17.

**Table 17.** Toxic to VOC ratios for diesel spillage emissions.

Pollutant	Toxic/VOC
2,2,4-Trimethylpentane	0.00974
Ethyl Benzene	0.00324
Hexane	0.01076
Toluene	0.01419
Xylene	0.01222
Benzene	0.00410

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<sup>1</sup> U. S. EPA. 2010. Motor Vehicle Emission Simulator (MOVES) 2010: User Guide. Report No. EPA-420-B-09-041. Available at <a href="http://www.epa.gov/otaq/models/moves/420b09041.pdf">http://www.epa.gov/otaq/models/moves/420b09041.pdf</a>.

<sup>4</sup>U. S. EPA. 1993. Final Regulatory Impact Analysis for Reformulated Gasoline. December 13, 1993. Available at <a href="http://www.epa.gov/otaq/regs/fuels/rfg/">http://www.epa.gov/otaq/regs/fuels/rfg/</a>

<sup>6</sup>Sierra Research, 2010. Development of Emission Rates for the MOVES Model. Prepared for the U. S. Environmental Protection Agency by Sierra Research, Sacramento, CA, July 2, 2010. Sierra Research Report No. SR2010-07-01.

<sup>&</sup>lt;sup>2</sup> U. S. EPA. 2004. MOBILE6 Vehicle Emissions Model. Available at http://www.epa.gov/otaq/m6.htm.

<sup>&</sup>lt;sup>3</sup> Michaels, H.; Brzezinski, D.; Cook, R. EPA's National Mobile Inventory Model (NMIM), A Consolidated Emissions Modeling System for MOBILE6 and NONROAD; EPA-420-R-05-003, U. S. Environmental Protection Agency, Office of Transportation and Air Quality, Assessment and Standards Division, Ann Arbor, MI, 2005. (Available at <a href="http://www.epa.gov/otaq/nmim.htm">http://www.epa.gov/otaq/nmim.htm</a>).

<sup>&</sup>lt;sup>5</sup> Michaels, H., Brzezinski, D., Cook, R. 2005. EPA's National Mobile Inventory Model (NMIM), A Consolidated Emissions Modeling System for MOBILE6 and NONROAD. U. S. EPA, Office of Transportation and Air Quality, Assessment and Standards Division, Ann Arbor, MI, March 2005; Report No. EPA-420-R-05-003. Available at <a href="http://www.epa.gov/otaq/nmim.htm">http://www.epa.gov/otaq/nmim.htm</a>.

<sup>&</sup>lt;sup>7</sup> U. S. EPA. 2009. Exhaust Emission Profiles for EPA SPECIATE Database: Energy Policy Act (EPAct) Low-Level Ethanol Fuel Blends and Tier 2 Light-Duty Vehicles. Assessment and Standards Division, Office of Transportation and Air Quality. Report No. EPA-420-R-09-002.

<sup>&</sup>lt;sup>8</sup> Michaels, H., Brzezinski, D., Cook, R. 2005. EPA's National Mobile Inventory Model (NMIM), A Consolidated Emissions Modeling System for MOBILE6 and NONROAD. U. S. EPA, Office of Transportation and Air Quality, Assessment and Standards Division, Ann Arbor, MI, March 2005; Report No. EPA-420-R-05-003. Available at <a href="http://www.epa.gov/otaq/nmim.htm">http://www.epa.gov/otaq/nmim.htm</a>.

<sup>&</sup>lt;sup>9</sup> Watson, J. D., E. Fujita, J. C. Chow, and B. Zielinska. 1998. Northern Front Range Air Quality Study. Desert Research Institute. See Table 4.4-4, page 4-41.

<sup>&</sup>lt;sup>10</sup> U. S. EPA, 2001. Revised Methodology and Emission Factors for Estimating Mobile Source PAH Emissions in the National Toxics Inventory. Memorandum from Rich Cook and Joseph Somers, Office of Transportation and Air Quality, to Laurel Driver, Office of Air Quality Planning and Standards, June 11, 2001.

<sup>11</sup>Sierra Research, 2010. Development of Emission Rates for the MOVES Model. Prepared for the U. S. Environmental Protection Agency by Sierra Research, Sacramento, CA, July 2, 2010. Sierra Research Report No. SR2010-07-01.

<sup>12</sup>U.S. EPA, 2009. SPECIATE 4.2 Speciation Database Development Documentation, Office of Research and Development. Report No. EPA/600-R-09/038, June 2009.

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

### **Calculation of Mercury Emission Factors from Vehicle Tests**

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

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

Evaporative losses of mercury from motor vehicles and loss of mercury during refueling were not measured and therefore not included in the National Emissions Inventory. The emission of mercury from these evaporative sources is expected to be small compared with the combustion exhaust emissions of mercury from mobile sources.

A description of the vehicles tested for which data were used in developing emission factors is provided in Table 1. The data collected from these vehicles in diluted exhaust in the constant volume sampler (CVS) included total hydrocarbon (THC), carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), methane (CH<sub>4</sub>), and carbon monoxide (CO). In raw, undiluted exhaust, data collected included elemental and total gas-phase mercury, particulate mercury and CO<sub>2</sub>. Gas-phase mercury was also measured in the intake air. Total air flow and standard temperature and pressure-corrected flows for all the sampling systems were measured. 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<sub>2</sub>, NO<sub>x</sub>, 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 in 5 minute intervals.

**Table 1.** Vehicles tested for Mercury Emissions

Model						
Year	Make	Model	Fuel Type	Odometer	Cylinders	Displacement
		GRAND MARQUIS				
2005	MERCURY	LS	Gasoline	9,953	8	4.6
		MUSTANG				
2005	FORD	CONVERTIBLE	Gasoline	5,424	6	4
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
2000	JEEP	CHEROKEE SPORT	Gasoline	48,468	6	4
1999	FORD	F250 XLT	Diesel	113,897	8	7.3
1999	FORD	F250 XLT SD	Diesel	109,429	8	7.3
1998	HONDA	CIVIC DX	Gasoline	204,983	4	1.6
1994	CHEVROLET	SILVERADO	Gasoline	129,521	8	5.7
1992	CHEVROLET	S10 BLAZER	Gasoline	162,249	6	4.3
1991	HONDA	ACCORD EX	Gasoline	143,289	4	2.2
1987	CHRYSLER	FIFTH AVENUE	Gasoline	72,573	8	5.2
1984	FORD	F150 PICKUP	Gasoline	36,727	8	5.8

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

### **Calculation of Emission Rates**

The data for regulated pollutants and mercury were time-aligned; however, emissions data were not attributed to vehicle specific power as the data are not to be used in modal emissions modeling at this time. Emission rates were calculated separately for elemental gasphase 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:

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

Exhaust flow = (CVS flow / dilution factor)

Exhaust flow calculation was initiated when the analytical equipment indicated that the dilute exhaust CO<sub>2</sub> concentration was greater than the background CO<sub>2</sub> concentration.

To calculate exhaust flow for the diesel vehicles, the dilution factor was calculated by simply dividing CO<sub>2</sub> in the raw exhaust by CO<sub>2</sub> in the CVS. This method was used because diesel engines operate across a very wide range of fuel to air mixtures and the CFR method described above was not appropriate.

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

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

### **Calculating Weighted Emission Test Results**

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

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

Equation used to calculate test-level emission rates:

Grams/mile emission factor =  $0.43*(C + R)/(C_m + R_m) + 0.57*(H+R)/(H_m + R_m)$ 

Where:

C = mercury mass collected in the first 300 seconds of the first morning test ('cold start')

 $C_{\rm m}$  = distance covered by the cold start

R = mercury mass collected in the last 1,135 seconds of all six cycles of the LA92 ('hot stabilized')

 $R_m$  = cumulative distance covered by all six cycles of the LA92 ('hot stabilized')

H = mercury mass collected in the first 300 seconds of the first afternoon test ('hot start')

 $H_m$  = distance covered by the hot start

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.

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

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

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

 Table 2. Mercury Emission Factors from Mobile Sources

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