Speciation of Total Organic Gas and Particulate Matter Emissions from On-road Vehicles in MOVES2014b

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

In addition to estimating emissions of pollutants that are discrete chemical compounds, such as carbon monoxide (CO) and sulfur dioxide (SO_2), MOVES2014 produces emission rates for aggregates of individual chemical compounds, including total hydrocarbons (THC), volatile organic compounds (VOC), total organic gases (TOG) and particulate matter (PM). These pollutants are operationally defined, meaning that their definition depends on the measurement technique(s) selected. For example, THC is defined as the hydrocarbons measured by a flame ionization detector (FID). TOG is intended to include all organic gases. Because THC measurements do not respond fully to carbon-oxygen bonds in oxygenated compounds, such as aldehydes, alcohols, and ketones, these oxygenates need to be measured separately by gas and liquid chromatography and added to the THC measurements to calculate TOG. Alternatively, TOG measurements can be made solely with gas and liquid chromatography methods. Thus, differences in measurement methods need to be considered when comparing THC to TOG emission measurements[1]. Similarly, particulate matter is operationally defined as the measured mass collected on a filter using EPA-defined sampling filter media, conditions, and practices[2,3]. $PM_{2.5}$ refers to particulate matter emissions collected downstream of a cyclone that removes the particles with aerodynamic diameter greater than 2.5 microns, while PM_{10} refers to particulate matter emissions with aerodynamic diameter less than 10 microns.

Previous versions of MOVES produced emission estimates for a subset of species that contribute to TOG and $PM_{2.5}$. These include important organic gaseous toxics (e.g., formaldehyde and benzene), and toxic particle-phase elements (e.g., nickel and manganese). These also include semi-volatile organic compounds, such as 15 individual polycyclic aromatic hydrocarbons (e.g., benzo(*g,hi,i*)perylene) that can exist in both the gaseous and particle phases under different measurement conditions. Individual toxic emission rates are detailed in the toxics report[4], but are peripherally discussed in this report in the context of their use in deriving speciated TOG and PM emissions.

For air quality modeling purposes, further chemical characterization of TOG and $PM_{2.5}$ is required. Prior to MOVES2014, the individual species produced by MOVES (e.g., benzene, elemental carbon) and aggregates (TOG and $PM_{2.5}$) were processed outside MOVES by emission pre-processors into a form suitable for air-quality modeling. The process of apportioning aggregate TOG and $PM_{2.5}$ into sets of separate components is called “speciation.” MOVES2014 incorporates the process of TOG and $PM_{2.5}$ speciation, and can produce the TOG and $PM_{2.5}$ species needed by air quality models.

The reason for bringing the speciation capability inside MOVES is improved accuracy and flexibility. Because the speciation of TOG and $PM_{2.5}$ depends on technology, fuels, and emission processes, speciation is approximate and cumbersome to implement outside MOVES. Pre-MOVES2014, speciation profiles were applied outside the model primarily by aggregate classifications called source classification code (SCC) that did not contain important distinctions of emission standards, fuel types, and emission process, such as between start and running exhaust. Pre-MOVES 2014 speciation profiles had to vary by county to account for combinations of ethanol fuel blends that vary by county. This outside-of-MOVES speciation was limited as it could not readily accommodate the application of technology-specific speciation profiles to concurrent categories of model-year group, regulatory class, fuel subtype (e.g., gasolines with different ethanol content), and MOVES emission process (see “process” in the glossary).

Inside MOVES, speciation (like all calculations) is done on a model-year, fuel, vehicle class, and emission-process basis, providing the ability to more easily reflect distinctions in different TOG and $PM_{2.5}$ profiles.

The purpose of this document is to describe how we have incorporated the speciation process, which previously occurred outside of the MOVES framework, into MOVES2014 to better provide model-ready species for air quality modeling. Limited data exist to support matching speciated emissions data with all combinations of MOVES classifications (model-year group, regulatory class, fuel subtype, emissions process), but we believe the speciated emissions data cited below are the best available at the time this document was created. Furthermore, the new structure allows us to continue to improve and expand the application of speciated emissions data in MOVES based on the research and emissions test programs as new data become available.

This report was revised for MOVES2014a from a previous version (EPA-420-R-14-020[5]). Those changes include: inclusion of the CB6 chemical mechanism into MOVES2014a (Section 4.3), a correction made to the TOG speciation profile assignment (Table 4-1 and Table B-1), corrections made to the NMOG and VOC factors (Sections 3.2 and 3.3), documentation of the values used to calculate NMOG and VOC emissions from diesel refueling processes (Section 3.4), and edits to Appendix C (Development of $PM_{2.5}$ speciation profiles in MOVES2014) in response to peer-review comments (Appendix E).

This report has also been updated for MOVES2014b. The only changes for MOVES2014b were updates to chemical mechanisms CB05 and CB6 and the addition of another chemical mechanism, SAPRC07T. For more details see Section 4.

2. Speciation Glossary

In the area of "speciation," many words have two or more meanings. The list below distinguishes these to avoid confusion. The report tries to use unambiguous terms that are close to common usage.

- Aggregate species: groups of chemical compounds (or “real species”). These are often defined operationally or may be defined for modeling purposes. For example, THC, TOG and VOC are aggregate gaseous species. NonEC is an aggregate particulate matter species.

- Elemental Carbon (EC): “A descriptive term for carbonaceous particles based on chemical composition rather than light-absorbing characteristics. Often used as a synonym for black carbon.”[6] Elemental carbon is measured through thermal optical techniques as particle-phase carbon that does not volatize at high temperatures in an oxygen-free environment.[7] In tailpipe exhaust, EC is one measure of carbonaceous soot formed from fuel pyrolysis occurring during combustion.[8]

- CMAQ: The Community Multiscale Air Quality system is a photochemical and transport air quality model. CMAQ is an open source development project sponsored by the US EPA Atmospheric Science Modeling Division (http://www.cmaq-model.org/).

- Chemical mechanism: In air-quality models, chemical mechanisms are simplified representations of the full panoply of atmospheric chemical reactions. They have been developed by air-quality modelers to speed up the atmospheric chemistry calculations in their models. An aspect of these chemical mechanisms is the use of a relatively small set of "chemical mechanism species," (CM species) into which all the real species can be mapped, and which serve to model the atmospheric reactions of importance. For the purposes of MOVES, a chemical mechanism may be thought of as a set of CM species and the mapping between regular MOVES output species and the CM species. In the original release of MOVES2014, we included only the CB05 version of the carbon-bond mechanism.[9] In MOVES2014a, we added CB6,[10] and in MOVES2014b we updated CB05 and CB6 (and updated the name to CB6CMAQ) and added SAPRC07T. However, since the mapping is table-driven, MOVES2014 has the structure in place to generate CM species for any chemical mechanism. OTAQ expects to add others over time.

- Integrated species: Real species for which MOVES produces emissions that are subtracted from TOG, leaving residual TOG. This residual TOG is speciated into CM species using a CM speciation profile constructed from the real speciation profile from which the integrated species have been removed. The integrated species, which are produced by MOVES, are individually speciated into CM species. At present, MOVES2014 integrates the 16 species shown in Table 2-1. MOVES is designed to accept different sets of integrated species, if desired.

Table 2-1. Integrated MOVES pollutants

pollutant ID	Pollutant Name
5	Methane (CH4)
20	Benzene
21	Ethanol
22	MTBE
24	1,3-Butadiene
25	Formaldehyde
26	Acetaldehyde
27	Acrolein
40	2,2,4-Trimethylpentane
41	Ethyl Benzene
42	Hexane
43	Propionaldehyde
44	Styrene
45	Toluene
46	Xylene
185	Naphthalene gas

- Intermediate $PM_{2.5}$ species: Groups of $PM_{2.5}$ species used to improve computation time, and reduce the size of the emission rate tables. They include the aggregate species: “non-

elemental carbon particulate matter" (NonECPM) and "non-elemental carbon non-sulfate particulate matter" (NonECnonSO4PM), elemental carbon (EC), sulfate (SO_4) and particulate water (H_2O). They are used to compute total $PM_{2.5}$ emissions and speciated $PM_{2.5}$ emissions. The EC, SO_4, and H_2O species are reported as MOVES outputs.

- Chemical Mechanism species (CM species): the species used by chemical mechanisms. CM species include both artificial constructs (sometimes referred to as "lumped species") and real species. CM species are unique to particular chemical mechanisms (e.g., CB05, SAPRC07T). All real TOG species are mapped to CM species. For a particular chemical mechanism, the associated group of CM species can be referred to by the name of the mechanism, for example, CB05 species.

- CM speciation profile: the mapping of a real species (e.g., hexane) or an aggregate species (e.g., TOG) into CM species. The mapping of real species into CM species has been created by the developers of chemical mechanisms for air quality modeling.[9] The mapping of real species is independent of process and fuel. The mapping of aggregate species (e.g., residual TOG) represents the sum of the mappings of the individual real species from the real speciation profiles. The mapping of aggregate species depends on process and fuel.

- Organic Mass (OM): Particle-phase organic mass. The mass of the organic material in particulate: OM = organic carbon (OC) + non-carbon organic matter (NCOM).

- Organic Carbon (OC): "The mix of compounds containing carbon bound with other elements; e.g., hydrogen and oxygen. Organic carbon may be a product of incomplete combustion, or formed through the oxidation of VOCs in the atmosphere."[6] Organic carbon is measured using thermal-optical methods as the particle-phase carbon collected on a filter that volatizes at high temperatures in an oxygen-free environment.

- Non-Carbon Organic Mass (NCOM): the mass of the oxygen, hydrogen, nitrogen and other elements present in particle-phase organic mass. OC and NCOM are modeled separately in air quality models in order to model the degree of oxidation of organic matter, which depends on the emission source and the chemical transformation in the atmosphere[11].

- Non-Elemental Carbon Particulate Matter (nonECPM): The $PM_{2.5}$ that is not elemental carbon. This is typically calculated as the difference between $PM_{2.5}$ mass filter-based measurements and elemental carbon measurements made using thermal optical measurements, or surrogate elemental carbon measurements such as photoacoustic sensors.

- Non-Elemental Carbon, Non-Sulfate Particulate Matter (nonECnonSO4PM): A MOVES intermediate species used to represent the $PM_{2.5}$ mass other than elemental carbon, sulfate, and associated water. NonECnonSO4PM includes organic matter, elements, and ions. NonECnonSO4PM is adjusted for fuel and temperature effects prior to speciation

due to limited data on temperature and fuel effects on individual $PM_{2.5}$ species in the exhaust, and to improve computational time.

- Non-Methane Hydrocarbons (NMHC): NMHC = THC – CH_4 (methane).

- Non-Methane Organic Gases (NMOG): NMOG = TOG – CH_4 (methane).

- Real species: "Species" in the normal chemical sense—a pure chemical substance. The word "real" helps distinguish these species from chemical mechanism species or aggregated species.

- Real speciation profile: ideally, a complete listing of the real species and their quantities of TOG. In practice, these profiles are incomplete; a certain fraction of the mass is unresolved. Such a profile is produced by laboratory analysis of emissions. This is not a CM speciation profile and is independent of chemical mechanism. Such a profile does, however, depend on process, fuel, and technology, since the mix of real species in TOG is different for different emission processes (e.g. evaporative and exhaust), for different fuels, and for different technologies. The SPECIATE database is the EPA repository for these profiles. (http://www.epa.gov/ttn/chief/software/speciate/index.html)

- Residual TOG: TOG that remains after subtracting integrated species.

- Process: MOVES2014 has twelve emission processes that are relevant for TOG speciation. The Process IDs and names are included in Table 2-2. Within each process, emission rates can potentially vary by operating mode. Running exhaust has different operating modes to represent idling, coasting, and operating with different engine loads. Start exhaust has different operating modes to differentiate a continuum of starts between cold, warm, and hot starts. The operating modes are defined in the MOVES2014 emission rate reports[30,33], and evaporative reports[12]. In MOVES2014, different TOG and PM speciation profiles can be applied to different processes, but not to individual operating modes.

Table 2-2. MOVES processes relevant for speciation profiles

Process ID	Process Name
1	Running Exhaust
2	Start Exhaust
11	Evap Permeation
12	Evap Fuel Vapor Venting
13	Evap Fuel Leaks
15	Crankcase Running Exhaust
16	Crankcase Start Exhaust
17	Crankcase Extended Idle Exhaust
18	Refueling Displacement Vapor Loss
19	Refueling Spillage Loss
90	Extended Idle Exhaust
91	Auxiliary Power Exhaust

- Source Classification Code (SCC): Standard code that identifies various emissions sources for inventory reporting and air quality modeling.

- SMOKE: Sparse Matrix Operator Kernel Emissions is a computer program used to provide model-ready inputs into CMAQ. SMOKE produces gridded, speciated, and hourly emissions input for use in CMAQ and other air-quality models. (http://www.smoke-model.org/index.cfm)

- Species: Distinct chemical compounds, ions, groups of compounds, or other chemical entities. In this report, we distinguish "real species," "aggregate species," "CM species," and "intermediate species," as explained in this glossary.

- Total Hydrocarbons (THC): "THC is the measured hydrocarbon emissions using a Flame Ionization Detector (FID) calibrated with propane. The FID is assumed to respond to all hydrocarbons identically as it responds to propane in determining the concentration of carbon atoms in a gas sample. Most hydrocarbons respond nearly identically as propane with notable exceptions being oxygenated hydrocarbons such as alcohols and aldehydes commonly found in engine exhaust." [1]

- Total Organic Gases (TOG): hydrocarbon emissions plus oxygenated hydrocarbons such as alcohols and aldehydes[1]

- Volatile Organic Compounds (VOC): TOG emissions minus those hydrocarbons that contribute little to ozone formation, such as methane, ethane, and acetone.[1] EPA may over time exclude additional organic compounds from the definition of VOC which have negligible photochemical reactivity. For the current list, see: Code of Federal Regulations, 40: Chapter 1, Subchapter C, Part 51, Subpart F, 51100(s). In mobile source testing, typically only a few compounds with negligible photochemical reactivity are measured in significant quantities. For the TOG speciation profiles used in MOVES, VOC is defined as TOG minus methane, ethane, and acetone.

3. Organic Gas Aggregations

MOVES provides estimates of organic gas emissions in a number of different aggregations. Table 3-1 shows the composition of the various organic gas aggregate classes in MOVES. As the table shows, the organic gas aggregations differ based on the presence or absence of methane, ethane, alcohols, and aldehydes. Definitions for these species are also included in the glossary. The term "FID-HC" refers to the total hydrocarbons detected by a Flame Ionization Detector (FID). MOVES THC (pollutandID=1) is defined as FID-HC, and thus includes methane and ethane. MOVES calculates emissions of total organic gases (TOG), nonmethane organic gases (NMOG) and volatile organic compounds (VOC) using information regarding the total organic gas speciation of emissions.

Table 3-1. Relationships among Organic Gas Aggregations in MOVES

PollutantID	PollutantName	FID-HC	Methane	Ethane	Acetone	Alcohols	Aldehydes
1	Total Hydrocarbons	Yes	Yes	Yes	No	No	No
79	Non Methane Hydrocarbons	Yes	No	Yes	No	No	No
87	Volatile Organic Compounds	Yes	No	No	No	Yes	Yes
86	Total Organic Gases	Yes	Yes	Yes	Yes	Yes	Yes
80	Non Methane Organic Gases	Yes	No	Yes	Yes	Yes	Yes

In MOVES, THC emission rates are the base emission rates (field meanBaseRate in the EmissionRateByAge table), from which each of the other hydrocarbon emissions are estimated. The following sections present the equations and parameters used to derive these other aggregate organic gas emission rates from THC.

3.1. Methane and Non-Methane Hydrocarbon Calculations

Exhaust regulations for hydrocarbons are often expressed in terms of non-methane hydrocarbons (NMHC). MOVES calculates both methane and NMHC from the THC emissions using methane/total hydrocarbon ratios (CH4THCRatio in the MethaneTHCRatio Table) as shown in Equation 1 and Equation 2.

$$NMHC = THC \cdot (1 - MethaneTHCRatio) \quad \textbf{Equation 1}$$

$$Methane = THC \cdot (MethaneTHCRatio) \quad \textbf{Equation 2}$$

The development of the methane/total hydrocarbon ratios is documented in the MOVES2014 Greenhouse Gas and Energy Consumption Rates Report.[13]

3.2. Non-Methane Organic Gases Calculation

Non-Methane Organic Gas (NMOG) is defined as all non-methane organic gases, including oxygenated hydrocarbons such as alcohols and aldehydes. To calculate NMOG from NMHC

requires accounting for the FID response factor for the oxygenated hydrocarbons. For example, formaldehyde generally has an FID response of ~0, so formaldehyde measurements need to be fully added to the NMHC value. An approximate FID factor for acetaldehyde is ~0.5, which means that only ½ of the measured acetaldehyde emissions need to be added to the FID measurements to calculate NMOG.

Within MOVES, the following equation is used to calculate NMOG.

$$NMOG = NMHC \cdot \left[speciationConstant + \sum_{i=1}^{4}(oxySpeciation \cdot volToWtPercentOxy_i \cdot oxyVolume_i)\right] \quad \textbf{Equation 3}$$

Where:

i = one of four gasoline oxygenates: ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), or tert-amyl methyl ether (TAME).

SpeciationConstant =NMOG/NMHC conversion factor when the gasoline has no oxygenate volume.

oxySpeciation = empirically derived value that adjusts the NMOG/NMHC according to oxygenate volume. The values represent the adjustment for a 1 b-1 increase in oxygenate volume.

$volToWtPercentOxy_i$ = term used to convert from the oxygenate percentage by volume (vol percent) to the mass percentage of oxygen in the fuel(mass percent). volToWtPercentOxy is calculated using Equation 4 and the values provided in Table 3-2. Equation 3 assumes that the relationship between the oxySpeciation factor is linearly proportional to the mass fraction of oxygen in the fuel.

$oxyVolume_i$ = the percent volume of each gasoline oxygenate in the respective fuel.

The methods used to derive the speciationConstant and the oxySpeciation terms are documented in Appendix A. The volume to weight percent oxygen values are calculated using Equation 4.

$$volToWtPercentOxy_i = Mass\ Fraction\ of\ Oxygen_i \times \frac{\rho_i}{\rho_F} \quad \textbf{Equation 4}$$

Where:

ρ_i = the density of the oxygenate (g/cm^3)

ρ_F = the density of the gasoline fuel, assume to be 0.75 g/cm^3

The mass fraction of oxygen, densities of the oxygenates, and calculated volToWtPercentOxy values are shown in Table 3-2.

Table 3-2. Volume to Weight Percent Oxygen for Gasoline Oxygenates

Oxygenate Name	Mass Fraction of Oxygen	Density of the Oxygenate (g/cm^3)	Volume to Weight Percent Oxygen (volToWtPercentOxy), assuming gasoline fuel density of 0.75 g/cm^3
Ethanol	0.3473	0.789	0.3653
MTBE	0.1815	0.7404	0.1792
ETBE	0.1566	0.7364	0.1537
TAME	0.1566	0.791	0.1651

Exhaust speciation factors for pre-2001 model year gasoline vehicles (pre-NLEV/Tier 2) remain unchanged from MOVES2010. The pre-2001 - gasoline NMOG/NMHC factors in MOVES were taken from MOBILE6.2 materials and were originally produced for MOBILE4.1 and MOBILE5.[14,15,16,17] These values are displayed in Table 3-3 for the pre-2001 model year groups. As indicated previously, oxySpeciation is an empirically derived value that adjusts the NMOG/NMHC relationship according to oxygenate volume. The pre-2001 oxySpeciation constants are based on data from speciation profiles incorporated into SPECIATE (profiles 1313 and 1314). There is no oxyspeciation factor for ethanol blends greater than 10 percent, since speciationConstant accounts for the oxygenate level.

Table 3-3. Parameters used to calculate NMOG/NMHC ratios for gasoline vehicle emissions

Fuel Subtype	Model Year Group	Process	speciationConstant	oxySpeciation
E0 to E10	1960-1974	Start and Running Exhaust	1.0352	0.0062
	1975-1986		1.02113	0.0062
	1987-1989		1.0179	0.0062
	1990-1993		1.0167	0.0062
	1994-2000		1.0163	0.0062
	2001-2050	Start	1.0078	0.0082
		Running	1.0149	0.0028
E15	1960-2050	Start	1.0495	0
		Running	1.0318	0
E20	1960-2050	Start	1.0703	0
		Running	1.0367	0
E70 to E100	1960-2000	Start and Running Exhaust	1.4858	0

The organic gas speciation factors for NLEV and Tier 2 gasoline (2001+) and ethanol blends are based on EPAct Phase 3 data.[18] The E0, E10, E15, E20 and E70-E100 values are based on data in SPECIATE profiles 8756, 8757, 8758, 8854, and 8855 profiles, respectively. For pre-2001 vehicles fueled on E70-E100 gasoline-ethanol blends, we calculate NMOG using the parameters

in Table 3-3[a]. For 2001 and later E70-E100 fueled vehicles, the NMOG emissions are set equal to the E10 emissions as discussed in the MOVES2014 fuel effects report.[32]

The NMOG/NMHC values for the pre-2007 trucks were based on more recent and extensive data than were available in earlier versions of MOVES.[19] MOVES2014 uses the pre-2007 NMOG/NMHC value for diesel auxiliary power units for all model years because they are not subject to the same control as on-highway diesel engines[b]. For 2007-and-later diesel engines, data were available from the Advanced Collaborative Emissions Study (ACES).[20]

MOVES2014 also includes updated NMOG speciation factors for compressed natural gas (CNG) transit buses. Two CNG speciation values are provided based on two model groups (pre-2004 and 2004-and-later), assuming full use of oxidation catalysts in 2004-and-later model year vehicles. CNG exhaust contains high formaldehyde emissions, particularly for uncontrolled compression ignition buses, which causes high NMOG/NMHC ratios. The derivation of the CNG NMOG/NMHC and VOC/NMHC rates are documented in the 2014 Heavy-Duty Emissions Report.[30] The new speciationConstant and oxySpeciation coefficients for diesel vehicles, and compressed natural gas vehicles are summarized in Table 3-4.

Table 3-4. Parameters used to calculate NMOG/NMHC ratios for diesel and CNG vehicle emissions

Fuel Type	Model Year Group	speciationConstant	oxySpeciation
Diesel	1960-2006	1.1455	0
	2007-2050	1.3431	0
CNG	1960-2003	1.9	0
	2004-2050	1.24	0

3.3. Volatile Organic Compound Calculation

In MOVES, Volatile Organic Compounds (VOC) are defined as the NMOG minus ethane and acetone. MOVES uses the same calculator and table to calculate VOC emissions as NMOG emissions. Equation 5 is used to calculate VOC emissions from NMHC, which has the same structure as Equation 3 used for NMOG calculations. However, the coefficients are different to account for the exclusion of ethane and acetone in the VOC emissions.

[a] MOVES2014 erroneously did not produce NMOG, VOC, and TOG emissions from MY 1998, 1998 and 2000 E85-fueled LDVs and LDTs. This has been fixed in MOVES2014a, which uses the NMOG/NMHC and VOC/NMHC values documented in Table 3-3 and Table 3-5.

[b] MOVES2014a corrected the NMOG/NMHC and VOC/NMHC values for APUs to use the pre-2007 values for 2007-2050 (instead of the 2007-2050 exhaust values as in MOVES2014), and corrected the MY 2007 extended idling values to use the 2007-2050 values (instead of the pre-2007 values).

$$VOC = NMHC \cdot \left[speciationConstant + \sum_{i=1}^{4}(oxySpeciation \cdot oxyMassFraction_i \cdot oxyVolume_i)\right] \quad \textbf{Equation 5}$$

Where:

i = one of four gasoline oxygenates: ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), or tert-amyl methyl ether (TAME).

SpeciationConstant = VOC/NMHC conversion factor when the gasoline has no oxygenate volume.

oxySpeciation = empirically derived value that adjusts the VOC/NMHC according to oxidation volume.

$oxyMassFraction_i$ = term used to convert from the oxygenate percentage by volume (vol percent) to the mass percentage of oxygen in the fuel(mass percent). volToWtPercentOxy is calculated using Equation 4 and the values provided in Table 3-2. Equation 5 assumes that the relationship between the oxySpeciation factor is linearly proportional to the mass fraction of oxygen in the fuel.

$oxyVolume_i$ = the percent volume of each gasoline oxygenate in the respective fuel.

The same data sources are used to derive the VOC/NMHC ratios as the NMOG/NMHC ratios presented earlier. The gasoline values are displayed in Table 3-5.

Table 3-5. Parameters used to calculate VOC/NMHC ratios for gasoline vehicle emissions

Fuel Subtype	Model Year Group	Process	speciationConstant	oxySpeciation
E0 to E10	1960-1974	Start and Running Exhaust	1.0239	0.0133
	1975-1986		0.9799	0.0133
	1987-1989		0.976	0.0133
	1990-1993		0.9787	0.0133
	1994-2000		0.9797	0.0133
	2001-2050	Start	0.9787	0.0068
		Running	0.9148	-0.0013
E15	1960-2050	Start	1.0162	0
		Running	0.9049	0
E20	1960-2050	Start	0.9233	0
		Running	1.0436	0
E70 to E100	1960-2000[a,c]	Start and Running	1.3981	0

[c] For 2001 and later model year gasoline vehicles fueled on E70-E100, the VOC emissions are set equal to VOC emissions from E10 vehicles, as discussed in the MOVES2014 fuel effects report.[32]

The diesel and CNG values are shown in Table 3-6. These were updated in MOVES2014 based on the data sources discussed in the NMOG section. As for NMHC, the diesel APUs use the 1960-2006 VOC/NMOG values for all model years[b].

Table 3-6. Parameters used to calculate VOC/NMHC ratios for diesel and CNG vehicle emissions

Fuel Type	Model Year Group	speciationConstant	oxySpeciation
Diesel	1960-2006	1.1243	0
	2007-2050	1.3058	0
CNG	1960-2003	1.6808	0
	2004 -2050	0.9471	0

3.4. NMOG and VOC Calculations for Evaporative, Refueling and Permeation Emissions

Since no significant methane, ethane, or acetone emissions are found in evaporative or permeation emissions, THC is equivalent to NMHC, and VOC is equivalent to NMOG and TOG for these emissions. Speciation factors are only needed to convert THC to NMOG to account for the mass of ethanol not measured by the FID. MOVES uses Equation 3 and Equation 5 with the parameters reported in Table 3-7.

THC to NMOG factors for vehicles with fuel ethanol content at or below 20 percent are unchanged from earlier versions of MOVES for fuel vapor venting, fuel leaks, and refueling evaporative emissions, and were derived from SPECIATE profiles 1301 and 1305. The speciation factors for E70-E100 were updated based on the analysis of the CRC E-80 program.[21]

Table 3-7. Gasoline Vehicle Evaporative THC to NMOG and VOC speciation factors

Engine Type	Fuel Subtype	Process	speciationConstant	oxySpeciation
Gasoline	<5% ethanol	Vapor Venting and Refueling Vapor Loss	1	0.0318
	E5 to E20		1	0.0318
	E70 to E100		1.511	0
Gasoline	<5% ethanol	Fuel Leaks and Refueling Spillage Loss	1	0.025
	E5 to E20		1	0.025
	E70 to E100		1.511	0

New permeation factors were developed for MOVES2014 for E0 to E10, E15, and E20 based on data from the CRC E-77 program.[22,23] The CRC E-77 program did not measure emissions for an E15 blend; therefore, it was interpolated from E10 and E20 profiles. For E70-E100, the speciation factor for permeation is identical to the factors for other evaporative processes (see Table 3-7), developed from CRC E-80 program. These factors are provided in Table 3-8.

Table 3-8 Gasoline Vehicle Permeation hydrocarbon THC to NMOG and VOC speciation factors

Engine Type	Fuel Subtype	Process	speciationConstant	oxySpeciation
Gasoline	E0 to E10	Permeation	1	0.036
Gasoline	E15	Permeation	1.1755	
Gasoline	E20	Permeation	1.2235	0
Gasoline	E70 to E100	Permeation	1.511	0

Currently, MOVES produces THC emissions from diesel vehicles for refueling spillage loss (processID 19), but not the other evaporative or refueling emission processes. The NMOG/NMHC and VOC/NMHC value for diesel spillage is set to 1, with no adjustment for oxygenate content, as shown in Table 3-9. These values are consistent with the chemical speciation measurements in SPECIATE profile 4547 'Diesel Headspace (Table 4-1), where no methane, ethane, acetone, formaldehyde, acetaldehyde, or ethanol were measured.

Table 3-9. Diesel Vehicle Refueling THC to NMOG and VOC speciation factors

Engine Type	Fuel Subtype	Process	speciationConstant	oxySpeciation
Diesel	Conventional Diesel and Biodiesel	Refueling Spillage Loss	1	0

3.5. Total Organic Gases Calculation

MOVES calculates Total Organic Gases (TOG) from NMOG by adding the methane emissions to NMOG as shown:

$$TOG = NMOG + Methane$$ **Equation 6**

4. Chemical Mechanism (CM) Speciation

4.1. Overview

MOVES2014b produces the output of the CM species of Total Organic Gases (TOG) in units of moles, for use by air-quality models. MOVES2014a was capable of producing chemical-mechanism species for two chemical mechanisms, CB05 and CB6. These have been updated in MOVES2014b. The update to CB05 is still called CB05. The update to CB6 is now called CB6CMAQ. A third mechanism, SAPRC07T, was added. Prior to MOVES2014, the mapping of MOVES output of individual organic species (e.g., benzene, 1,3-butadiene) and aggregates (e.g., TOG) into CM species was done outside MOVES by emission pre-processors to air quality models. Beginning with MOVES2014, this mapping is done inside MOVES. In this report, the mapping process is referred to as TOG speciation.

The component of TOG that remains after subtracting MOVES gaseous organic species is called residual TOG:

Residual TOG = TOG - MOVES gaseous organic species **Equation 7**

The MOVES gaseous organic species that are subtracted are referred to as "integrated species." Currently, we are integrating 16 MOVES species, listed in Table 2-1. The MOVES species we do not integrate are primarily the PAHs and the dioxins.

TOG speciation required for air quality models is different than PM speciation, due to the concept of chemical mechanisms. Chemical mechanisms (defined in the glossary) are used to simplify the thousands of individual organic compounds into a manageable set of CM species used for air quality modeling. The profiles used in this process, and the mapping of real species into CM species is discussed below. PM, on the other hand, is not mapped into CM species, but is split into various real species and some aggregated groups for use in air quality models.

4.2. Real Speciation Profiles

A real speciation profile is, in principle, a complete listing of all the real species and their quantities that make up an aggregate species such as TOG. Of course, the hundred or so compounds listed in these profiles are not a complete listing, which would likely include thousands of species. But they are the major species by mass and reactivity. Such a profile is produced by laboratory analysis of emissions. These are not CM speciation profiles and are independent of chemical mechanism. Table 4-1 summarizes the speciation profiles we are using in MOVES, together with the fuels, regulatory classes, and MOVES emission processes to which they apply. The emission processes associated with the MOVESProcessIDs are identified in Table 2-2. MOVES processes relevant for speciation profiles.

The source of all the profiles listed in Table 4-1 is SPECIATE 4.4. SPECIATE is the EPA's repository of volatile organic gas and particulate matter (PM) speciation profiles from air pollution sources.[24] The Speciate Database Project began at EPA in 1988; the current version, SPECIATE 4.4, was released in February 2014. In 2005, an EPA SPECIATE Workgroup was formed to assure inclusion of the most current data and to quality-assure the content.[25] The SPECIATE database contains a record of each profile including its referenced source, testing methods, a subjective rating of the quality of the data, and other detailed data that allow researchers to decide which profile is most suitable for model input. Table 4-2 lists the referenced sources of the real speciation profiles used in MOVES.

Table 4-1. Speciation profiles used for onroad TOG emissions[d]

Profile	Profile Description	Fuel	Affected Vehicles	MOVES ProcessID
1001	CNG Exhaust	CNG	All CNG Transit Buses	1,2,15,16
4547	Diesel Headspace	Diesel	All Diesel	11, 12,13,18,19
8753	E0 Evap	E0	All Gas	12,13,19
8754	E10 Evap	E10	All Gas	12,13,19
8756	Tier 2 E0 Exhaust	E0	2001+ LD Gas	1,2,15,16
8757	Tier 2 E10 Exhaust	E10	2001+ LD Gas	1,2,15,16
8758	Tier 2 E15 Exhaust[e]	E15, E20	All Gas	1,2,15,16
8766	E0 evap permeation	E0	All Gas	11
8769	E10 evap permeation	E10	All Gas	11
8770	E15 evap permeation	E15, E20	All Gas	11
8774	Pre-2007 MY HDD exhaust	Diesel	Pre-2007 HD Diesel	1,2,15,16,17,90
8774	Pre-2007 MY HDD exhaust	Diesel	All APU	91
8774	Pre-2007 MY HDD exhaust	Diesel	Pre-2007 LD Diesel	1,2,15,16
8775	2007+ MY HDD exhaust	Diesel	2007+ LD Diesel	1,2,15,16
8775	2007+ MY HDD exhaust	Diesel	2007+ HD Diesel	1,2,15,16,17,90
8855	Tier 2 E85 Exhaust	E85	All Ethanol	1,2,15,16
8869	E0 Headspace	E0	All Gas	18
8870	E10 Headspace	E10	All Gas	18
8871	E15 Headspace	E15, E20	All Gas	18
8872	E15 Evap	E15, E20	All Gas	12,13,19
8934	E85 Evap	E85	All Ethanol	11, 12,13,18,19
8750a	Pre-Tier 2 E0 exhaust	E0	Pre-2001 LD Gas	1,2,15,16
8750a	Pre-Tier 2 E0 exhaust	E0	All MC and non-LD Gas	1,2,15,16
8751a	Pre-Tier 2 E10 exhaust	RFG, E10	Pre-2001 LD Gas	1,2,15,16
8751a	Pre-Tier 2 E10 exhaust	RFG, E10	All MC and Non-LD Gas	1,2,15,16

[d] Appendix B Provides a complete mapping of the TOG speciation profiles to modelYearGroupID, processID, fuelSubTypeID, and regClassID.

[e] MOVES2014, as well as the MOVES2014 October release with CB6 installer, incorrectly assigned two speciation profiles (8751a and 8758) to start and running exhaust associated with pre-2001 MY gasoline vehicles and E15 or E20 fuels. In MOVES2014a, only speciation profile 8758 is assigned to this vehicle/process/fuel combination as shown in Table 4-1 and Table B-1. In MOVES2014 runs where this vehicle/process/fuel combination was assigned the incorrect speciation profiles, the CB05 and CB6 chemical mechanism emissions are incorrect.

Table 4-2. Data sources for the MOVES profiles

Profile ID	Profile Name	Source Data	Additional Documentation
1001	Internal Combustion Engine - Natural Gas	Oliver, W. R. and S. H. Peoples, Improvement of the Emission Inventory for Reactive Organic Gases and Oxides of Nitrogen in the South Coast Air Basin, Volumes I and II, Final Report (Prepared for California Air Resources Board), May 1985.	
4547	Gasoline Headspace Vapor - Circle K Diesel - adjusted for oxygenates	Internal data collection effort, Charles Lewis, U.S. EPA Office of Research and Development, with Ying Hsu, E.H. Pechan & Associates, Inc., personal communication (t), June 29, 2004.	SPECIATE 4.2. Speciation Database Development Documentation. Report No. EPA/600-R-09/038, U.S. EPA, June 2009. Available at: http://www.epa.gov/ttn/chief/software/speciate/
8750a	Gasoline Exhaust - Reformulated gasoline (pre-Tier 2)	Kansas City PM characterization Study. Final Report. EPA 420-R-08-009. U.S. EPA, April 2008. Available at: http://www.epa.gov/oms/emission-factors-research/index.htm.	Emission Profiles for EPA SPECIATE Database. EPA Contract No. EP-C-06-094. Environ Corporation, January 2008. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2710.
8751a	Gasoline Exhaust - E10 ethanol gasoline (pre-Tier 2)	Kansas City PM characterization Study. Final Report. EPA 420-R-08-009. U.S. EPA, April 2008. Available at: http://www.epa.gov/oms/emission-factors-research/index.htm.	Emission Profiles for EPA SPECIATE Database. EPA Contract No. EP-C-06-094. Environ Corporation, January 2008. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2710.
8753	Gasoline Vehicle - Evaporative emission - Reformulated gasoline	Auto/Oil Air Quality Improvement Research Program. Coordinating Research Council, 1990-1997. List of reports at: http://www.crcao.com/reports/auto-oil/default.htm	Emission Profiles for EPA SPECIATE Database. EPA Contract No. EP-C-06-094. Environ Corporation, January 2008. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2710.
8754	Gasoline Vehicle - Evaporative emission - E10 ethanol gasoline	Auto/Oil Air Quality Improvement Research Program. Coordinating Research Council, 1990-1997. List of reports at: http://www.crcao.com/reports/auto-oil/default.htm	Emission Profiles for EPA SPECIATE Database. EPA Contract No. EP-C-06-094. Environ Corporation, January 2008. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2710.
8756	Gasoline Exhaust - Tier 2 light-duty vehicles using 0% Ethanol - Composite Profile	Data Collected in EPAct Fuel Effects Study Pilot Phases 1 and 2. Memorandum to the Tier 3 Docket. U.S. EPA, 2013 Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135.	Exhaust Emission Profiles for EPA SPECIATE Database: Energy Policy Act (EPAct) Low-Level Ethanol Fuel Blends and Tier 2 Light-Duty Vehicles. EPA Report No. EPA-420-R-09-002. U.S. EPA, 2009. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2711.
8757	Gasoline Exhaust - Tier 2 light-duty vehicles using 10% Ethanol - Composite Profile	Data Collected in EPAct Fuel Effects Study Pilot Phases 1 and 2. Memorandum to the Tier 3 Docket. U.S. EPA, 2013 Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135.	Exhaust Emission Profiles for EPA SPECIATE Database: Energy Policy Act (EPAct) Low-Level Ethanol Fuel Blends and Tier 2 Light-Duty Vehicles. EPA Report No. EPA-420-R-09-002. U.S. EPA, 2009. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2711.
8758	Gasoline Exhaust - Tier 2 light-duty vehicles using 15% Ethanol - Composite Profile	Data Collected in EPAct Fuel Effects Study Pilot Phases 1 and 2. Memorandum to the Tier 3 Docket. U.S. EPA, 2013 Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135.	Exhaust Emission Profiles for EPA SPECIATE Database: Energy Policy Act (EPAct) Low-Level Ethanol Fuel Blends and Tier 2 Light-Duty Vehicles. EPA Report No. EPA-420-R-09-002. U.S. EPA, 2009. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2005-0161, Document ID: EPA-HQ-OAR-2005-0161-2711.

Profile ID	Profile Name	Source Data	Additional Documentation
8766	Diurnal Permeation Evaporative Emissions from Gasoline Vehicles using 0% Ethanol - Combined - Composite Profile	Evaporative Emissions from In-use Vehicles: Test Fleet Expansion. CRC E-77-2b. SWRI Project No. 03.14936.05. Final report. Available at: http://www.epa.gov/otaq/emission-factors-research/	
8769	Diurnal Permeation Evaporative Emissions from Gasoline Vehicles using 10% Ethanol - Combined - Composite Profile	Evaporative Emissions from In-use Vehicles: Test Fleet Expansion. CRC E-77-2b. SWRI Project No. 03.14936.05. Final report. Available at: http://www.epa.gov/otaq/emission-factors-research/	
8770	Diurnal Permeation Evaporative Emissions from Gasoline Vehicles using 15% Ethanol - Combined	Evaporative Emissions from In-use Vehicles: Test Fleet Expansion. CRC E-77-2b. SWRI Project No. 03.14936.05. Final report. Available at: http://www.epa.gov/otaq/emission-factors-research/	
8774	Diesel Exhaust Emissions from Pre-2007 Model Year Heavy-Duty Diesel Trucks	Heavy-duty Vehicle Chassis Dynamometer Testing for Emissions Inventory, Air Quality Modeling, Source Appointment and Air Toxics Emissions Inventory. CRC Project No. E-55/E-59, Phase II Final Report. Coordinating Research Council, July 2005. Available at: http://www.crcao.com/publications/emissions/index.html	
8775	Diesel Exhaust Emissions from 2007 Model Year Heavy-Duty Diesel Engines with Controls	Phase 1 of the Advanced Collaborative Emissions Study. Coordinating Research Council, July 2009. Available at: http://www.crcao.com/publications/emissions/index.html	
8855	Gasoline Exhaust - Tier 2 light-duty vehicles using 85% Ethanol - Composite Profile	EPAct/V2/E-89: Assessing the Effect of Five Gasoline Properties on Exhaust Emissions from Light-Duty Vehicles Certified to Tier-2 Standards:–Final Report on Program Designand Data Collection. EPA-420-R-13-004. U.S. EPA, April 2013. Available at: http://www.epa.gov/otaq/models/moves/epact.htm.	
8869	Gasoline Headspace Vapor - 0% Ethanol (E0) Combined - EPAct/V2/E-89 Program	Hydrocarbon Composition of Gasoline Vapor Emissions from Enclosed Fuel Tanks, Report No. 420-R-11-018. U.S. EPA, December 2011. Available at: http://www.regulations.gov, Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0027.	Mobile Source Hydrocarbon Speciation Profiles for the Tier 3 Rule NPRM and Anti-backsliding Study Air Quality Modeling. Memorandum to the Docket. U.S. EPA, 2013. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0089.

Profile ID	Profile Name	Source Data	Additional Documentation
8870	Gasoline Headspace Vapor - 10% Ethanol (E10) Combined - EPAct/V2/E-89 Program	Hydrocarbon Composition of Gasoline Vapor Emissions from Enclosed Fuel Tanks, Report No. 420-R-11-018. U.S. EPA, December 2011. Available at: http://www.regulations.gov, Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0027.	Mobile Source Hydrocarbon Speciation Profiles for the Tier 3 Rule NPRM and Anti-backsliding Study Air Quality Modeling. Memorandum to the Docket. U.S. EPA, 2013. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0089.
8871	Gasoline Headspace Vapor - 15% Ethanol (E15) Combined - EPAct/V2/E-89 Program	Hydrocarbon Composition of Gasoline Vapor Emissions from Enclosed Fuel Tanks, Report No. 420-R-11-018. U.S. EPA, December 2011. Available at: http://www.regulations.gov, Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0027.	Mobile Source Hydrocarbon Speciation Profiles for the Tier 3 Rule NPRM and Anti-backsliding Study Air Quality Modeling. Memorandum to the Docket. U.S. EPA, 2013. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0089.
8872	Gasoline Vehicle - Evaporative emission - E15 ethanol gasoline - Calculated	Auto/Oil Air Quality Improvement Research Program. Coordinating Research Council, 1990-1997. List of reports at: http://www.crcao.com/reports/auto-oil/default.htm EPAct/V2/E-89: Assessing the Effect of Five Gasoline Properties on Exhaust Emissions from Light-Duty Vehicles Certified to Tier-2 Standards: Final Report on Program Design and Data Collection. EPA-420-R-13-004. U.S. EPA, April 2013. Available at: http://www.epa.gov/otaq/models/moves/epact.htm.	Mobile Source Hydrocarbon Speciation Profiles for the Tier 3 Rule NPRM and Anti-backsliding Study Air Quality Modeling. Memorandum to the Docket. U.S. EPA, 2013. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0089.
8934	Evaporative Emissions from Flexible-Fuel Gasoline Vehicles using 85% Ethanol	Exhaust and Evaporative Emissions Testing of Flexible-Fuel Vehicles. Final report. CRC Report CRC-E-80. Coordinating Research Council, Inc. August 2011. Report and program data available at http://www.crcao.org/publications/emissions/index.html	

4.3. Mapping of Real Species to Chemical Mechanism Species and of Residual TOG to Chemical Mechanism Speciation Profiles

The mapping of real species to CM species is mechanism-specific. Each chemical mechanism maps real organic gas species to one or more CM species. Air quality models use these CM species to model atmospheric chemistry. CB05, CB6CMAQ, and SAPRC07T are three widely used chemical mechanisms for air quality modeling that are incorporated into MOVES2014b. Emission estimates for species calculated directly by MOVES are based on more detailed and accurate information than those estimated using the TOG speciation profiles; therefore, we use a process called "integration" to subtract these species from the TOG speciation profiles. In MOVES2014b, the integration process removes the 16 pollutants in Table 2-1 from the TOG speciation profiles to leave residual-TOG (often called NONHAPTOG) speciation profiles, which are renormalized without the integrated species. The mapping of both integrated species and NONHAPTOG to chemical mechanism species is initially performed outside of MOVES by a program called the Speciation Tool.[26] This mapping is then incorporated into a table in the MOVES2014b default database that maps both integrated species and NONHAPTOG to chemical mechanism species during MOVES runs. After MOVES performs this mapping, all the occurrences of each CM species are summed to produce the final output of chemical mechanism species.

Regular MOVES output is unchanged. All chemical mechanism species are in units of moles. Because this process is table driven, MOVES is capable of providing CM species for multiple chemical mechanisms. In MOVES2014b, the CB05, CB6CMAQ, and SAPRC07T mechanisms are implemented. Figure 1 is a diagram of the process of TOG speciation for air quality modeling.

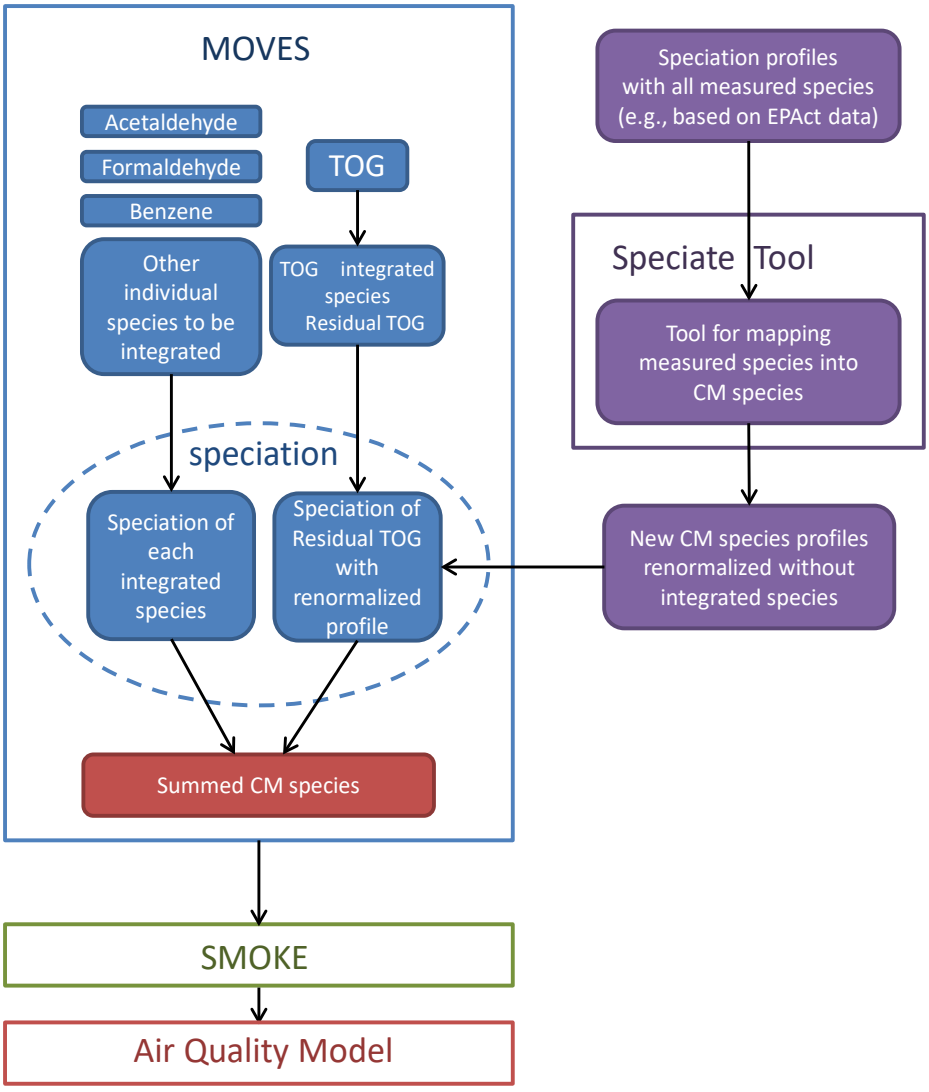

Figure 1. Diagram of the process of TOG speciation for air quality modeling as it occurs with MOVES2014

5. $PM_{2.5}$ Speciation

5.1. Overview

Modeling $PM_{2.5}$ in CMAQ does not use simplifying chemical mechanisms, and the $PM_{2.5}$ species are input directly into the model. CMAQv5.0, which uses the CMAQ Aerosol Module, version 6, or "AE6", requires 18 $PM_{2.5}$ species as outlined in Table 5-1[27]. Theses PM species are compatible with previous versions of CMAQ and with the Comprehensive Air Quality Model with Extensions (CAMx) as shown in Table 5-1, and will be beneficial to air-quality agencies and researchers who use different air quality models.

Table 5-1. $PM_{2.5}$ species required in CMAQv5.0 (this version uses the CMAQ Aerosol Module, version 6, or "AE6")[27] , CMAQv4.7.1 (this version uses the CMAQ Aerosol Module, version 5, or "AE5"), and CAMx5.4[28]

$PM_{2.5}$ Species	CMAQv5.0 Species Name	Required in CMAQv4.7.1	Required in CAMx5.4
Primary organic carbon	POC	x	x
Elemental carbon	PEC	x	x
Sulfate	PSO4	x	x
Nitrate	PNO3	x	x
Ammonium	PNH4	x	x
Non-carbon organic matter	PNCOM		x
Iron	PFE		
Aluminum	PAL		
Silicon	PSI		
Titanium	PTI		
Calcium	PCA		
Magnesium	PMG		
Potassium	PK		
Manganese	PMN		
Sodium	PNA		x
Chloride	PCL		x
Particulate water	PH2O		x
Primary unspeciated $PM_{2.5}$[f]	PMOTHR	x	x

MOVES2014 is designed to produce all $PM_{2.5}$ species required by CMAQv5.0. Previous versions of MOVES (2010b and earlier) produced $PM_{2.5}$ in the form of three $PM_{2.5}$ species: elemental carbon (EC), organic carbon (OC) and sulfate (SO_4). Substantial post-processing of MOVES $PM_{2.5}$ outputs was needed to provide PM emissions inventories that could be transformed by SMOKE into ready-inputs of speciated $PM_{2.5}$ for CMAQ. For example, MOVES2010b did not output nitrate, ammonium, and metals. These compounds were assumed

[f] The definition of the unspeciated $PM_{2.5}$ depends on the set of identified $PM_{2.5}$ species in each air quality model.

to be included in the OC emission rates of $PM_{2.5}$. This division required post-processing the MOVES2010b OC emissions using $PM_{2.5}$ speciation profiles, and created differences between OC as defined by MOVES2010b and the post-processed OC used for air quality modeling. MOVES2014 removes the distinction by defining OC consistently with air quality models as defined in the glossary.

5.2. Steps

Figure 2 and Figure 3 provide an overview of the algorithm used to calculate speciated and total exhaust PM emission rates in MOVES2014. The steps used to calculate $PM_{2.5}$ emissions and $PM_{2.5}$ speciation are outlined in nine steps below. Additional details are provided in the MOVES2014 Software Design Reference Manual[29]. Steps 1 – 4 are outlined in Figure 2.

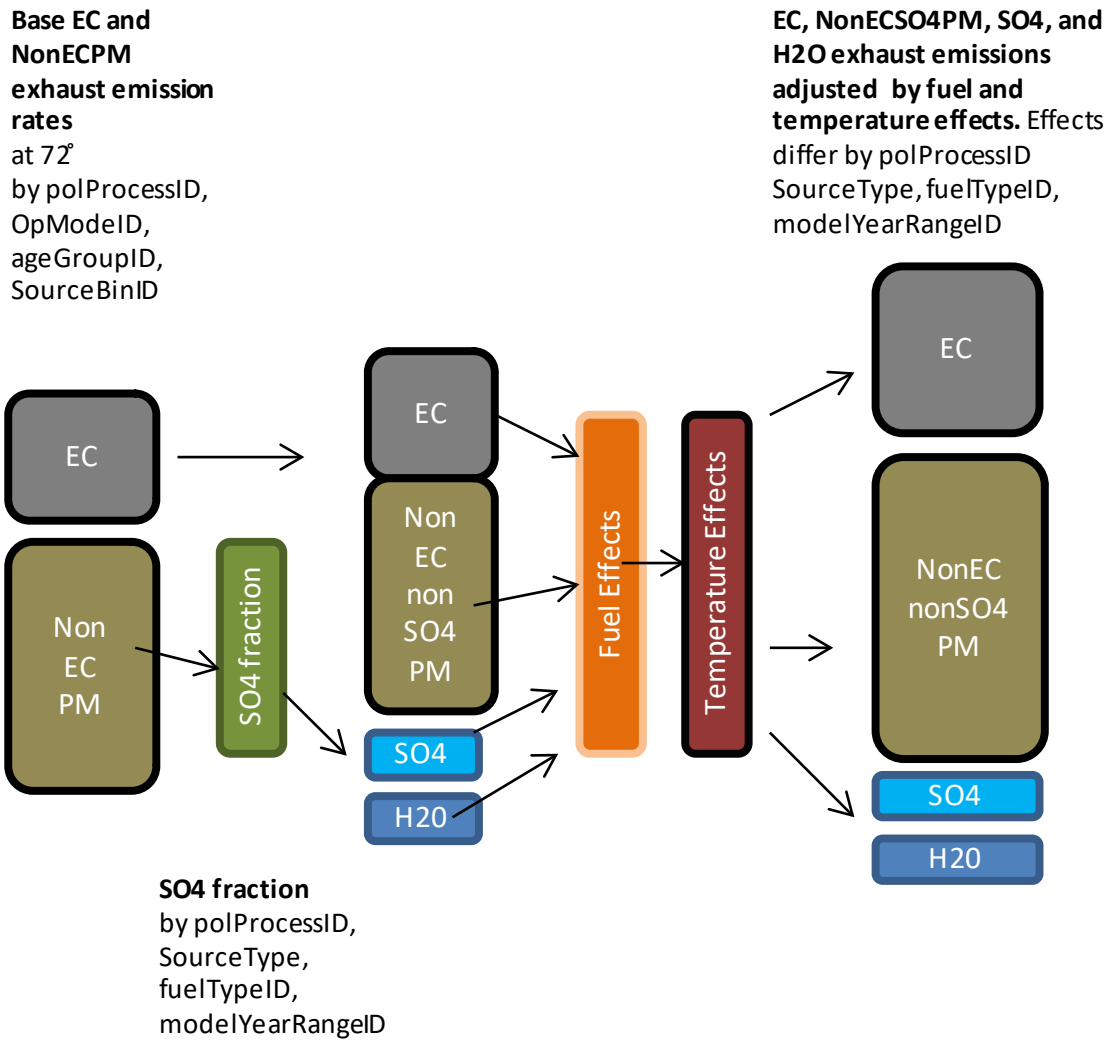

Figure 2. Flow Chart of Calculation of the Intermediate $PM_{2.5}$ Emission Rates

Step 1. MOVES2014 stores $PM_{2.5}$ exhaust emission rates by pollutant process (start, running, extended idle), operating mode, sourcebin (fuelType, engine technology, regulatory class, model year), and vehicle age. MOVES2014 stores base exhaust rates for $PM_{2.5}$ divided into two primary components (EC and nonECPM). The base rates are stored by EC and nonECPM so that the $EC/PM_{2.5}$ ratio can vary across operating modes. EC is formed within the engine due to pyrolysis of fuel droplets in the engine, and researchers have determined that EC emissions from conventional diesel engines are strongly correlated with the air-fuel ratio[30]. Within MOVES, modal EC/PM ratios were developed as documented in the Exhaust Emission Rates for Heavy-Duty On-road Vehicles in MOVES2014 Report[30]. Modal $EC/PM_{2.5}$ ratios have not been developed for other vehicle types (gasoline, CNG, ethanol, and modern diesel), so the EC and NonECPM emission rates for these soucetypes and fuels have a constant ratio across operating modes.

Step 2. MOVES2014 calculates sulfate and particulate water emissions from the nonECPM using values obtained from the $PM_{2.5}$ speciation profiles. SO4 and H2O (particulate water) emissions are calculated as a function of the nonECPM rates using the fuel sulfur level for the model run, the fuel sulfur level used to develop the base PM emission rates, and the fraction of sulfate coming from the fuel in the base PM emission rates, as described in the sulfate calculator.[32] The remaining nonECPM is renamed nonECnonSO4PM. This intermediate species contains organic matter, elements, ions, and the unspeciated portion of $PM_{2.5}$.

Step 3. The intermediate PM species are adjusted for temperature effects such as inefficient oxidation of emissions at cool catalyst temperatures and additional fuel needed to start an engine at cold temperatures. The temperature effects can differ by intermediate species, process (e.g. start exhaust, running exhaust, extended idle), model year groups, and fuel type. Currently, temperature effects only apply to gasoline and ethanol-blend fueled vehicles. Currently, the EC, nonECnonSO4PM, SO4, and H2O emissions are each adjusted using the same temperature adjustments, because our data does not support individual temperature adjustments.[37] The temperature effects are documented in the report: Emission Adjustments for Temperature, Humidity, Air Conditioning and Inspection and Maintenance for On-road Vehicles in MOVES2014.[31]

Step 4. MOVES2014 adjusts the intermediate species (EC and NonECnonSO4PM) according to fuel effects. EC and nonECnonSO4 are adjusted according to fuel properties depending on the applicable model (e.g. EPAct model for 2001 and later light-duty gasoline). The fuel adjustments and calculators are described in the Fuel Effects Report.[32]

Steps 5 – 8 are outlined in Figure 3.

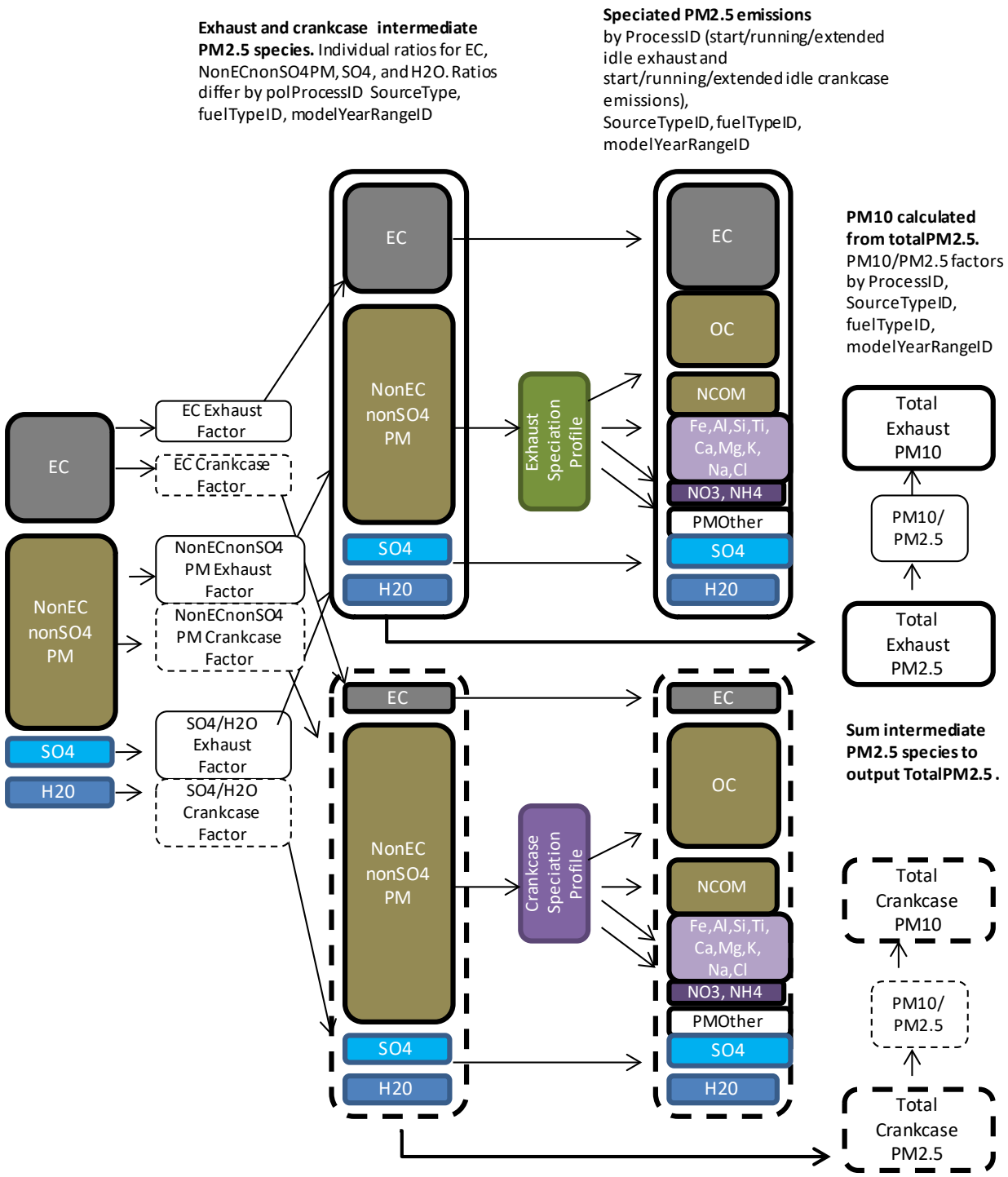

Figure 3. Flow Chart of Calculation of exhaust and crankcase $PM_{2.5}$ and PM_{10} emission rates, and $PM_{2.5}$ exhaust and crankcase speciation

Step 5. Exhaust and crankcase emissions are calculated from the intermediate exhaust $PM_{2.5}$ species (EC, NonECnonSO4PM, SO4, and H2O), after the intermediate exhaust species have been adjusted for fuel effects and temperature effects. The exhaust and crankcase emissions are calculated from the intermediate exhaust rates with exhaust and crankcase ratios that can vary

according to pollutant, process, source type, fuel type, and model year range as shown in Table 5-2.

For 2007 and later diesel engines, crankcase emissions are measured with exhaust emissions in the certification data. The exhaust and crankcase emission ratios are used to split the PM rates into exhaust and crankcase emissions. For 2007-and-later diesel, the exhaust and crankcase ratios sum to one for each PM subspecies.

For other vehicles types (pre-2007 diesel, gasoline, CNG vehicles), this step accounts for the PM crankcase emissions that are not measured in the exhaust emission rates (i.e., the exhaust and crankcase ratios sum to greater than one for each PM subspecies). The exhaust emissions remain constant in this step.

The sources of the diesel crankcase emission factors are documented in the heavy-duty exhaust emissions rates report[30] and the gasoline crankcase emission factors are documented in the light-duty exhaust emissions rates report[33]. The factors are applied by intermediate subspecies, to account for differences in $PM_{2.5}$ speciation between crankcase and tailpipe particulate matter emissions. MOVES2014 models different PM composition between exhaust and crankcase emissions for pre-2007 conventional diesel, using the exhaust and crankcase ratios as shown in Table 5-2.

Table 5-2. Exhaust and Crankcase Ratios by Pollutant, Process, Model Year Group, and Fuel Type, and Source Type

		Motor-cycles	1960-1968 Gasoline, 1960-2000 Light-Duty Diesel	1969-2050 Gasoline/CNG, 2000-2050 Light-Duty Diesel	1960-2006 Heavy-Duty Diesel			2007-2050 Heavy-Duty Diesel
Pollutant		All	All	All	Start	Running	Extended Idle	All
EC	Exhaust	1	1	1	1	1	1	0.62
nonECnonSO4-PM		1	1	1	1	1	1	0.62
SO4		1	1	1	1	1	1	0.62
H2O		1	1	1	1	1	1	0.62
EC	Crankcase	0	0.2	0.008	0.009	0.004	0.012	0.38
nonECnonSO4-PM		0	0.2	0.008	0.295	0.954	0.268	0.38
SO4		0	0.2	0.008	0.295	0.954	0.268	0.38
H2O		0	0.2	0.008	0.295	0.954	0.268	0.38

Step 6. The exhaust intermediate species and the crankcase intermediate species are summed to calculate primary exhaust $PM_{2.5}$ emissions. The intermediate species are used instead of the fully speciated $PM_{2.5}$ emissions to save computational time during MOVES runs.

Step 7. MOVES2014 calculates primary exhaust and crankcase PM_{10} emissions from the primary $PM_{2.5}$ emissions using $PM_{10}/PM_{2.5}$ ratios. The MOVES2014 $PM_{10}/PM_{2.5}$ ratio used for primary

exhaust and crankcase emissions are listed in Table 5-3. MOVES2014 has the capability to apply separate ratios by source type, emission process, and model year. At present, a single value of the $PM_{10}/PM_{2.5}$ ratio is used for all source types, emission processes, and model years for primary exhaust and crankcase emissions. No speciation is conducted within MOVES2014 for PM_{10} emissions, because it is not needed for air quality modeling purposes[g,34]. The derivation of the $PM_{10}/PM_{2.5}$ ratio is presented in Appendix D.

Table 5-3 $PM_{10}/PM_{2.5}$ Ratios for Primary Exhaust and Crankcase Emissions

	$PM_{10}/PM_{2.5}$
gasoline	1.130
diesel	1.087

Step 8. MOVES2014 calculates speciated $PM_{2.5}$ emissions, by applying speciation profiles to the adjusted nonECnonSO4 fraction to calculate the individual $PM_{2.5}$ species. The data sources and documentation for the $PM_{2.5}$ profiles are included in Table 5-4. Each of the $PM_{2.5}$ profiles for use in MOVES2014 was created or updated recently, thus we included documentation of their development in Appendix C.

Table 5-4. MOVES2014 $PM_{2.5}$ Speciation Profiles

Profile ID	Profile Name	Profile Source	Source Data
8992	Light-duty Gasoline Exhaust - Start	SPECIATE 4.4	Kansas City PM characterization Study. Final Report. EPA 420-R-08-009. U.S. EPA, April 2008. Available at: http://www.epa.gov/oms/emission-factors-research/index.htm.
8993	Light-duty Gasoline Exhaust- Hot Stabilized Running	SPECIATE 4.4	Kansas City PM characterization Study. Final Report. EPA 420-R-08-009. U.S. EPA, April 2008. Available at: http://www.epa.gov/oms/emission-factors-research/index.htm.
8994	Conventional HDD - Idle	SPECIATE 4.4	Clark, N.N. and Gautam, M. HEAVY-DUTY Vehicle Chassis Dynamometer Testing for Emissions Inventory, Air Quality Modeling, Source Apportionment and Air Toxics Emissions Inventory. August 2007. CRC Report. No. E55/59
8995	Conventional HDD – Hot Stabilized Running	SPECIATE 4.4	Clark, N.N. and Gautam, M. HEAVY-DUTY Vehicle Chassis Dynamometer Testing for Emissions Inventory, Air Quality Modeling, Source Apportionment and Air Toxics Emissions Inventory. August 2007. CRC Report. No. E55/59
8996	2007 and Newer Diesel Exhaust Composite	SPECIATE 4.4	Khalek, I. A.; Bougher, T. L; Merrit, P. M.; Phase 1 of the Advanced Collaborative Emissions Study. CRC Report: ACES Phase 1, June 2009.
95219	CNG transit bus exhaust from a lean-burn engine - no aftertreatment	Next release of SPECIATE	Okamoto, R. A.; Kado, N. Y.; Ayala, A.; Gebel, M.; Rieger, P.; Kuzmicky, P. A.; Kobayashi, R.; Chemical and Bioassay Analyses of Emissions from Two CNG Buses with Oxidation Catalyst. http://www.arb.ca.gov/research/veh-emissions/cng-diesel/cng-diesel.htm.
95220	CNG transit bus exhaust from a lean-burn engine – oxidation catalyst	Next release of SPECIATE	Okamoto, R. A.; Kado, N. Y.; Ayala, A.; Gebel, M.; Rieger, P.; Kuzmicky, P. A.; Kobayashi, R.; Chemical and Bioassay Analyses of Emissions from Two CNG Buses with Oxidation Catalyst. http://www.arb.ca.gov/research/veh-emissions/cng-diesel/cng-diesel.htm.

[g] Within CMAQv5.0, the US EPA assumes a single speciation profile for all anthropogenic coarse PM[34].

The $PM_{2.5}$ profiles used for the applicable source type, fuel, pollutant process, and model year ranges are shown in Table 5-5.

Table 5-5. Application of MOVES2014 $PM_{2.5}$ Speciation Profiles

Profile ID	Description	Fuel	Affected Vehicles	MOVES ProcessID
8992	Light-duty Gasoline Exhaust - Start	All gasoline vehicles (E0 to E85)	All model years	2,16
8993	Light-duty Gasoline Exhaust- Hot Stabilized Running	All gasoline vehicles (E0 to E85)	All model years	1,15
8994	Conventional HDD - Idle	Diesel	Pre-2007 and all MY auxiliary power units	2,16,17,90,91
8995	Conventional HDD – Hot Stabilized Running	Diesel	Pre-2007	1,15
8996	2007 and Newer Diesel Exhaust Composite	Diesel	2007+	1,2,15,16,17,90
95219	CNG transit bus exhaust from a lean-burn engine - no aftertreatment	CNG	pre-2002 transit buses	1,2,15,16,17,90
95220	CNG transit bus exhaust from a lean-burn engine – oxidation catalyst	CNG	2002+ transit buses	1,2,15,16,17,90

MOVES2014 uses two light-duty gasoline profiles to characterize $PM_{2.5}$ emissions from all gasoline vehicles, including motorcycles, light-duty passenger cars and trucks, and medium and heavy-duty gasoline trucks and buses.

The pre-2007 diesel profiles are used to represent all pre-2007 on-highway diesel vehicles in MOVES, including light-duty passenger cars and trucks, medium, and heavy-duty trucks, and diesel buses. Tailpipe exhaust and crankcase nonECnonSO4 emissions emitted during extended idle and start are speciated using the Idle Profile (8994). Tailpipe exhaust and crankcase nonECnonSO4emissions emitted during running operation are speciated using the running profile (8995). In addition, the idle profile (8994) is used to characterize nonECnonSO4emissions from diesel-powered auxiliary power units used on heavy-duty diesel trucks.

The ACES Phase 1 profile (8996) is used for all 2007-and-later diesel sources, including light-duty passenger cars and trucks, medium and heavy-duty trucks and diesel buses. The ACES Phase 1 16-hour cycle is used to develop the profile, which includes both exhaust and crankcase emissions, as well as start, extended idle and running emission processes. For this reason, the composite profile is also used to speciate all emission processes for 2007-and-later diesel engines.

The CNG compression ignition profile is applied to the pre-2002 model CNG transit buses, and the CNG profile with oxidation catalyst profile is applied to the 2002+ model year CNG transit buses. This technology is determined to be most representative of the available $PM_{2.5}$ speciation data according to the analysis conducted in the heavy-duty vehicle emissions rate report[30].

Step 9. (Not shown in Figure 2 or 3). MOVES2014 calculates additional particulate-phase species, required for the National Emission Inventory (NEI) and National Air Toxics Assessment (NATA). Listed in Table 5-6, these include: manganese, nickel, chromium, arsenic, and particulate mercury. The metals are emitted in exhaust as $PM_{2.5}$, but are calculated with a separate calculator than the other $PM_{2.5}$ species. The emission rates for these metals are not chained from NonECSO4PM, but are provided with their own mass/distance rates as documented in the Air Toxic Emissions Report[4]. The mass of these compounds is not used in the summation to calculate $PM_{2.5}$ due to the very small mass, but they are important $PM_{2.5}$ exhaust species from a health effects perspective. Of the toxic metals, CMAQv5.0 only requires manganese as a required $PM_{2.5}$ species. By default, MOVES2014 calculates manganese emission rates when the user requests $PM_{2.5}$ speciation. Chromium, nickel, arsenic, and particulate mercury emission rates are produced when requested by the user.

Table 5-6. Metal Air Toxics produced by MOVES2014

Pollutant
Chromium 6+
Manganese
Nickel
Particulate Hg
Arsenic

Appendix A Methods used to derive NMOG/NMHC and VOC/NMHC parameters

A.1 Background

In MOVES, the base organic gas emission rates are in terms of total hydrocarbon emissions (THC). THC emissions are operationally defined by a FID. Other measures of organic gas emissions include nonmethane hydrocarbon (NMHC) emissions, non-methane organic gas (NMOG) emissions, volatile organic gas emissions (VOC), and total organic gas emissions (TOG). Definitions for each of these emissions are provided in the glossary in the main chapter. NMHC, NMOG, VOC, and TOG are referred to as 'chained pollutants' because we calculate their emissions based on the emissions of THC and other variables. Two important inputs to these calculations are the NMOG/NMHC ratio and the VOC/NMHC ratio. The sections below explain how these ratios are used and how they were derived.

A.2 NMOG/NMHC Method Description

NMOG emissions are calculated from NMHC emissions using Equation 3, provided below.

$$NMOG = NMHC \cdot \left[speciationConstant + \sum_{i=1}^{4}(oxySpeciation \cdot oxyMassFraction_i \cdot oxyVolume_i)\right] \quad \textbf{Equation 3}$$

Where:

i = one of four gasoline oxygenates: ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), or tert-amyl methyl ether (TAME).

SpeciationConstant =the NMOG/NMHC conversion factor when the gasoline has no oxygenate volume.

oxySpeciation = an empirically derived value that adjusts the NMOG/NMHC according to oxidation volume.

$oxyMassFraction_i$ = the mass fraction of oxygen within each of the gasoline oxygenates. The oxygen mass fraction is included in Equation 3 to adjust the oxySpeciation factor relative to the mass fraction of oxygen in the fuel. Due to limited data, we assume that the oxySpeciation relationship is linearly proportional to the oxygen content of the fuel oxygenate.

$oxyVolume_i$ = the percent volume of each gasoline oxygenate in the respective fuel.

Two methods were used to calculating the SpeciationConstants and oxySpeciation constants for Equation 3. The formulation of Equation 3 is generic enough to use ratios calculated using either methods. For fuel with similar fuel properties, the two methods give equivalent results.

A.2.1 Method 1

The first method is documented in a technical report used to develop VOC emission inventories for Mobile4.1.[14] This method was used in subsequent versions of MOBILE and MOVES. It is used to derive the NMOG/NMHC ratio for all light-duty gasoline vehicles, and diesel vehicles in MOVES. This method is based on the relative carbon fraction within each species. This method calculates the measured mass per carbon molecule by the FID (as NMHC in the denominator), and compares it to the true mass per carbon molecule of the exhaust (calculated as NMOG in the nominator). The equation form is shown below. It uses measurements of three oxygenated species: formaldehyde (HCHO), acetaldehyde (C2H4O), and ethanol (C2H5OH), and all other organic emissions are classified as NMHC.

The equation form of this method is below:

$$\frac{NMOG}{NMHC_{FID}} = \frac{(CF_{HCHO}\,MPC_{HCHO}) + (CF_{acetald}\,MPC_{acetald}) + (CF_{EtOH}\,MPC_{EtOH}) + (CF_{NMHC}MPC_{NMHC})}{[(CF_{acetald}\,FID_{acetald}) + (CF_{EtOH}\,FID_{EtOH}) + (CF_{NMHC}FID_{NMHC})] \times MPC_{NMHC}} \qquad \textbf{Equation 8}$$

Where:

CF = carbon fraction

MPC = mass per carbon

FID_X = FID response factor

As documented in the Mobile4.1 technical memorandum[14] describing this method, the assumed values for the mass per carbon, and the FID response factors are:

Table A-1. Mass per Carbon and FID response factors

Compound	Mass per carbon (MPC) (g/gC)	FID response factor
Gasoline Exhaust HC	13.8758	1.0
Formaldehyde	30.0264	0
Acetaldehyde	22.0267	0.50
Ethanol	23.0347	0.80
MTBE	17.6301	0.90

For Tier 2 vehicles, the original values from MOBILE4.1 were used, with the exception that the FID response for ethanol was updated with analysis done at Southwest Research Institute for the EPAct test program[35] using a FID response of 0.74, and mass/carbon of 23.0347.

This method was used for the development of the NMOG/NMHC ratios for per-Tier 2 gasoline vehicles, and pre and post-2007 diesel vehicles in MOVES2014.

A.2.2 Method 2

The second method used to develop NMOG/NMHC parameters is the measurement method outlined in the Code of Federal Regulations[36]. Rather than using relative concentrations of each species, this method uses the absolute concentrations to calculate NMOG/NMHC. Using the same notation as the federal register, the mass of NMOG is calculated from the mass of NMHC, the important oxygenated species, the FID response of the oxygenated species, and the density of each of the species, as shown in Equation 9 (Equation 1066.635-1 in the Federal Register):

$$m_{\text{NMOG}} = m_{\text{NMHC}} - \rho_{\text{NMHC}} \cdot \sum_{i=1}^{N} \frac{m_{\text{OHCi}}}{\rho_{\text{OHCi}}} \cdot RF_{\text{OHCi[THC-FID]}} + \sum_{i=1}^{N} m_{\text{OHCi}} \qquad \textbf{Equation 9}$$

Where:

m_{NMOG} = the sum of the mass of NMOG in the exhaust.

m_{NMHC} = the mass of NMHC and all oxygenated hydrocarbons (OHCs) in the exhaust, as determined using Eq. 1066.605-1. Calculate NMHC mass based on ρ_{NMHC}.

ρ_{NMHC} = the effective C_1-equivalent density of NMHC as specified in §1066.1005(f):.

m_{OHCi} = the mass of oxygenated species *i* in the exhaust calculated using Eq. 1066.605-1.

ρ_{OCHi} = the C_1-equivalent density of oxygenated species *i*.

$RF_{\text{OHCi[THC-FID]}}$ = The response factor of a THC-FID to oxygenated species *i* relative to propane on a C_1-equivalent basis as determined in 40 CFR 1065.845.

In this method, the NMOG is estimated from the NMHC. The NMOG/ NMHC ratio is then calculated by dividing the estimated NMOG from the NMHC measurements. This method is used to calculate the NMOG/NMHC ratio for CNG vehicles as documented in the Exhaust Emission Rates for Heavy-duty On-Road Vehicles in MOVES2014 Report.[30]

A.2.3 Comparison of the Two Methods

The first method is based on the relative carbon mass fraction of each species, while the second method is based on the absolute mass of each species. Because both methods are used to supply NMOG/NMHC ratios in MOVES2014, we applied both methods to demonstrate that they provide consistent NMOG/NMHC ratios. We used summary data reported for LDGV (3-way) catalysts in the MOBILE4.1 documentation[14], shown in Table A-2 below.

Table A-2. Mass fraction, mass/carbon, and carbon fraction of four components of 3-way catalyst exhaust

	Mass fraction	Mass/carbon	Carbon fraction
Ethane	0.0350	1.2518	0.3913
Formaldehyde	0.0119	30.0264	0.0055
Acetaldehyde	0.0056	22.0267	0.0036
Gasoline NMHC	0.9825	13.8758	0.9909

Example, Method 1:

$$\frac{NMOG}{NMHC} = \frac{(0.0056 \times 30.0264) + (0.0036 \times 22.0267) + (0.9909 \times 13.8758)}{[(0.0036 \times 0.5) + (0 \times 0.8) + (0.9909 \times 1)] \times 13.8758}$$

$$\frac{NMOG}{NMHC} = \frac{13.9940}{13.7742} = 1.01599$$

Example, Method 2:

Assume 0.9825 grams of NMOG, 0.0119 grams of Formaldehyde, and 0.0056 grams of Acetaldehyde, to be equivalent masses with the relative mass fractions in Table A-2.

$$\frac{NMOG}{NMHC} = \frac{0.9825 - 576.816 \times \left[\left(\frac{0.0119}{1248.21}\right) \times 0 + \left(\frac{0.0056}{915.658}\right) \times 0.5\right] + 0.119 + 0.0056}{0.9825}$$

$$\frac{NMOG}{NMHC} = \frac{0.9982}{0.9825} = 1.01602$$

As shown, the two methods yield the same NMOG/NMHC fractions to five significant figures. The comparability of the methods depends on the exhaust composition of the fuels, and this comparison is not comprehensive. However, considering that different assumptions were used regarding the carbon fraction/density of the NMHC, we believe the agreement of the methods to be well within the uncertainty of the emission measurements used as input into MOVES. As such, we have used both methods in MOVES for developing NMOG/NMHC ratios.

A.3 VOC/NMHC Method Description

Volatile Organic Compounds (VOC) are defined as the reactive organic gases that contribute to ozone formation. For MOVES, VOCs are defined as NMOG minus ethane and acetone. Within MOVES, VOC emissions are calculated from NMHC emissions using Equation 5, provided below.

$$VOC = NMHC \cdot \left[speciationConstant + \sum_{i=1}^{4}(oxySpeciation \cdot oxyMassFraction_i \cdot oxyVolume_i)\right] \quad \textbf{Equation 5}$$

Where:

i = one of four gasoline oxygenates: ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), or tert-amyl methyl ether (TAME).

SpeciationConstant = VOC/NMHC conversion factor when the gasoline has no oxygenate volume.

oxySpeciation = empirically derived value that adjusts the VOC/NMHC according to oxidation volume.

$oxyMassFraction_i$ = the mass fraction of oxygen within each of the gasoline oxygenates (shown in Table A-1). The oxygen mass fraction is included in Equation 5 to adjusts the oxySpeciation

factor relative to the mass fraction of oxygen in the fuel. Due to limited data, we assume that the oxySpeciation relationship is linearly proportional to the oxygen content of the fuel oxygenate.

oxyVolume$_i$ = the percent volume of each gasoline oxygenate in the respective fuel.

As for NMOG, the VOC/NMHC ratio coefficients are calculated using two methods. Both methods are described using examples.

A.3.1 Method 1

Method 1 is the method documented in the Mobile4.1 documentation[14], and uses the same methodology as for NMHC, except the ethane fraction is subtracted from the nominator term, as shown in Equation 10.

$$\frac{VOC}{NMHC_{\mathrm{FID}}} = \frac{(CF_{\mathrm{HCHO}}\,MPC_{\mathrm{HCHO}}) + (CF_{\mathrm{acetald}}\,MPC_{\mathrm{acetald}}) + (CF_{\mathrm{EtOH}}\,MPC_{\mathrm{EtOH}}) + (CF_{\mathrm{NMHC}}MPC_{\mathrm{NMHC}}) - (CF_{ethane}MPC_{ethane})}{[(CF_{\mathrm{acetald}}\,FID_{\mathrm{acetald}}) + (CF_{\mathrm{EtOH}}\,FID_{\mathrm{EtOH}}) + (CF_{\mathrm{NMHC}}FID_{\mathrm{NMHC}})] \times MPC_{\mathrm{NMHC}}} \quad \textbf{Equation 10}$$

Where:

CF = carbon fraction

MPC = mass per carbon

FID$_X$ = FID response factor

A.3.2 Method 2

Method 2 is consistent with the Federal Register method in calculation of NMOG. After NMOG is calculated using Equation 9, VOC is calculated by subtracting ethane and acetone from NMOG as shown in Equation 11. We assume that the FID response factor for ethane is 1.0.

$$m_{VOC} = m_{NMOG} - m_{ethane} - m_{acetone} \quad \textbf{Equation 11}$$

A.3.3 Comparison of the Two Methods:

Again, we used the data presented in Table A-2 to evaluate the two methods.

Example, Method 1:

$$\frac{VOC}{NMHC} = \frac{(0.0056 \times 30.0264) + (0.0036 \times 22.0267) + (0.9909 \times 13.8758) - (0.3913 \times 1.2518)}{[(0.0056 \times 0) + (0.0036 \times 0.5) + (0.9909 \times 1)] \times 13.8758}$$

$$\frac{NMOG}{NMHC} = \frac{13.5046}{13.7742} = 0.98043$$

Example, Method 2:

$$\frac{VOC}{NMHC} = \frac{0.9982 - 0.350}{0.9825} = \frac{0.9632}{0.9825} = 0.98039$$

As shown, the two methods yield the same VOC/NMHC fractions to four significant figures in the example calculation. Numerically, the methods are shown to give equivalent VOC/NMHC parameters for emission modeling purposes.

A.3.4 Estimating the OxySpeciation Constant

Equation 3 and Equation 5 enable the calculation of NMOG/NMHC and VOC/NMHC as a function of gasoline oxygenates (primarily ethanol), using the oxySpeciation constant, an empirically derived value that adjusts the NMOG/NMHC or VOC/NMHC ratio according to the oxygen content.

While either of the methods in the previous section could be used to derive this constant, we used Method 1 to estimate NMOG/NMHC and VOC/NMHC at E0 and E10. The effect of the oxygenate blend level was estimated using a linear interpolation between these two values with the intercept term representing the NMHC/NMOG ratio (or VOC/NMOG) at E0. The oxySpeciation constants for pre-2001 model year vehicles were derived from data used in SPECIATE profiles 1313 and 1314, and for 2001+ model year vehicles were derived from data used in SPECIATE profiles 8756 and 8757. The gasoline oxySpeciation factors for NMOG and VOC are displayed in Table 3-3 and Table 3-5, respectively.

The scalar oxyMassFraction is included in Equation 3 and Equation 5 so that relationships developed from one oxygenate (e.g. ethanol) can be applied to other gasoline oxygenates in MOVES. We assume that the gasoline oxygenate impact on the NMOG/NMHC and VOC/NMHC ratio is directly related to the oxygen mass content. As such, the impact of the gasoline oxygenates in Equation 3 and Equation 5 are directly proportional to the oxygenate fuel volume, and the mass fraction of oxygen in the oxygenate (oxyMassFraction).

Appendix B TOG Speciation Map

Table B-1 provides a complete speciation map between MOVES profiles and the distinguishing factors used in MOVES: modelYearGroupID, processID, fuelSubTypeID, and regClassID. This is more complete than the more readable Table 4-1 provided in the text.

Table B-1. TOG Speciation Map

Profile	Profile Description	modelYear-GroupID	processID	fuelSubTypeID	regClassID
1001	CNG Exhaust	19602050	1,2,15,16	30	48
4547	Diesel Headspace	19602050	11	20,21,22	0
4547	Diesel Headspace	19602050	12,13,18,19	20,21,22	10,20,30,40,41,42,46,47,48
8753	E0 Evap	19602050	12,13,19	10	10,20,30,40,41,42,46,47,48
8754	E10 Evap	19602050	12,13,19	12,13,14	10,20,30,40,41,42,46,47,48
8756	Tier 2 E0 Exhaust	20012050	1,2,15,16	10	20,30
8757	Tier 2 E10 Exhaust	20012050	1,2,15,16	12,13,14	20,30
8758	Tier 2 E15 Exhaust[e]	19602050	1,2,15,16	15,18	10,20,30,40,41,42,46,47,48
8766	E0 evap permeation	19602050	11	10	0
8769	E10 evap permeation	19602050	11	12,13,14	0
8770	E15 evap permeation	19602050	11	15,18	0
8774	Pre-2007 MY HDD exhaust	19602006	1,2,15,16,17,90	20,21,22	40,41,42,46,47,48
8774	Pre-2007 MY HDD exhaust	19602050	91	20,21,22	46,47
8774	Pre-2007 MY HDD exhaust	19602006	1,2,15,16	20,21,22	20,30
8775	2007+ MY HDD exhaust	20072050	1,2,15,16	20,21,22	20,30
8775	2007+ MY HDD exhaust	20072050	1,2,15,16,17,90	20,21,22	40,41,42,46,47,48
8855	Tier 2 E85 Exhaust	19602050	1,2,15,16	50,51,52	10,20,30,40,41,42,46,47,48
8869	E0 Headspace	19602050	18	10	10,20,30,40,41,42,46,47,48
8870	E10 Headspace	19602050	18	12,13,14	10,20,30,40,41,42,46,47,48
8871	E15 Headspace	19602050	18	15,18	10,20,30,40,41,42,46,47,48
8872	E15 Evap	19602050	12,13,19	15,18	10,20,30,40,41,42,46,47,48
8934	E85 Evap	19602050	11	50,51,52	0
8934	E85 Evap	19602050	12,13,18,19	50,51,52	10,20,30,40,41,42,46,47,48
8750a	Pre-Tier 2 E0 exhaust	19602000	1,2,15,16	10	20,30
8750a	Pre-Tier 2 E0 exhaust	19602050	1,2,15,16	10	10,40,41,42,46,47,48
8751a	Pre-Tier 2 E10 exhaust	19602000	1,2,15,16	11,12,13,14	20,30
8751a	Pre-Tier 2 E10 exhaust	19602050	1,2,15,16	11,12,13,14	10,40,41,42,46,47,48

Appendix C Development of $PM_{2.5}$ speciation profiles in MOVES2014

MOVES2014 includes updated $PM_{2.5}$ exhaust speciation profiles. For MOVES2014, updated $PM_{2.5}$ profiles were developed for gasoline sources and conventional diesel sources. The new profiles were developed to be consistent with the data used to derive the $PM_{2.5}$ emission rates, and to take advantage of the added capability of MOVES2014. This report includes the derivation of each $PM_{2.5}$ profiles used in MOVES2014.

Details on the $PM_{2.5}$ species are provided in this report because 1) the new $PM_{2.5}$ profiles were developed specifically for MOVES2014 and 2) the updated $PM_{2.5}$ speciation profiles change the EC, OC, and the total $PM_{2.5}$ emission rates. MOVES2014 applies separate fuel effects to $PM_{2.5}$ components and then sums the components to calculate the total exhaust $PM_{2.5}$. Thus, the updated speciation profiles change the primary $PM_{2.5}$ exhaust emission rates from MOVES2014 compared to MOVES2010b. The $PM_{2.5}$ profiles are presented here so that users can understand the reasons for these differences.

For comparison purposes, the seven $PM_{2.5}$ profiles developed for MOVES are presented in Table C-1. In the following subsections, the analyses to derive each of these profiles are presented.

Table C-1. $PM_{2.5}$ Profiles developed for MOVES2014

	Light-duty Gasoline Exhaust – Start (8992)	Light-duty Gasoline Exhaust- Hot Stabilized (8993)	Conventional HDD- Idle (8994)	Conventional HDD- Hot Stabilized Running (8995)	2007 and Newer Diesel Exhaust Composite (8996)	CNG transit bus exhaust from a lean-burn engine - no aftertreatment (95219)	CNG transit bus exhaust from a lean-burn engine - no aftertreatment (95220)
Elemental Carbon (EC)	44.37%	14.00%	46.40%	78.97%	9.98%	9.25%	11.12%
Organic Carbon (OC)	42.64%	55.70%	34.74%	14.52%	22.33%	36.99%	37.45%
Non-carbon Organic Matter (NCOM)	8.53%	11.14%	6.95%	2.90%	4.47%	7.40%	7.49%
SO4	0.95%	7.19%	5.27%	1.03%	59.91%	0.64%	1.04%
NO3	0.26%	0.29%	1.25%	0.18%	0.00%		
NH4	0.43%	2.78%	1.74%	0.36%	0.00%		
Fe	0.31%	1.83%	0.34%	0.13%	0.64%	0.25%	0.25%
Al		0.32%	0.06%	0.06%	0.11%	0.89%	0.89%
Si		0.32%	0.30%	0.22%	0.09%	0.46%	0.59%
Ti		0.03%	0.01%	0.01%	0.02%		
Ca	0.39%	1.44%	0.58%	0.35%	0.47%	0.21%	0.44%
Mg	0.02%	0.14%	0.13%	0.01%	0.14%		
K		0.09%	0.26%	0.02%	0.05%		
Na	0.01%	0.04%	0.31%	0.03%	0.99%		
Cl	0.02%	0.10%	0.38%	0.13%	0.04%		
CMAQ5.0 unspeciated (PMOTHR)	2.09%	4.58%	1.28%	1.09%	0.78%	43.90%	40.74%

C.1 Development of Gasoline Profiles from the Kansas City Light-duty Vehicle Emissions Study

The Kansas City Light-duty Vehicle Emissions Study (KCVES) is the primary source of $PM_{2.5}$ emission rates for light-duty vehicles in MOVES2014[33]. The KCVES sampled $PM_{2.5}$ emissions from 496 vehicles recruited in a stratified random sample. The KCVES also measured speciated $PM_{2.5}$ on a subset of 99 of these vehicles. An overview of the vehicles included in the chemical subset is included in Table C-2.

Table C-2. Vehicle sample size in the Kansas City Light Duty Vehicle Emissions Study

Vehicle Type[1]	Strata	Model Year Group	% of KC LDGV Vehicle Population	% of KC LDGV Vehicle Miles Traveled (VMT)	Summer Round Sample		Winter Round Sample	
					Full Sample	Chemical Subset	Full Sample	Chemical Subset
Truck	1	pre-1981	1.1%	0.6%	2	2	10	3
	2	81-90	3.7%	2.4%	21	4	33	3
	3	91-95	7.2%	6.5%	18	6	33	7
	4	96-2005	28.6%	34.2%	39	8	59	11
Car	5	pre-1981	1.3%	0.7%	6	5	17	3
	6	81-90	7.4%	4.6%	49	4	40	5
	7	91-95	13.4%	11.2%	39	6	44	9
	8	96-2005	37.3%	39.8%	87	14	41	9
		Sum =	100%	100%	261	49	277	50

The derivation of the $PM_{2.5}$ gasoline profile for MOVES2014 is documented in Sonntag *et al.* (2013)[37]. A summary of the speciation derivation is included in this report, as well as a discussion on implementing the profile into the MOVES2014 framework. Two gasoline profiles are developed to maintain differences between start and running processes. Minor differences were detected between the $PM_{2.5}$ compositions between seasons, which were confounded by the different vehicles tested in each season. The data used equally weighted data from the summer and winter tests to calculate a profile that incorporates data from both seasons.

We discovered high concentrations of silicon in some of the $PM_{2.5}$ measurements, likely due to contamination from silicone rubber couplers used in KCVES. The silicone contamination occurred primarily on bag 2 of the LA-92 drive cycle which was used for developing the running $PM_{2.5}$ speciation profile and emission rates. The silicone contamination was larger for trucks than cars due to their higher exhaust temperatures. The effect of the silicone contamination was removed from the developed profile using the silicon emissions measurement by X-ray florescence. The primary exhaust $PM_{2.5}$ emission rates were corrected in MOVES2014 to account for the silicone contamination.[33] After removing the silicone contamination from the speciated data, no significant differences were detected between passenger cars and light-duty trucks, and the data from the cars and trucks were pooled together to develop single start and running $PM_{2.5}$ speciation profiles for all light-duty gasoline vehicles.

Important differences in the $PM_{2.5}$ composition were detected among model year groups. Rather than calculating model-year-group-specific profiles, fleet-average profiles were calculated to better capture the impact of deterioration within all model year groups and to avoid over-fitting the data to model year group trends. Malfunctioning high-emitting vehicles are known to contribute a significant share of in-use PM emissions from light-duty vehicles.[38,39,40,41] High-emitting gasoline emissions have a highly variable PM composition due to failed emission control systems, excessive oil consumption, and poor fuel control. Previous analysis of the KCVES suggested that the speciation subsample (102 tests) provides a reasonable estimate of the total PM mass compared to the full sample (522 tests), but the speciation sample underestimated the high emitting vehicles in the newer model year groups.[42] Other test programs have confirmed

that high emitting gasoline vehicles also occur in modern vehicle fleets such as 1990-era vehicles with electronic fuel injection.[38,39,40] The speciation sample size was deemed too limited to accurately capture the impact of deterioration and high-emitting vehicles within each model-year group. By using all the data in a fleet-average approach, we incorporated the impact of deteriorated vehicles on the fleet-average $PM_{2.5}$ emissions.

The fleet-average PM speciation profiles are calculated using seasonal, vehicle-miles-traveled (VMT), and PM mass-weighting. The PM profile is calculated using the ratio of the means, also referred to as a mass-normalized emission profile.[43] The ratio of means is calculated by first calculating the mean emission rate of the total $PM_{2.5}$, and the mean emission rate of each PM species (EC, OC, Fe, etc.). Then the speciation profile is calculated, by calculating the ratio of the mean emission rate from each species, to the mean $PM_{2.5}$ emission rate, e.g., mean(EC)/mean(PM). The vehicle tests from each season are equally weighted, and averaged according to the calculated contribution to annual VMT in the Kansas City MSA (Table C-2). By using VMT and mass weighting, the profile scales up the contribution of older and higher emitting vehicles according to their high PM emissions, but also scales their down their contribution based on the relatively small number of vehicle miles traveled associated with these vehicles. For application in MOVES2014, the fleet-average profile is used to characterize $PM_{2.5}$ emissions across all model year groups, and all ages of vehicles used to represent deterioration.

Because the $PM_{2.5}$ speciation varied significantly by model year group,[37] the fleet average speciation profile is sensitive to the averaging assumptions. As mentioned above, we did not maintain the difference in speciation in model year groups, due to concern that the model-year groups would not be representative of the PM emissions as the vehicles aged. Given the uncertainty of the PM speciation profiles, we thought it would be unreasonable to model differences in PM speciation according to different ages of vehicle fleets in different areas in the US. For simplicity, we assume that the fleet-average $PM_{2.5}$ profile from Kansas City to be representative of the US gasoline fleet.

We recognize the need to incorporate speciation data on newer vehicles. For the next generation of vehicles, the composition of PM is expected to become increasingly dominated by black carbon emissions from both low-emitting port-fuel injected vehicles[38,44,45,46] and gasoline-direct injection (GDI) vehicles[47,48,49]. We plan on incorporating light-duty gasoline PM profiles to MOVES and SPECIATE as such data on representative, in-use vehicles becomes available.

The developed $PM_{2.5}$ profiles used in MOVES2014 for gasoline exhaust are included in Table C-3. The number of samples for each $PM_{2.5}$ species are also shown in Table C-3. EC was measured on each vehicle test and has a much greater sample size than the other species. The EC and nonECPM emission rates in MOVES2014[33] are updated to be consistent with the EC fractions developed in Table C-3.

For application in MOVES2014, only the $PM_{2.5}$ species required by CMAQv5.0 are reported. A revision of the metal emission rates for Mn, Cr, and Ni for gasoline vehicles based on the KCVES is provided in the Fuels and Toxics Report. The $PM_{2.5}$ ratios that were not significantly greater than 0 at the 95 percent confidence intervals were reported as 0, which removed five $PM_{2.5}$ species pollutants from the start profile. Fuel samples analyzed for 171 of the vehicles tested in KCVES yielded an average fuel sulfur content of 161.2 ppm. Fuel sulfur content in the US is now lower after implementation of the Tier 2 Vehicle & Gasoline Sulfur Program Final Rule (effective beginning 2006-2008), which set a gasoline sulfur fuel limit of 30 ppm. In

MOVES2014, the baseline sulfate emissions estimated from the $PM_{2.5}$ profile are adjusted according to the user-supplied fuel sulfur content as discussed in the Fuel Effects on Exhaust Emissions from On-road Vehicles in MOVES2014.[32]

Details on the data, quality control measures, and statistical methods used to develop the profile are documented in the Sonntag *et al.* (2013).[37] The paper also introduces methods to identify significant measurements, correct for organic carbon positive artifact, control for contamination from the testing environment on the $PM_{2.5}$ speciation profiles, and impute missing $PM_{2.5}$ species in the KCVES measurements from other light-duty gasoline PM emission studies. Speciation factors for additional $PM_{2.5}$ species (P, Cu, Zn, Br, Mo, and Pb) that are not included in MOVES2014 are also presented.

Table C-3. Gasoline $PM_{2.5}$ Profile for Start and Running Emissions weighted average using Vehicle Miles Traveled (VMT)

PM Species	Start (8992)				Running (8993)			
	n	mean ratio +/- 95% CI			n	mean ratio +/- 95% CI		
Elemental Carbon (EC)	484	44.37%	+/-	4.30%	531	14.00%	+/-	2.68%
Organic Carbon (OC)	66	42.64%	+/-	6.63%	99	55.70%	+/-	4.02%
Non-carbon Organic Matter (NCOM)	66	8.53%	+/-	1.33%	99	11.14%	+/-	0.80%
SO4	66	0.95%	+/-	0.24%	99	7.19%	+/-	1.90%
NO3	66	0.26%	+/-	0.08%	99	0.29%	+/-	0.08%
NH4	66	0.43%	+/-	0.10%	99	2.78%	+/-	0.73%
Fe	66	0.31%	+/-	0.21%	99	1.83%	+/-	0.53%
Al					99	0.32%	+/-	0.10%
Si					99	0.32%	+/-	0.10%
Ti					99	0.03%	+/-	0.01%
Ca	66	0.39%	+/-	0.14%	99	1.44%	+/-	0.26%
Mg	66	0.02%	+/-	0.02%	99	0.14%	+/-	0.02%
K					99	0.09%	+/-	0.03%
Mn					99	0.02%	+/-	0.02%
Na	66	0.01%	+/-	0.00%	99	0.04%	+/-	0.01%
Cl	66	0.02%	+/-	0.01%	98	0.10%	+/-	0.04%
CMAQ5.0 unspeciated (PMOTHR)	66	2.09%	+/-	1.75%	99	4.56%	+/-	1.10%

C.2 Development of E55/59 Profile for Use in MOVES2014 for Pre-2007 Conventional Diesel

An updated $PM_{2.5}$ profile for pre-2007 conventional diesel trucks was developed from the CRC E55/59 Study: Heavy-Duty Vehicle Chassis Dyno Testing for Emissions Inventory[50]. The E55/59 program is the current source for $PM_{2.5}$ emission rates for medium and heavy-duty conventional diesel trucks in MOVES2014, and is the source of the conventional diesel TOG speciation profiles (Table 4-2). By using the E55/59 study for $PM_{2.5}$ speciation profiles we are using a consistent study with both the $PM_{2.5}$ emission rates and the TOG speciation profiles in MOVES2014.

The E55/59 profile replaces SPECIATE profile # 91106 used to conduct $PM_{2.5}$ speciation based on the Northern Front Range Study Air Quality Study (NFRAQS) [51] conducted in the late 1990's. The MOVES2014 E55/59 $PM_{2.5}$ profile includes measurements from eight heavy-duty trucks, ranging from a 1985 to 2004 model year as shown in Table C-4. The E55/59 fuel properties are more aligned with those in-use today, with sulfur content ~ 172 ppm, as opposed to ~ 340 ppm sulfur used in NFRAQS.[41,51] The CRC E55/59 study was conducted from 2001-2005 in several phases. Chemical characterization of $PM_{2.5}$ emissions was conducted for nine of the 75 trucks tested in the E55/59 study, ranging from 1985 to 2004 model year.

Table C-4. Vehicle Information from the Speciated E55/59 Trucks

Phase	ID	Medium/ Heavy Duty	Vehicle Model Year	Vehicle Manufacturer	Engine Model Year	Engine Model	Engine Power (hp)	Engine Disp. (Liter)	Engine Manufacturer	Odometer Reading (mi)
1	1	H	1994	Freightliner	1994	Series 60	470	12.7	Detroit	639105
1	2	H	1995	Freightliner	1995	3406B	375	14.6	Caterpillar	241843
1	3	H	1985	International	1985	NTCC-300	300	14	Cummins	501586
2	39	H	2004	Volvo	2003	ISX	530	14.9	Cummins	45
2	40	H	2004	Freightliner	2003	Series 60	500	14	Detroit	8916
2	41	M	1998	Ford	1997	B5.9	210	5.9	Cummins	13029
2	42	H	2000	Freightliner	1999	3406	435	14.6	Caterpillar	576998
2	43	H	1995	Peterbilt	1994	Series 60	470	12.7	Detroit	899582
2	44	H	1989	Volvo	1989	3406	300 (est.)	14.6	Caterpillar	811202

In all, 65 tests were conducted on the nine trucks selected for PM speciation. Phase 1 tested three heavy heavy-duty diesel trucks (HHDTs) for PM speciation on four modes of the Urban Dynamometer Driving Schedule (UDDS), including: Idle, Creep, Transient, and Cruise. Phase 2 tested six additional heavy heavy-duty diesel trucks, and one medium heavy-duty truck (MHDT). In Phase 2, the HHDTs were also tested on the UDDS, as well as a high speed cruise mode added after Phase 1. The MHDT was tested on MHDT schedule developed by the California Air Resources Board that included two transient modes and a cruise mode. For chemical speciation, some tests were repeated in sequence to collect additional mass on the filter, including extended idle and extended creep. In Phase 2, the speciation data was not collected for the creep mode.[50]

The total and speciated $PM_{2.5}$ emissions data from the E55/59 study was compiled from the speciation database compiled in CRC Report No. E75-2: Diesel Unregulated Emission Characterization Report[52] and from Table 17 of the E55/59 Phase 1 report.[53] The data reduction steps used to develop a $PM_{2.5}$ speciation profile from the E55/59 speciated data are outlined in the following paragraphs.

Step 1. We first calculated the average $PM_{2.5}$ profile for each individual truck and four generic classifications of test cycle, namely: idle, creep, cruise, and transient. The composite UDDS cycle is classified as a transient cycle, similar to the classification conducted of speciation profiles by E75-2.[51] The truck and test cycle average PM profiles are calculated as ratios of the means, also called a PM mass-weighted profile. In this manner, idle tests that contain three repeat idle cycles contribute more to the average than tests that include only one idle cycle. The average profile for each vehicle/test cycle classification is shown in Figure C-1. Thirty average speciation profiles were calculated from the 65 tests as shown in Figure C-1. Typically, each truck/cycle average contains two tests.

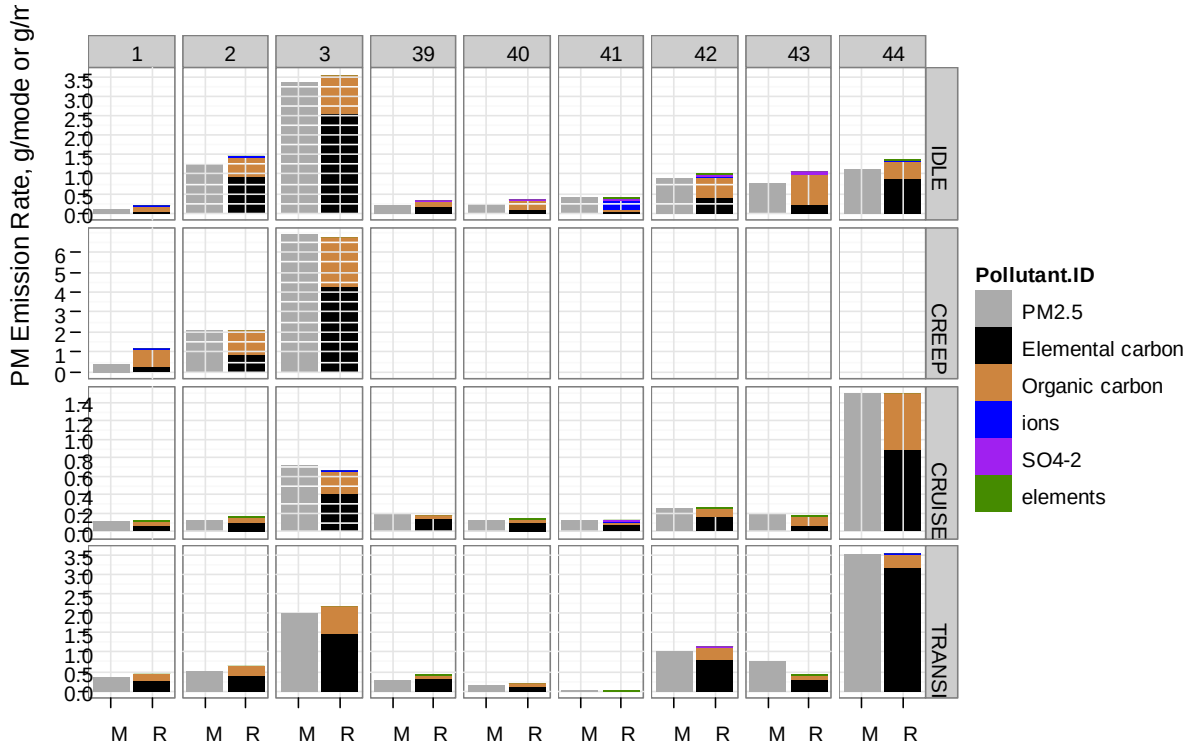

Figure C-1. Average $PM_{2.5}$ Speciation Profiles by Truck and Test Cycle from the E55/59 Program. M = Measured total $PM_{2.5}$, R = Reconstructed total $PM_{2.5}$ from the speciated measurements

Step 2. We removed the average $PM_{2.5}$ profiles with suspect data. As shown in Figure C-1, the MMHDT truck (Truck 41) had very low PM emissions on the transient cycle, and a very large contribution of ammonium to the idle cycle. This PM composition does not compare well with previous data in the literature[54], so the medium-duty truck was removed from further analysis.

Step 3. We calculated a median PM profile using the individual truck/test-cycle PM profiles calculated in steps 1 and 2. The median is used rather than the mean due to the small sample (eight trucks), in contrast to the variety of truck technologies, exhaust control systems, and ages of the trucks in the real-world fleet. A mass-weighted mean would have been dominated by the results for Truck 3 and Truck 44, which had the highest PM emission rates. Instead we calculated the median of the PM fractions, and not a fraction of the median emission rates. In this manner, the final PM speciation profile is not overly dependent on any one vehicle. Additionally, there

may be systematic differences between the Phase 1 and Phase 2 measurements that could impact a mass-weighted profile. By calculating the $PM_{2.5}$ species fraction before computing the median, any differences impacted the absolute $PM_{2.5}$ emission rates between phases do not impact the resulting speciation profile.

Step 4. We adjust the median profile to account for unmeasured $PM_{2.5}$ species including metal-bound oxygen and non-carbon organic matter. The additional oxygen mass associated with the metal oxides are calculated using the oxide state assumptions in Sonntag *et al.* (2013)[37] reproduced in Table C-5.

Table C-5. Oxide states assumed for calculation of metal-bound oxygen

Element	Oxide Form 1	Oxide Form 2	Oxide Form 3	Oxide/Element Mass Ratio
Na	Na_2O			1.35
Mg	Mg			1.0
Al	Al_2O_3			1.89
Si	SiO_2			2.14
P	PO_4			3.07
Cl	Cl			1.0
K	K_2O			1.20
Ca	Ca			1.0
Ti	TiO_2			1.67
Cr	Cr_2O_3	CrO_3		1.69
Mn	MnO	MnO_2	Mn_2O_7	1.63
Fe	FeO	Fe_2O_3		1.36
Ni	NiO			1.27
Cu	CuO			1.25
Zn	Zn			1.0
Rb	Rb_2O			1.09
Br	Br			1.0
Mo	MoO_2	MoO_3		1.42
Pb	PbO	PbO_2		1.12

For the Phase 1 samples, the molar concentration of ammonium balances within 5 percent of the molar concentrations of $2*SO_4 + NO_3$. This is what would be expected if the ammonium exists as ammonium sulfate $[NH_4]_2SO_4$ and ammonium nitrate, NH_4NO_3. For the Phase 2 samples, ammonium balances within 25 percent of the molar concentrations of $2*SO_4 + NO_3$. Due to the relatively good agreement between the measurements, it appears that the sulfate on the filter exists as ammonium sulfate. As such, we did not account for sulfate-bound water contributing to filter mass.

The sum of the PM fractions from the median profiles is greater than one. To achieve mass balance, we are scaled down the organic carbon fraction to correct for positive artifact inherent in organic carbon (OC) filter measurements, as was done in previous work including for the light-duty gasoline profile[37] and analysis of emissions from other combustion sources[55]. We calculated the organic matter (OM) as the remainder of the $PM_{2.5}$ using Equation 12.

$$OM\% = 100 - EC\% - elements\% - metal\ bound\ oxygen\% - ions\% \quad \textbf{Equation 12}$$

Then we split the OM into OC and non-carbon organic matter (NCOM) using the following relationship: OM = 1.2 * OC used by Kleeman *et al.* (2000)[56] and developed from work conducted on medium-duty diesel emissions.[54]

$$OC\% = \left(\frac{5}{6}\right) OM\% \quad \textbf{Equation 13}$$

$$NCOM\% = \left(\frac{1}{6}\right) OM\% \quad \textbf{Equation 14}$$

The initial and corrected OC/PM factors are shown in Table C-6. The adjusted OC speciation factors are smaller than the initially measured OC/PM fraction, which is expected due to the higher affinity for OC artifact to collect on the quartz fiber filters, as compared to the Teflon filters used to measure $PM_{2.5}$ mass.[57]

Table C-6. Impact of mass-balance correction on organic carbon and organic matter emission rates

PM factors	IDLE	CRUISE	TRANSIENT
Initial OC/PM factor	54.1%	36.3%	30.1%
Mass-balance OM/PM factor	41.7%	36.1%	17.4%
Corrected OC/PM factor	34.7%	30.1%	14.5%

The resulting profiles for the $PM_{2.5}$ species are located in Table C-7. The Start/Extended Idle profile is based on the idle test cycles, and the running emissions are based on the transient cycles. These cycles are selected for use for modeling these emission processes because they have similar PM characteristics (EC/PM) ratio as the $PM_{2.5}$ MOVES emission rates for conventional diesel as discussed next.

Table C-7. $PM_{2.5}$ Profiles for Conventional Diesel Exhaust developed for MOVES2014

	Start/Extended Idle (Profile 8994)	Running (Profile 8995)
Elemental Carbon	46.40%	78.97%
Organic Carbon	34.74%	14.52%
NonCarbon OM	6.95%	2.90%
SO4	5.27%	1.03%
NO3	1.25%	0.18%
NH4	1.74%	0.36%
Fe	0.34%	0.13%
Al	0.06%	0.06%
Si	0.30%	0.22%
Ti	0.01%	0.01%
Ca	0.58%	0.35%
Mg	0.13%	0.01%
K	0.26%	0.02%
Na	0.31%	0.03%
Cl	0.38%	0.13%
CMAQ5.0 unspeciated	1.28%	1.09%

As discussed in $PM_{2.5}$ overview, the exhaust $PM_{2.5}$ speciation profiles are used to speciate the non-EC emission rates in MOVES2014. In the case of conventional diesel, the EC emission rates were developed separately by weight class, and operating mode bin as discussed in the MOVES2014 Heavy-duty report.[30] The EC fraction from a MOVES calendar year 2014 model run are compared to the EC fraction in the developed profile in Table C-8. The MOVES2014 EC/PM factor varies by operating mode and regulatory class, and thus changes for different MOVES scenarios depend on the age distribution, fleet characteristics, and driving mix on different road types. MOVES2014 reflects the lower EC/PM fraction for extended idle and start emissions, which was also shown in the E55/59 profile. Running emissions represent over 80 percent of the $PM_{2.5}$ emissions from conventional diesel trucks. The EC/PM ratio for running compares very well (<1 percent) between the MOVES estimates and the E55/59 running $PM_{2.5}$ speciation profile. The comparison validates the consistency in using the operating mode specific values in MOVES for the EC emission rates, and using the E55/59 profile to calculate the remaining $PM_{2.5}$ species.

Table C-8. MOVES EC/$PM_{2.5}$ fraction from conventional Diesel (pre-2007) calendar year 2014, compared to the EC/$PM_{2.5}$ fraction from the developed profile from E55/59

	Extended Idle	Start	Running
MOVES2014 EC/PM Rates	26.6%	33.2%	79.4%
E55/59 $PM_{2.5}$ Speciation profile	46.4%	46.4%	79.0%

The MOVES2014 conventional diesel profiles developed from the E-55/59 Study are compared to composite profile developed by Schauer *et al.* (2006)[43] from measurements taken from the DOE Gasoline/Diesel PM Split Study, as well as the NFRAQS heavy-duty diesel profile (SPECIATE Profile 91106) in Table C-9. The EC/PM fraction from the transient cycle compares well to both the composite profiles. The MOVES2014 idle profile has a substantially lower EC/PM fraction than the composite profiles, with a corresponding higher fraction of organic matter. The MOVES2014 sulfate fractions appear are more aligned with the DOE Split study, which could be due to newer technology diesel and lower altitude testing. Elements and ion emission rates compare well to the DOE gasoline/diesel PM split study. Even though the E55/59 speciation sample is limited, it appears valid in comparison to other available studies.

Table C-9. Comparison of MOVES2014 Conventional Diesel Profiles with other $PM_{2.5}$ Conventional Diesel Profiles

	MOVES2014 E55/59		DOE Gasoline/ Diesel PM Split Study	Northern Front Range Air Quality Study
	Start/ Extended Idle (8994)	Running (8995)	Composite	Composite (91106)
Elemental carbon	46.4%	79.0%	72.7%	77.1%
Organic matter	41.7%	17.4%	24.1%	17.6%
SO_4	5.3%	1.0%	1.3%	0.3%
Cl, NH_4, NO_3	3.4%	0.7%	0.4%	0.1%
Elements	2.1%	1.1%	1.5%	0.5%

C.3 Development of the ACES $PM_{2.5}$ Profile for 2007 and Newer Technology Diesel

The $PM_{2.5}$ speciation profile for 2007-and-later technology is based on Phase 1 of the Advanced Collaborative Emissions Study (ACES) Report[58]. The purpose of the ACES report was to characterize criteria and toxic emissions from advanced technology diesel engines and control systems. Phase 1 of ACES tested four heavy-duty diesel engines each equipped with a catalyzed diesel particulate filter (C-DPF). The $PM_{2.5}$ profile is based on a 16-hour cycle which is composed of FTP and CARB 5-Modes, developed specifically to gain sufficient PM mass to measure the emission rates of trace metals and toxics and to capture diesel particulate filter regeneration events. The $PM_{2.5}$ measurements from the 16-hour cycle include the exhaust measurements downstream of the C-DPF and crankcase blow-by emissions. Crankcase blow-by emissions contributed 38 percent of the combined crankcase and tailpipe $PM_{2.5}$ emissions on the FTP cycle.

The SPECIATE contractor (Abt Associates) developed the $PM_{2.5}$ profile from the ACES program Phase 1 with input from the US EPA, with the intent of maintaining consistency with the summarized results in the ACES Phase 1 report. The 16-hour results yielded the most accurate measurements at the low levels of $PM_{2.5}$ and are used to represent all $PM_{2.5}$ emission processes from 2007-and-newer on-highway diesel vehicles.

The following decisions were made to develop a profile to be consistent with the results in the ACES Phase 1 report.

1. The original measurements were used rather than background or tunnel corrected measurements. EC and OC were not corrected for background, or backup quartz filters. Background correcting the EC/OC filters caused negative EC/OC emission rates on three of the four engines. The ACES researchers did not report OC corrected by a backup-quartz filter because of concern of under-representing OC emissions[59]. Similarly, species for elements and ions were not corrected for tunnel blanks. Using uncorrected OC measurements likely contributed to the mass of the sum of the speciated measurements being higher than Teflon filter measurements[60]. By using the original measurements, rather than the background or tunnel corrected measures, we are likely overestimating the emissions from some of the individual species that are subject to positive artifact like OC. The ACES researchers discuss possible approaches for correcting the measured OC emission rates, and mention this as an area for future work for 2007 diesel engines.

2. Unmeasured species that likely contribute to particulate matter were not included in the profile, including sulfate-bound water and metal-bound oxygen from the profile. The PM collected on the filter were analyzed for nitrate and ammonium, however no ammonium or nitrate was detected[58]. In the absence of these species, the sulfate is expected to exist as hydrated sulfuric acid. Khalek *et al.* 2011[59] reported that accounting for the water-bound sulfate would increase the summed mass of the individual species 37 percent beyond the measured filter mass. Rather than lowering the factors for other species by including the sulfate-bound water, it was excluded from the profile. Converting the measured organic carbon to organic matter and accounting for the oxide state of the elements was considered by Khalek *et al.* (2011)[59], but was not conducted due to the uncertainty of reconciling the filter mass and the sum of the measured species

3. According to the SPECIATE database, the profile was normalized to the gravimetric mass of PM. Gaseous and particulate phase sulfate are combined in the PM profile. More information on the profile itself can be found in the SPECIATE database, and the database's supporting documentation outlines specific procedures for creating PM profiles.[61]

The ACES Profile is included in the SPECIATE database as profile #5680. This profile is the basis of SPECIATE profile 8996 used in MOVES2014 with one adjustment. CMAQ5.0 needs organic matter reported as OC and non-carbon organic matter (NCOM). We treated the reported OC in the SPECIATE profile 5680 as OM, and calculate OC and NCOM using the same split (5:1) as used for conventional diesel and light-duty gasoline. The species not needed by CMAQ5.0 from the ACES Phase 1 profile are summed into the CMAQ5.0 unspeciated fraction. Metal emission rates for manganese, chromium, and nickel from MOVES2014 are derived from the ACES Phase 1 data[4]. They are estimated using the metals calculator with mass/distance emission rates, and are not reported in the SPECIATE profiles.

Table C-10. SPECIATE $PM_{2.5}$ Profile 8996 developed from the 16-hour cycle from four heavy-duty diesel engines with C-DPFs in the ACES Phase 1 Program

	Weight %
Elemental Carbon	9.98%
Organic Carbon	22.33%
Non Carbon Organic Matter	4.47%
Sulfate	59.91%
Nitrate	0.00%
Ammonium	0.00%
Iron	0.64%
Aluminum	0.11%
Silicon	0.09%
Titanium	0.02%
Calcium	0.47%
Magnesium	0.14%
Potassium	0.05%
Sodium	0.99%
Chlorine	0.04%
CMAQ5.0 unspeciated	0.78%

The 2007+ diesel EC/PM fraction in MOVES2014 is a constant 8.61 percent based on previous analysis documented in the heavy-duty diesel report. This value is quite similar to the 9.98 percent EC/PM fraction estimated from Phase 1 of the ACES program. Due to the similarity in the EC/PM fraction, the previous value of 8.61 percent is also used in MOVES2014. However, the ACES Phase 1 data is used to speciate the remaining species listed in Table C-10.

C.4 Development of the Compressed Natural Gas (CNG) Transit Bus Profile

The California Air Resource Board (CARB) conducted several emission characterization studies on compressed natural gas vehicles. We used test data collected on CNG New Flyer bus with a 2000 MY Detroit Diesel (DDC) Series 50G engine, equipped with and without an oxidation catalyst to develop $PM_{2.5}$ speciation profiles. CARB also conducted tests on a CNG bus with a 2001 Cummins Westport engine. We developed the profile on the DDC engine, with and without catalyst to estimate the impact of oxidation catalyst control, without introducing differences in engine technology. CARB characterized the PM emissions on a steady-state cycle, and a central business district cycle (CBD). We used the CBD data, which was consistent with the criteria pollutant analysis in the MOVES2014 Heavy-duty Emissions Report[30], and was considered more representative of typical transit bus behavior.

We elected to use only the data reported by CARB on the DDC 50G engine to develop the profile. Using a single profile provides consistency in the PM characterization estimates and assures that the organic carbon emissions are reduced with implementation of oxidation catalyst controls. Other studies that reported EC/OC did not measure emission rates for elements[62]. We used measurements made on the same tests to construct the profile in Table C-11. The PAH/OC ratios documented in the MOVES2014 toxics report[4] were also developed from the CARB measurements on the DDC 50 G.

Table C-11. $PM_{2.5}$ Speciation Profiles for CNG Compressed Ignition Transit Bus Exhaust

Pollutant	Uncontrolled (95219)	Oxidation Catalyst (95220)
Elemental Carbon (EC)	9.25%	11.12%
Organic Carbon (OC)	36.99%	37.45%
Non-carbon Organic Matter (NCOM)	7.40%	7.49%
SO4	0.64%	1.04%
aluminum	0.89%	0.89%
calcium	0.21%	0.44%
chromium	0.25%	0.25%
cobalt	0.39%	0.40%
iron	0.25%	0.25%
nickel	0.04%	0.00%
phosphorus	0.04%	0.15%
silicon	0.46%	0.59%
zinc	0.14%	0.20%
Unspeciated $PM_{2.5}$	43.04%	39.74%

We used PM, EC, OC, and element emission rates for two repeat tests both with and without the oxidation catalyst.[63,64] CARB measured 13 elements by X-ray fluorescence but no ions (sulfate, ammonium, or nitrate) were measured. The sulfate emissions were estimated by assuming that all elemental sulfur is in the form of sulfate. This assumption is consistent with sulfate and

elemental sulfur measurements reported for natural gas combustion in the speciate database (SPECIATE 91112). We assume that the missing ammonium and nitrate emissions are zero, based on the negligible ammonium and nitrate measurements from modern spark-ignition CNG buses equipped with three-way catalysts.[65] Sodium and magnesium were the largest elements measured (sodium was over 7 percent of the $PM_{2.5}$ measured in the uncontrolled test), which is likely due to known measurement artifact for XRF measurements of sodium and magnesium. As such the sodium and magnesium emission rates are reported as zero.

The use of the oxidation catalyst reduced the $PM_{2.5}$ emission rates from 28 mg/mile to 20.3 mg/mile on the CBD cycle (a 27.5 percent decrease). As shown in Table C-11, the composition of the $PM_{2.5}$ stayed fairly constant. The EC and OC fractions between the two control conditions are not statistically different. The estimated sulfate emissions are significantly higher with the oxidation catalyst, which is to be expected. Both profiles contain a large amount of unspeciated $PM_{2.5}$ emissions. The source of the large unspeciated $PM_{2.5}$ emissions is unknown, but may be attributed to the different sampling media for the total and speciated $PM_{2.5}$ emissions, which is amplified at the low $PM_{2.5}$ concentrations measured from CNG exhaust. The absence of ion measurements may also be a contributing factor.

The real-world variability in the $PM_{2.5}$ composition is larger than the developed profiles suggest. The OC/PM fraction for the 2001 Cummins Westport with oxidation catalyst was 61.9 percent, which is much larger than that measured on the 2000 Detroit diesel engine. Lanni *et al.* (2003)[62] reported that the OC/PM fraction on three CNG transit buses with DDC Series 50 G engines ranged from 29 percent to 74 percent of the $PM_{2.5}$. The EC emissions measured by Lanni *et al.* (2003)[62] were below the detection limit, but the presented results compare well with the 2001 Cummins Westport measured by CARB (12.7 percent EC/PM). The sulfate fraction for the oxidation catalyst presented in Table C-11 compares well with the sulfate fraction reported for the 2001 Cummins Westport by CARB[64] (2.8 percent), and by Lanni *et al.* (2003)[62] (1.5 percent to 2.4 percent).

Appendix D $PM_{10}/PM_{2.5}$ Factors

The gasoline $PM_{10}/PM_{2.5}$ factor is based on measurements of 1991-1997 model year vehicles tested by Norbeck *et al.* (1998)[66]. This ratio estimates that roughly 10 percent of the PM emitted from gasoline vehicles is in the coarse range, which agrees with the size-distributions reported from cascade impactor measurements on light-duty gasoline exhaust from Schauer *et al.* (2008)[67].

The diesel $PM_{10}/PM_{2.5}$ factor is based on a 1985 EPA report[68], which reports that 92 percent of particulate mass is measured below a 2.5 µm cut-off. Although derived from measurements on older technologies, the diesel $PM_{10}/PM_{2.5}$ ratio compares well with observations of the particle size distribution of diesel exhaust by Kittelson *et al.* (1998)[69], who states that the coarse mode contains 5-20 percent of the total aerosol mass. Unfiltered crankcase emissions published by Donaldson Company Inc. (2011)[70] have similar reported mass distributions with ~ 93 to 97 percent of the cumulative mass particles smaller than 2.5 µm. In contrast, Tatli and Clark (2008)[71] report that the particle mass size distribution is significantly different from crankcase and tailpipe diesel emissions for particles below 1 µm. Due to the limited information on coarse-mode crankcase particulate emissions, we assume the same $PM_{10}/PM_{2.5}$ fraction for diesel crankcase emissions.

Filtered diesel crankcase and exhaust emissions are expected to have smaller $PM_{10}/PM_{2.5}$ ratios, due to the higher filter capture efficiency of coarse mode particles.[70,72] However, the same $PM_{10}/PM_{2.5}$ ratios are used for the later model year groups, due to limited coarse mode particulate exhaust measurements, and limited information on the failure rates of these technologies in real-world use.

No information was available on the $PM_{10}/PM_{2.5}$ ratio for CNG emissions, and the gasoline ratio is used for CNG emissions. Table D-1 contains the selected exhaust $PM_{10}/PM_{2.5}$ ratios used in MOVES.

Table D-1. $PM_{10}/PM_{2.5}$ Ratios for primary exhaust and crankcase emissions by fuel type

Fuel	$PM_{10}/PM_{2.5}$
Gasoline, E85, CNG	1.130
Diesel	1.087

Appendix E Peer-Review Comments and Responses

This report was reviewed for the MOVES2014 release. The draft report that was subject to peer-review and the peer-review comments are available at EPA's science inventory webpage.[73] The peer-review comments and EPA responses are summarized below, and were originally included in the MOVES2014 version of this report.[5] The speciation updates made for MOVES2014a and MOVES2014b were not peer-reviewed.

E.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?

E.1.1 Dr. Tom Durbin

For the "TOG and PM Speciation in MOVES for Air Quality Modeling" and the "Appendix: PM2.5 Speciation in MOVES" reports, there are several other data sets should be considered for inclusion in the model as the model continues to be developed. The California Air Resources Board has been looking at the toxicity of advanced technology diesel vehicles, and some of this data has sulfate emissions that could be of relevance here. The South Coast Air Quality Management District has also conducted a study to evaluate the in-use emission rates of 2007+ technology, heavy-duty diesel and natural gas vehicles. These data will probably not be available until the first part of next year, but they could be considered for future application to the model. Phase 2 of the ACES program is another data set that could be of value for future model revisions.

For CARB studies, see http://www.arb.ca.gov/research/veh-emissions/veh-emissions.htm noting that there have been some publications more recent that those listed on the website.

UC Riverside program with the South Coast Air Quality Management District (SCAQMD), "Determining the Physical & Chemical Composition & Associated Health Effects of Tailpipe PM Emissions"

UC Riverside program with the Coordinating Research Council (CRC), "Biodiesel and Renewable Diesel Characterization & Testing in Modern LD Diesel Passenger Cars & Trucks"

UC Riverside program with the South Coast Air Quality Management District (SCAQMD), "Determining the Physical & Chemical Composition & Associated Health Effects of Tailpipe PM Emissions"

UC Riverside and West Virginia University program with the SCAQMD, "In-Use Emissions Testing and Demonstration of Retrofit Technology for Control of On-Road Heavy-Duty Engines"

Durbin, T.D., Karavalakis, G., Johnson, K.C., Miller, J.W., and Hajbabaei, M. (2013) Evaluation of the Performance and Air Pollutant Emissions of Vehicles Operating on Various Natural Gas Blends – Heavy-Duty Vehicle Testing – Regulated Emissions and PM, Final Report for the California Energy Commission by the University of California at Riverside, June.

Durbin, T.D., Karavalakis, G., Miller, J.W., Hajbabaei, M., Bumiller, K., Villela, M., and Xu, K.H., 2012. Effects of Olefins Content on Exhaust Emissions: CRC Project E-83, Final report for the Coordinating Research Council by the University of California at Riverside, June.

Durbin, T.D., Miller, J.W., Johnson, K.C., Hajbabaei, M., Kado N.Y., Kobayashi, R., Liu, X., Vogel, C.F.A., Matsumura, F., Wong, P.S., and Cahill, T. (2011) Assessment of the Emissions from the Use of Biodiesel as a Motor Vehicle Fuel in California - Biodiesel Characterization and NOx Mitigation Study, Final report for the California Air Resources Board by the University of California at Riverside, the University of California at Riverside, and Arizona State University, October.

Durbin,T.D., J.W. Miller, T. Younglove, T. Huai, and K. Cocker. 2006. Effects of Ethanol and Volatility Parameters on Exhaust Emissions: CRC Project No. E-67. Final report for Coordinating Research Council, CRC Project No. E-67, January.

Durbin, T. D., J. W. Miller, J. T. Pisano, C. Sauer, T. Younglove, S. H. Rhee, T. Huai, and G.I. MacKay. 2003. The Effect of Fuel Sulfur on NH3 and Other Emissions from 2000-2001 Model Year Vehicles. Final report for Coordinating Research Council, CRC Project No. E-60, CE-CERT Technical Report No. 02-VE-59971-E60-04, May.

Response: We appreciate these references to past and future emission test programs. These references will be considered for the next update to MOVES.

E.1.2 Dr. Allen Robinson

The report provides some description of data sources. For example Table 12 points the reader to different EPA reports. That is valuable, but it is not clear that the information in the Table is sufficient if a reader wanted to truly understand where the source profile came from. I have been frustrated in the past trying to track down the source data for speciation profiles used in EPA models. Sometimes there are no references (not a problem here), but other times the references point to a large report (the case here). However, these reports can be massive documents that describe lots of data, but the reader has no idea which specific data were actually used to develop the input for the model (or how they were used). Maybe that is not an issue here (I have not gone and looked at the underlying reports), but I would encourage the authors to make sure the reader truly can figure out where the source profiles came from so that can start with the actual data and recreate the actual profiles. For example, the report could refer to specific emissions data form the underlying report.

The report seems to do a better on the PM side of things (PM speciation appendix, which is built upon this unpublished paper). It is very helpful that the PM appendix includes the actual profiles. I would encourage EPA to write a similar Appendix for the TOG speciation.

Response: The source for speciation profiles used in MOVES is EPA's SPECIATE database. SPECIATE is an EPA-maintained database of VOC and particulate matter (PM) speciation profiles for various emission sources, including mobile sources. This database comprises the record of each profile including its referenced source, testing methods, a subjective rating of the quality of the data, and other detailed data that allow researchers to decide which profile is most suitable for model input.

We note that the purpose of this MOVES document is not to replicate the SPECIATE documentation, but to describe the incorporation of the speciation process into MOVES2014 to provide model-ready species for air quality modeling, whereas previously the process occurred in SMOKE or as a pre-processor to SMOKE. The advantage of this change in approach is improved accuracy in speciation by regulatory class and fuel. The TOG profiles themselves are not new, nor is their use in air quality modeling, i.e., they have all been used previously to develop air quality modeling inventories for various rule makings. Because the PM speciation profiles were new at the time we submitted this document for review, we included these profiles in the appendix. One of the new PM profiles has since been published in peer-reviewed literature.

I was surprised that there modeling assumes that a constant EC/PM emission ratio for LDGV. This may be because the KCVES did not test many Tier 2/LEV2 vehicles. The CRC A74/E96 project found a pretty significant increase in the EC/PM for newer Tier 2/LEV2 vehicles. This has been presented in project reports and will be published shortly.

Response: We plan on examining these studies and may utilize their data to create speciation profiles for use with future versions of MOVES.

It also seems like default LDGV EC/PM ratio is not appropriate for GDI, which are becoming a larger part of the fleet. ARB has been doing a fair bit of testing of GDI – presumably those data are available. This will be critical for MOVES to be able to predict emissions from future fleets.

Response: We had limited data on speciation of GDI vehicles. We plan on including data on representative Tier 2/LEV II and later technology vehicles (including GDI vehicles) in the future.

E.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?

E.2.1 Dr. Tom Durbin

Sections 3.1 to 3.5 – The description here is not clear. In equation 1, defines a "speciation factor". Then later on the page there is a "speciationConstant" that is not defined. Similarly, "oxySpeciation" does not appear to be defined. The equations above table 4 are also not clear. Does this mean that the speciation is defined separately for the pure gasoline as opposed to the oxygenate part of the fuel. What is the voltowtpercentoxy term?

Response: This section was significantly revised in response to this comment, and similar comments from Dr. Allen Robinson. We removed former equation 1 from the main text to the appendix (as discussed in responses Robinson's comments, E.3.2).We reduced the equations referenced above from four to one, to help clarify that MOVES is using the same calculation for all oxygenates. We also included definitions for each of the terms, which were missing in the draft report. We added the complete derivation of the volume to Weight Percent Oxygen term to provide transparency on the assumptions used to derive this term. .

Table 13 is useful, providing a link with other models, as our Figure 2 and Figure 3.

Section 5.1 step 1 – It would be useful to provide a one sentence explanation as to why the EC/PM2.5 ratios vary across operating modes.

> *Response: We added a sentence explaining that EC is dependent on engine conditions, and varies accordingly. However, at this time we have only developed modal EC/PM emission rates for conventional diesel vehicles.*

Step 2 – last sentence "the nonECnonSO4PM as a whole…. (potential suggestion)

> *Response: The reviewer suggested new text to clarify the explanation of Step 2. We incorporated the suggestion.*

Step 4 – It would be useful to give a simple example of a basis temperature effect (effect on catalyst temp, for example).

> *Response: We added a simple example of temperature effects on PM emissions, (cool catalyst and additional fueling needed to start an engine at cold temperatures).*

Step 5 – For the crankcase emissions for the pre-2007 diesel, there are some important factors that are left out that would be useful in interpreting Table 14. In particular, from the MOVES2014 Heavy-duty Emissions Rate Report it indicates that "The crankcase emission factors shown in Table 51 are derived such that the crankcase PM2.5 emissions are 20 percent of the PM2.5 exhaust measurements, and have an EC/PM split of 1.57 percent."

> *Response: We added text clarifying why the ratios were derived differently for 2007-2050 diesel and other sources. We also added the text that the reviewer suggested, and we referenced the Heavy-Duty Report where the crankcase emission factors are discussed in more detail.*

Top of page 28 – refers to Table 7, but this deals with VOC/NMHC not PM.

> *Response: The cross-references to Tables and Figures were reviewed and updated where necessary.*

Step 8 – It seems like since there are only 7 categories that a table could actually be included with the speciation profiles used for each of the categories.

> *Response: We added Table C-1 which includes the seven $PM_{2.5}$ profiles used in MOVES2014.*

p. 3 Why was EC measured for considerably more vehicles for the KCVES than OC. What method was used for the EC?

> *Response: As discussed in more detail in Sonntag et al. (2013)[37], we used the photoacoustic black carbon measurements made on each vehicle as a surrogate for elemental carbon (EC). Sonntag et al. (2013)[37] contains further discussion that supports this decision, including a comparison of the IMPROVE-TOR elemental carbon and photoacoustic black carbon made on the same vehicle tests.*

The comparisons in Table A-8 [*now Table C-9*] and the associated discussion is valuable in that it ties the current estimates to earlier model estimates and data in the literature.

Under Table A-4 [*now under Table C-5*]. The discussion needs to be clarified about how OM is split into organic carbon and non-carbon organic matter using the relationship: OM = 1.2 * OC. The table seems to show that the OC is scaled down and then renamed OM, which is subsequently modified by the 1.2 factor. It seems that it would be best to start out by saying that the initial OC includes organic carbon, a positive artifact, and other non-carbon species associated with the organic carbon (such as hydrogen, oxygen, etc.).

Response: We added Equations 12, 13, and 14 with accompanying text to clarify how the corrected OC and NCOM values are calculated.

E.2.2 Dr. Allen Robinson

No response.

E.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.

E.3.1 Dr. Tom Durbin

The methods and procedures appear to be reasonable for this document. The bigger question is probably the description of the methods and the evaluation of the data sets, as described above. One major category that is missing is pre-2007 retrofit heavy-duty diesel engines and how these are modeled. Also, GDI vehicles for future years.

Response: See response E.4.2 and E.5.2 (Regarding GDI vehicles)

Although the silicone contamination from the connecting pieces from the transfer line can be removed, is it possible that some other PM species relating the transfer line heating/burning. I see in another section that there is some compensation for other species, but it reinforces the idea that EPA should consider a broader range of data sources in its modeling.

Response: Comparisons with literature on individual PM species measured from the KCVES are made within Sonntag et al. (2013)[37]*. We agree that including additional data sources in the future will improve the robustness of MOVES.*

Although the Kansas City study is one of the more recent comprehensive studies of gasoline PM, it is not obvious that fleet average composition profiles would be representative of the fleet going into the future. On page 2, it does indicate that there were differences in PM2.5 composition between different model year groups. If there are differences between Tier 0, Tier 1, and NLEV/Tier 2 vehicles, will a fleet average profile be adequate for the fleet going into the future? Of course, future generations of the model will need to include GDI vehicles, as more information on their PM species profiles become more available.

Response: As mentioned on page 40 and page 41, we used a fleet-average profile because it incorporates vehicles at representative deterioration, and we did not want to

extrapolate forward the PM speciation values based only on newer model year groups. Additionally, we plan to incorporate PM speciation data on GDI vehicles as mentioned.

Additionally, how are light-duty diesel vehicles accounted for in the model?

Response: The light-duty diesel emission rates for PM (EC and NonECPM) are identical to the light-duty gasoline emission rates in MOVES2014 as documented in the light-duty emission rate report[33]. MOVES2014 uses diesel PM speciation profiles to speciate the NonECPM emissions from light-duty diesel vehicles, as shown in Table 5-5.

E.3.2 Dr. Allen Robinson

I like the approach of defining nonECPM because EC is refractory while other components, in particular OC, are semivolatile. This addition is an important step towards implementing a more physically realistic treatment of OC. However, I am concerned that the model continues to treat OC as an inert, non-volatile component of the exhaust. Presumably MOVES is supposed to estimate the PM emissions at typical atmospheric conditions (not those in CVS). The problem is that the low levels of dilution commonly often used in vehicle testing campaigns such as the KCVES create high PM concentrations in the CVS. This biases the gas-particle partitioning of the OC. Few studies have quantified the behavior, but the recent CRC A74/E96 project demonstrates the issues with fleet of 60+ LDGV and MDDV/HDDV vehicles (see May et al. dx.doi.org/10.1021/es400782j | Environ. Sci. Technol. 2013, 47, 8288−8296, May et al. Atmospheric Environment 77 (2013) 128e139). At a minimum the report should point out this limitation that the emission rates may be overestimated because of partitioning biases. I would encourage EPA to start explicating accounting for these biases in both the MOVES emission rates and source profiles. This can be done using the volatility distributions in the May et al. papers and the measured CVS concentrations.

Response: As mentioned in the Toxics report (Section 2.1.2 Polycyclic Aromatic Hydrocarbons)4, the particulate matter (PM) emission rates are derived from emission test programs, but the gas-particle partitioning is not adjusted to be representative of ambient conditions. We agree that differences between the dilution conditions of the emission test programs and ambient conditions, introduce differences in the PM emissions. However, a comprehensive reevaluation of the PM emission rates was not within the scope of the updates for MOVES2014.

I was confused with section 3 which describes the method for converting between different classes of gas phase organics (NMOG, TOG, THC, etc.).

Response: This section has been significantly revised to improve clarity. Dr. Robinson's concern is addressed in more detail in his following comments.

First, Title of section 3. Hydrocarbon speciation. I found this confusing. Hydrocarbons are organic compounds that contain carbon and hydrogen. This is a subset of the organic, which can contain compounds in addition to C and H. This should be called total organic gas speciation.

Response: Title has been changed to Organic Gas Aggregations

Second I am concerned with defining the THC emissions based on what is measured by the FID. I realize that this is standard definition but it is not scientifically correct. The FID measures

carbon. A problem is that the measurement efficiency is species dependent (as mentioned in the document). The FID quantitatively measure carbons in hydrocarbons (organic compounds comprised of carbon and hydrogen) and the standard propane calibration works well. However, the FID can also measure some of the carbon in oxygenated organics (especially carbons not associated with oxygen atoms) so some of the signal in the FID comes from oxygenated organics, which are not hydrocarbons. Therefore, there is no straightforward interpretation of the FID signal, but it does detect more than just the hydrocarbon emissions.

Response: We have kept our current definition of total hydrocarbons. We discuss the issues regarding partial responses to FID measurements from oxygenated organics in the main document (Section 3) and we added details on calculating other organic gas classes from THC in Appendix A.

Third, I could not follow the equations used to convert between the different classes of organic gases (NMOG to NMHC, etc. – e.g. section 3.2). This correction seems to be relatively straightforward – it appears that you are simply using different ratios of, e.g. NMOG to FID defined THC. Not surprisingly, these ratios depend on vehicle MY and type of fuel.

Response: Only the equations that are used in MOVES are presented. Definitions of the terms (that were previously undefined) have been included in the report. The equations used for the derivation of parameters have been moved to Appendix A, as discussed in the next response. The parameters for all gasoline vehicles are presented together to improve interpretation and comparison of parameters between different fuel types and model years.

I will focus my comments on section 3.2 but the same comments to apply to the other sections (e.g. 3.3) that perform the same analysis. What is the basis of equation (1)? Some underlying physical or chemistry principle? How is equation (1) used? Is equation (1) used to derive un-numbered equations later on page 9? What is the definition CF is molar or mass carbon fraction? MPC is mass of what? per carbon? Where is FIDx defined – give table or reference? Is the speciation constant listed in Table 5 the same as the speciation factor defined by equation 1? If so then you need to reconcile the names. I tried played with equation with equation (1) but could not figure out some of the inputs. It should be clear that I found this whole section pretty confusing and do not have a basic understanding of what MOVES is doing, never mind being able to reproduce the calculations.

Response: Equation 1 in the draft report is an equation used to derive the NMOG/NMHC parameters, which are subsequently used in the MOVES calculation. This equation is not used within MOVES, but is one method to derive the speciation factors used in the MOVES calculations.

The derivation of the NMOG/NMHC ratios has been moved to a new appendix (Appendix A), where the equation, terms, are explained in much more detail. Example calculations are also added to demonstrate how the NMOG/NMHC parameters are calculated, to enable readers to reproduce the calculations using their own data. The NMOG/NMHC ratios are calculated using two methods. We also demonstrated that equivalent results can be obtained using both methods.

Similar changes were also made to the section concerning VOC/NMHC. The former equation 2 was removed from the main text, and more in depth discussion of the former equation 2 is included in Section A.3.

It seems that the key to calculating the needed ratios is not equation (1) but the un-numbered equations listed on page 9. The inputs for these equations appear to be given in Table 4 and 5. I assume that these values are fixed (or can the user input a difference volume to weight percent oxygen)? Where did these values come from? Derived from fuel analyses? Derived from fitting experimental data? If they are fixed, then it seems like one could get rid of Table 4 and simply replace Table 5 with the actual ratios used to convert between NMHC and NMOG for the different model year groups. That would be much simpler. I think that the equations make it appear that what is being done is more sophisticated then it is.

Response: We removed the former equation (1), and moved it to Appendix A. (see previous comment). In the revised report main text, we emphasize the equations MOVES uses, by changing them from a set of previously unnumbered equations, to a single equation (Equation 3), with defined variables. We did this to clarify that MOVES is using the same calculation for all oxygenates.

We added the complete derivation of the volume to Weight Percent Oxygen term (Equation 4), and added information in Table 3-2, to provide transparency on the assumptions used to derive this term.

We also added references to provide the data sources from which the parameters were derived for each model year group and fuel type.

Page 25 "Step 2" states that sulfate and particulate water emissions were obtained by speciation profiles. However, I thought these were calculated with the sulfate model?

Response: We added clarification that the sulfate and particulate water emissions are adjusted according to the sulfate calculator in Step 2.

The report should define what is meant by the ratios of means (or mass weighted means) used to create average profiles. Right now the report assumes the reader can knows this.

Response: We added clarification by adding the following sentence, defining the ratio of means.

"The ratio of means is calculated by first calculating the mean emission rate of the total $PM_{2.5}$, and the mean emission rate of each PM species (EC, OC, Fe, etc.). Then the speciation profile is calculated, by calculating the ratio of the mean emission rate from each species, to the mean $PM_{2.5}$ emission rate, e.g., mean(EC)/mean(PM)."

E.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.

E.4.1 Dr. Tom Durbin

Again, the most critical assumption appears to be where the datasets sufficiently cover the vehicle categories that are needed for the model. Additional categories that could be added include pre-2007 retrofit heavy-duty diesel engines and GDI vehicles for future years, as well as some of the data sets described above.

Response: See response to E.4.2 and E.5.2 (Regarding GDI vehicles)

Although the silicone contamination from the connecting pieces from the transfer line can be removed, is it possible that some other PM species relating the transfer line heating/burning.

Response: See our response to E.3.1 regarding silicone contamination.

It seems reasonable that the sample size might be too [low] ~~high~~ to capture high emitters in each of the model year groups, especially for newer model years. It would be interesting to know if the population of high emitters in the KCVES was comparable to that found in previous studies of high emitters, although many of those estimates were made in older studies.

Response: Nam et al. (2008)[74]conducted comparisons of the CO and HC measurements from the KCVES compared to I/M data, and concluded that the high emitter rates for older vehicles were comparable, but there was less certainty regarding the high emitter rates vehicles within the newer model year groups.

How different is the PM2.5 composition by model year groups? As this would be an important consideration in terms of using the fleet average approach.

Response: Sonntag et al. (2013)[37] provides a detailed comparison of the PM2.5 composition by model year groups, cold and hot starts, and pollutant. We felt the large amount of information is best presented in that paper rather than in this report.

There are some differences between the cruise and transient OC/PM factors. How was it determined that the transient cycle is more representative than the cruise for heavy-duty vehicles. Is this based on more urban driving?

Response: As shown in Table C-8 *the EC/PM fraction from the transient cycle (79 percent) compares very well with the EC/PM emission rates produced from MOVES (79.4 percent). As discussed on page 47, we used the transient cycle, because it is consistent with PM values produced by MOVES2014.*

For the 2007+ heavy-duty vehicles, while it is understandable to utilize measurements that are not background corrected and the associated negative numbers, it should be noted and understood that this would likely overestimate the contributions of different individual species. Nevertheless, the breakdown in Table A-9 [*now Table C-10*], with a predominantly sulfate contribution and minimal contribution from minor species seems reasonable.

Response: We added text on page 50, discussing that by not conducting background correction, we ae likely overestimating PM species that are subject to positive artifact like OC.

The discussion relating to the exclusion of sulfate-bound water provides a good basis for this assumption and is adequately described.

E.4.2 Dr. Allen Robinson

Limited data for GDI. This is not mentioned in report. ARB has been doing some work on this.

Limited data for CNG. This is acknowledged in the report. Not clear how critical a gap that is given the limited number of CNG vehicles (maybe important in places like LA or NYC with lots of CNG buses?).

Limited data for post-2007 diesels, especially on long-term performance on aftertreatment devices.

These limitations are expensive to address. They should be pointed out in the report.

> *Response: The purpose of this document is to describe how we have incorporated the speciation process, which previously occurred outside of the MOVES framework, into MOVES2014 to better provide model-ready species for air quality modeling. Limited data exist to support matching speciated emissions data with all combinations of MOVES' classifications (model-year group, regulatory class, fuel subtype, emissions process, etc.). We plan continue to improve and expand the application of speciated emissions data in future versions of MOVES as new data become available. We have added text in the report that describes our intention to improve future versions of the model with newer speciated emissions data.*
>
> *Additionally, see response to E.5.2 (Regarding GDI vehicles).*

E.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?

E.5.1 Dr. Tom Durbin

The resulting model inputs appear to be consistent with exhaust emissions formation and the associated literature.

The intercomparisons between the model inputs and the available data for the pre-2007 heavy-duty vehicles indicate that the model inputs are reasonably representative. The relatively low sulfate contribution in these profiles may not be appropriate for retrofit heavy-duty diesel vehicles, however.

> *Response: At this time, MOVES does not incorporate effects of retrofits on the default emission rates or speciation of PM emissions of pre-2007 trucks. MOVES has a retrofit importer[75] which can be used to adjust the emissions of pre-2007 trucks, but it does not change the TOG or PM Speciation of the retrofitted vehicles.*

E.5.2 Dr. Allen Robinson

The PM profiles were weighted using Kansas City MSA VMT data. How sensitive are the profiles to that assumption? If they are sensitive then that potentially creates a number of

concerns. How representative is that of other areas in the country? How representative are they of future vehicle fleets?

Response: We added two paragraphs in response to this point, regarding the sensitivity to the averaging assumptions, selection with Kansas City to represent the fleet average, and the need for incorporating data on newer port-fuel injected vehicles, and gasoline-direct (GDI) injected vehicles.

Section 4.2 – "But they are the major species by mass and reactivity" I am concerned about the gaps between speciated and total emissions. The standard approach (adopted here), assumes that the unspeciated portion of the NMOG behaves the same as the speciated. This likely is not the case when it comes to secondary organic aerosol (SOA) formation. The unspeciated emissions are likely a complex mixture of higher molecular weight species – these species contribute disproportionately to SOA formation relative to lighter species (e.g. propane).

Response: The purpose of this MOVES document is to describe the incorporation of the speciation process into MOVES2014 to provide model-ready species for air quality modeling (previously the process occurred in SMOKE or as a pre-processor to SMOKE). Issues involving the treatment of unknowns or unspeciated emissions pertain to sample measurement and analysis, speciation profile development, and chemical mechanism development and, as such, fall beyond the scope of this document. We will note that OTAQ's approach to developing real TOG speciation profiles from mobile source emissions data is to retain the unknown portion of the mass reported by analytical laboratory.

For $PM_{2.5}$ profiles, our current modeling needs only require organic carbon as a broad category, which does not require resolving the organic carbon into individual species and unknown species. Discussion on achieving mass-balance for the $PM_{2.5}$ profiles is in Appendix C for each profile.

"while assuring that the PM2.5 species achieved a 100 percent mass balance" I find these sorts of statements very concerning, especially given that these sorts of renormalizations are often poorly documented resulting in users not being aware of these assumptions. It is important to document if there are significant mass balance discrepancies, not just normalize them away. I realize that the profiles don't have a PM_unknown species, but enforcing mass balance may create other problems.

Other studies with diesel (e.g. Schauer et al. 1999 EST, Subramanian et al. 2009 EST) show a pretty significant gap in PM mass balance for diesels (sum of speciated low).

Response: We added the following text in Appendix C.3 to explain why we had over 100 percent mass closure species, because we did not use background corrected OC.

"Using uncorrected OC measurements likely contributed to the mass of the sum of the speciated measurements being higher than Teflon filter measurements (Subramanian et al. 2009)"

We incorporated the Subramanian et al. 2009 reference, which includes the references to Schauer et al (1999) work.

We give reasons in Section C.3 for why Khalek et al. (2011) did not background correct the OC measurements.

We also clarified the way in which the profile achieved mass balance, by adding paragraph (3) in Section C.3 by clarifying that the sum of the individual species were all renormalized to the $PM_{2.5}$ filter measurements, and citing the SPECIATE 4.2 documentation that provides information on how this is done.

E.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.

E.6.1 Dr. Tom Durbin

extra space – page 3 1st sentence (THC) ,; page 4 elemental carbon " 5; Page 7 last sentence 1 ." might be extra space; page 8 under table 3 (field meanbase rate in..; page 14 section heading … for Evaporative

add space – page 8 (TOG): h;

add comma – page 3 3rd sentence , such as; page 6 nonECPM , such as; page 28 2nd full paragraph (i.e., ;

page 3 sentence 4 add "to make TOG" to end of sentence.

page 3 last sentence first paragraph ..seems to be missing something

page 3 second paragraph 3rd sentence – under different measurement

page 4 elemental carbon – can a reference to the TOR method be provided?

page 4 chemical mechanism – to speed up the atmospheric…

page 5 integrated species – 3rd sentence CM-speciate is unclear

page 8 Table 4 not centered – some headings are centered but not others throughout

page 12 and 13 – there is an issue with the paging

page 14 & 15– issue with section numbering should be 3.4 and 3.5

page 15– section 4.1 1st sentence – MOVES2014 produces an or the output

page 28– 3rd full paragraph there is a reference in (EPA, 2014) and not number format

page 28– last paragraph "capability"

Response:

These suggestions regarding additional clarity in text, added references to the TOR method, and grammar were addressed.

Comments on the $PM_{2.5}$ Appendix C

p. 2. Missing high emitter study

page 1 2nd paragraph – updated speciation profiles changes

the references are numbered in the main document, but use the name/year format in the Appendix

add comma – page 3 (effective beginning 2006-2008),;

page 3 3rd paragraph. Missing period after …..161.2 ppm. Fuel sulfur….

page 3 2nd to last sentence. imnpute

page 5 The CRC E-55/59 is listed three different was ….E55/59, -55/59, E-55/59

page 6 first sentence – extra space 2010). [1]; and 1st full sentence begins with number; 2nd to last full sentence on page beings with a number

page 7 2nd paragraph "Instead we used calculated"; last sentence in paragraph impacteding

page 8 last sentence – the adjusted OC speciation factors are

Response: These suggestions regarding grammar, consistent formatting, and clarifying text were addressed.

E.6.2 Dr. Allen Robinson

Page 5 Intermediate PM section -- EC is not a "real" species in that it is not a distinct chemical substance but something that is operational defined. Although not defined, I assumed a real species was an actual chemical species like CO.

Response:

We clarified the definition of EC, in that it a measurement from thermal optical methods. We removed the 'real' for EC, and instead classify it more correctly as a CMAQ $PM_{2.5}$ species in the context in which it is discussed.

Page 7 Real speciation profile – A key shortcoming is that these real profiles are incomplete – they are typically missing around a quarter of the TOG mass. This point is mentioned later but should be mentioned here as well.

Response: The wording has been changed:

"Real speciation profile: ideally, a complete listing of the real species and their quantities for TOG. In practice, these profiles are incomplete; a certain fraction of the mass is unresolved."

The qualifier "start" is often used to characterize the emissions. Every instance of that should be further classified as cold or hot start, as that can make a big difference on emissions. Many times it was not clear what type of start the text was referring too.

Response: We added the following clarification regarding starts under "Process" in the glossary term.

Within each process, emission rates can potentially vary by operating mode. Running exhaust has different operating modes to represent, idle, coast, and different engine loads. Start exhaust has different operating modes to differentiate a continuum of starts between cold, warm, and hot starts. Definitions of the operating modes are contained in the MOVES2014 emission rate reports[30],[33], and evaporative reports.[12] For TOG and PM

speciation in MOVES, different speciation profiles can be applied to each processes, but not individual operating modes.

Page 3 defined **by** discrete – missing by

Response: We changed " which are defined discrete chemical species" to " which are discrete chemical species."

Page 3 although "county"? Not sure what county is

Response: Text changed to:

"Sometimes speciation profiles varied by county to account for combinations of ethanol fuel blends that varied by county."

Page 9 "as the all" delete the

Page 14 – "3.1 NMHC and VOC calculations …" this section heading is misnumbered.

Response: Corrected.

PM fractions of median profile greater than 1 → how much greater than 1?

Response: We added the following text. "The sum of the PM fractions from the median profiles is greater than one (112 percent of the Teflon mass for the Idle cycle, and 113 percent of the Teflon mass for the Transient Cycle)."

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