Speciation of Total Organic Gas and Particulate Matter Emissions from Onroad Vehicles in MOVES3

EPA United States Environmental Protection Agency

Speciation of Total Organic Gas and Particulate Matter Emissions from Onroad Vehicles in MOVES3

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

NOTICE

This technical report does not necessarily represent final EPA decisions or positions. It is intended to present technical analysis of issues using data that are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments.

EPA United States Environmental Protection Agency

EPA-420-R-22-017
July 2022

Table of Contents

1 Introduction

The United States Environmental Protection Agency's Motor Vehicle Emission Simulator—commonly referred to as MOVES—is a set of modeling tools for estimating air pollution emissions produced by onroad (highway) and nonroad mobile sources. MOVES estimates the emissions of greenhouse gases (GHGs), criteria pollutants and selected air toxics. The MOVES model is currently the official model for use for state implementation plan (SIP) submissions to EPA and for transportation conformity analyses outside of California. The model is also the primary modeling tool for estimating the impact of mobile source regulations on emission inventories, and thus, provides important inputs to air quality models.

In MOVES, some pollutant emissions are computed directly, based on measured emission rates[1,2]. Other pollutants are estimated as a function of the directly computed emissions. This is true of many of the air toxics, as described in the MOVES air toxics report[7]. For air quality modeling purposes, further chemical characterization of TOG and $PM_{2.5}$ is required. The process of apportioning aggregate organic gases and particulate matter into sets of separate components is called "speciation."

Note that MOVES applies speciation to all onroad sources and processes, except for brake and tire wear particulate matter emissions as discussed in Section 5.4. For nonroad, speciation is handled differently. Toxics are estimated in the nonroad portion of the model, similar to what is done for highway sources. However, detailed TOG speciation and speciation of PM2.5 are conducted as part of post-processing of MOVES nonroad results.[3]

1.1 Measuring Hydrocarbons and Particulate Matter

In addition to estimating emissions of pollutants that are discrete chemical compounds, such as carbon monoxide (CO) and sulfur dioxide (SO_2), MOVES 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 defined to include all organic gases.[4] 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.[a]

Similarly, particulate matter is operationally defined as the measured mass collected on a filter using EPA-defined sampling filter media, conditions, and practices.[5,6] $PM_{2.5}$ 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.

[a] Thus, differences in measurement methods need to be considered when comparing THC to TOG emission measurements.

1.2 MOVES Speciation Approach

MOVES produces 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[7], but are peripherally discussed in this report in the context of their use in deriving speciated TOG and PM emissions.

MOVES applies TOG and $PM_{2.5}$ speciation to produce the species need for air quality modeling. Generally, this speciation is done through a combination of estimation, subtraction of known pollutants and allocation of the remaining emissions based on profiles from EPA's SPECIATE database.[8] Air quality models such as CMAQ[b] need MOVES emission rates aggregated by source classification code (SCC), which is defined in MOVES by emission process, source type, fuel type and road type. However, as discussed in Section 4.2, the speciation profiles used for allocation are defined at a finer level of detail than SCC. By incorporating the speciation process within MOVES, MOVES can accurately calculate the speciated components of TOG and $PM_{2.5}$ at the appropriate level of detail of the speciation profiles and then aggregate the emissions to SCC.

1.3 Data Uncertainty and Limitations

Speciated emissions are collected in laboratory conditions using laboratory bench instruments that can analyze bag measurements of volatile organic compounds and can properly handle particulate matter filters for chemical analysis. Speciated measurements also are based on time-aggregated bag or filter measurements from engine or chassis dynamometer tests rather than time-resolved emission measurements (e.g. second-by-second measurements) that are used to inform emission rates in MOVES from vehicles operating in different operating modes.

As such, the number of vehicles and the range of vehicle operation conditions from which we have speciated data are more limited than the vehicle samples and operating conditions used to estimate emission rates of total hydrocarbon and $PM_{2.5}$ emission rates as documented in the emission rate reports.[1,2] Thus, the speciation results may be heavily impacted by test-to-test and vehicle-to-vehicle variability, For example, THC emissions for light-duty gasoline vehicle are based on hundreds or thousands of vehicles for each model year[1], and heavy-duty diesel vehicles measurements are based on hundreds of vehicles operating in real-world operation.[2] On the other hand, the speciation profile for model year 2001 and later light-duty gasoline vehicles is based on only three vehicles as discussed in Section 3.3[c], and the speciation profiles applied to model year 2010 and later diesel vehicles are based on three heavy-duty engines as discussed in Section 3.2.

In addition, available vehicle exhaust speciated measurements tend to be sampled from relatively new engines or vehicles. However, speciation likely changes as vehicles age. For example, new

[b] Defined in Section 2.5

[c] As discussed in the Toxics report, many of the key toxics are estimated from the fifteen vehicles tested in the Phase 3 of the Epact program.

vehicles with fully active catalysts likely have higher CH_4/THC ratios than older vehicles due to the relative effectiveness of newer aftertreatment systems in oxidizing the NMHC species as comparted to more difficult to oxidize methane.[9,10] However, we do not have sufficient data to model age-varying speciation ratios (CH_4/THC, NMOG/NMHC and VOC/NMHC) or speciation profiles, nor have we designed MOVES to handle varying speciation as vehicle age. Similarly, speciation testing is often conducted using regulatory cycles, while real-world speciation may differ. For now, our best approach is to select speciation data that are deemed the most representative of the vehicle fleet by emission process, fuel type, regulatory class, and model year.

Additional uncertainty comes from applying speciation profiles to technologies and processes that differ from what was tested. For example, we apply the diesel speciation profile developed from heavy heavy-duty engines to light-duty diesel emissions. Also, with the exception of the light-duty gasoline $PM_{2.5}$ speciation discussed in Appendix E, the speciation profiles are developed from vehicles that are properly functioning and with low accumulated mileage, but we apply them to fleet-average emission rates which include higher emissions due to aged and deteriorated engine and emission control systems. Similarly, the EPAct light-duty gasoline speciation profile is based on combined emission of start and running emissions. As a result, there is no resolution between start and running emissions in the speciation profile.

In addition to small sample sizes and limited testing scope, measurement deficiencies contribute to the uncertainty of MOVES speciated emission emissions. For example, as discussed in Section 3.2, the 2010-and-later model year heavy-duty diesel total organic gas speciation profile was corrected to remove three erroneous measurements artifacts. Speciation profiles also may not measure pollutants because the concentrations were below the detection limits of the measurement. As discussed in the toxics report[7], many individual species are emitted below detection limits during hot-running operation.

We have attempted to include qualitative discussions of the sources of uncertainty and application of the speciation data for each of the relevant sections of the report.

1.4 Updates to MOVES3

This document describes all the data and calculations used by MOVES3 in speciation calculations, including those that are unchanged from previous versions of MOVES. We have highlighted the updates made in MOVES3 from MOVES2014b.[11] These changes include: updates to total organic gases calculations (Section 3), and incorporation of a new TOG speciation profile for diesel exhaust for 2010 and later model years (Section 3.2 and Section 4.2). These updates were peer-reviewed in September 2017. Updates to the report in response to the peer-review are summarized in the peer-review materials on the EPA's science inventory webpage.[12]

Subsequent to the peer-review, we conducted a further analysis of the speciation of diesel exhaust for 2010-and- later model years. We adjusted the methane fraction (Section 3.6), and made revisions to the diesel 2010-TOG speciation profile (Appendix D). We also updated the speciation profile assigned to diesel refueling emissions as discussed in Section 3.2 and made clarifications to the text of the report.

1.5 Updates to MOVES3.0.4

Starting with version 3.0.4, MOVES3 offers the capability of speciating onroad emissions as a post-processing step with the objective of facilitating the use of state-of-the-science speciation profiles and chemical mechanisms without waiting for new public versions of MOVES that incorporate the latest speciation data. This new feature is geared in particular towards air quality modelers that wish to translate onroad emissions into chemical mechanism species. The post-processing of onroad emissions in MOVES3.0.4 is done via post-processing script incorporated in the Tools menu of the MOVES graphical user interface (GUI).

In terms of the speciation process in MOVES3, the model continues to provide speciated TOG and PM pollutants and users can continue selecting these pollutants when building the RunSpec. The only GUI changes that the user will notice is the addition of two new pollutants (Total Organic Matter and Residual PM) and the removal of chemical mechanisms options in favor of a single option to generate Residual TOG (NONHAPTOG). These new pollutants must be selected if the user desires to perform speciation of onroad emissions as a post-processing step. We note that the addition of new pollutants did not require changes to model calculations as MOVES already calculated these quantities implicitly during runtime; the effective changes in this version simply allow the selection of these pollutants as part of the model output. For further details on speciation outside of MOVES, see Appendix G.

2 Speciation Glossary

In the area of "speciation," many terms have multiple meanings. The definitions below provide the terms as they are used in the context of speciation in MOVES. We have grouped the terms into General, Organic Gas, Chemical Mechanism, Particulate Matter, and Databases, Models and Tools Terms.

2.1 General Terms

- 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 below

- Aggregate species: Groups of chemical compounds. 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.

- 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 or Particulate Matter. 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 or PM 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.[8]

2.2 Organic Gas Terms

- Hydrocarbon (HC): compound containing only carbon and hydrogen[13]. Because we cannot precisely measure emissions from combustion emissions using this strict definition, we often refer to hydrocarbon (HC) emissions synonymously with total hydrocarbon (THC) emissions which is a defined by the measurement method. For example, the National Emissions Inventory reports MOVES total hydrocarbon emissions (THC) as hydrocarbon (HC) emissions. At other times, we also use the term hydrocarbon more generally to include multiple measurements and definitions of organic gases that are primarily composed of hydrocarbons, including: non-methane hydrocarbons (NMHC), non-methane organic gases (NMOG), and total organic gases (TOG). When discussing HC emission in the MOVES technical reports, we typically only refer to gaseous HC emissions, and not HC emissions in the particulate phase, which is measured as organic carbon (OC) and non-carbon organic matter (NCOM).

- 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."[4] In MOVES, THC is often used synonymously with hydrocarbon (HC) emissions.

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

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

- Total Organic Gases (TOG): Total hydrocarbon (THC) emissions plus oxygenated hydrocarbons such as alcohols and aldehydes.[4]

- Volatile Organic Compounds (VOC): EPA defines VOC as any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate) which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity.[14] In mobile source testing, typically only a few compounds with negligible photochemical reactivity are measured in significant quantities. For use in MOVES in defining emission rates and application of speciation profiles, VOC is defined as TOG minus methane, ethane, and acetone (Equation 9).

2.3 Chemical Mechanism Terms

For MOVES3.0.4 we have removed the option of generating chemical mechanism species. However, this document will maintain the technical documentation for users that might still be using earlier versions of MOVES3.

Chemical mechanism (CM): In air-quality models, chemical mechanisms are simplified representations of the full array 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. Since the mapping is table-driven, MOVES has the structure in place to generate onroad vehicle CM species for any chemical mechanism. MOVES3 produces emissions output for CM species for the four chemical mechanisms listed in Table 2-1. CB6AE7 is newly added to MOVES3, the other chemical mechanisms are unchanged from MOVES2014b.

Table 2-1 Chemical Mechanisms in MOVES3

Chemical Mechanism	Description	MOVES Status
CB05	Carbon Bond developed in 2005[15]	Unchanged from MOVES2014b
CB6CMAQ	Carbon Bond Version 6[16] updated to model naphthalene as a separate species from XLK[17]	Unchanged from MOVES2014b
SAPRC07T	SAPRC07 updated with additional toxic species[18]	Unchanged from MOVES2014b
CB6AE7	CB6CMAQ updated for the AE7 Aerosol Module in CMAQ[19]; the largest impact for the MOVES speciation profiles is the addition of a new chemical mechanism species IVOC[d]	New in MOVES3

- 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, SAPRC07). All integrated species are mapped to CM species. For each chemical mechanism, the associated group of CM species can be referred to by the name of the mechanism, for example, CB05 species.

- Chemical mechanism 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. The mapping of real species is independent of emission 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, and is conducted using the Speciate Tool (Section 2.5)

- Integrated species: Real species for which MOVES produces emissions that are subtracted from TOG emissions to calculate "Residual TOG." The integrated species are individually speciated into CM species. MOVES3 integrates the 15 species shown in Table 2-2. The integrated species include all the organic gases estimated by MOVES, including naphthalene gas, but excepting all other polycyclic aromatic hydrocarbons

[d] In addition to adding IVOC to each MOVES profile, CB6AE6 added APIN to profile 8774 (Pre-2007 MY diesel exhaust)

Table 2-2 Integrated MOVES Pollutants

pollutantID	Pollutant Name
5	Methane (CH_4)
20	Benzene
21	Ethanol
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

- Residual TOG or NonHAPTOG: TOG that remains after subtracting integrated species. 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. MOVES reports emission rates of residual TOG as NonHAPTOG with pollutantID 88.

2.4 Particulate Matter Terms

- Primary Exhaust $PM_{2.5}$ - Total ($PM_{2.5}$). Primary particulate matter emissions from vehicle exhaust collected using a filter, measured downstream of a cyclone that removes particles with mean aerodynamic diameters greater than 2.5 microns. $PM_{2.5}$ = EC + nonECPM.

- Primary Exhaust PM_{10} - Total ($PM_{2.5}$). Primary particulate matter emissions from vehicle exhaust collected using a filter, measured downstream of a cyclone that removes particles with mean aerodynamic diameters greater than 10 microns.

- Intermediate $PM_{2.5}$ species: Groups of $PM_{2.5}$ species used to simplify calculations, improve computation time, and to 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, nonECPM, SO_4, and H_2O species are reported as MOVES outputs.

- Elemental Carbon (EC): "A descriptive term for carbonaceous particles based on chemical composition rather than light-absorbing characteristics. This term is often used as a synonym for black carbon."[20] Elemental carbon is measured through thermal optical techniques as particle-phase carbon that does not volatize at high temperatures in an

oxygen-free environment.[21] In tailpipe exhaust, EC is one measure of carbonaceous soot formed from fuel pyrolysis occurring during combustion.[22]

- 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." 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.

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

- Non-Carbon Organic Matter (NCOM): the mass of the oxygen, hydrogen, nitrogen and other elements present in particle-phase organic matter. 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.[23]

- 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. nonECPM = nonECnonSO_4PM + SO_4 + H_2O.

- Non-Elemental Carbon, Non-Sulfate Particulate Matter (nonECnonSO_4PM): MOVES intermediate species used to represent the $PM_{2.5}$ mass other than elemental carbon, sulfate, and associated water. NonECnonSO_4PM includes organic matter, elements, and ions. NonECnonSO_4PM 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.

2.5 Databases, Models and Tools

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

- SPECIATE: EPA's repository of organic gas and particulate matter (PM) speciation profiles from air pollution sources.[8] 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 (https://www.epa.gov/air-emissions-modeling/speciate)

- Speciation Tool: Estimates "split-factors" to translate inventory pollutants such as VOC to chemical mechanisms species. The Speciation Tool creates the mapping of

NONHAPTOG emissions from MOVES to the chemical mechanism species, using the relevant speciation profiles from SPECIATE, re-normalized without the integrated species.[24]

- 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. For onroad emissions, MOVES provides the emissions already speciated into the chemical mechanism species. (https://www.cmascenter.org/smoke/)

- SMOKE-MOVES: "A set of methodologies and software tools to help use output from MOVES as inputs to SMOKE."[25] MOVES is run in rates-mode to produce emission rates for different meteorological conditions, vehicle speeds (for running emissions), emission processes, road types, fuel types, and source types at different temporal and geographical domains to account for local differences in emissions. SMOKE-MOVES combines MOVES emission rates with respective vehicle activity to estimate emissions that are input into SMOKE.

3 Organic Gas Aggregations and Ratios

MOVES provides estimates of organic gas emissions in a number of different aggregations. Table 3-1 shows the composition of 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 of these species are also included in the glossary. In MOVES, total hydrocarbons (THC) is defined as hydrocarbons measured with a Flame Ionization Detector and includes methane and ethane. MOVES calculates emissions of total organic gases (TOG), non-methane organic gases (NMOG) and volatile organic compounds (VOC) using information regarding the organic gas speciation of emissions.

Table 3-1 Relationships among Organic Gas Aggregations in MOVES

pollutantID	pollutantName	Acronym	FID-HC	Methane	Ethane	Acetone	Alcohols	Aldehydes
1	Total Hydrocarbons	THC	Yes	Yes	Yes	No	No	No
79	Non-Methane Hydrocarbons	NMHC	Yes	No	Yes	No	No	No
87	Volatile Organic Compounds	VOC	Yes	No	No	No	Yes	Yes
86	Total Organic Gases	TOG	Yes	Yes	Yes	Yes	Yes	Yes
80	Non-Methane Organic Gases	NMOG	Yes	No	Yes	Yes	Yes	Yes

In MOVES, THC emission rates are the base organic gas emission rates as documented in the MOVES light-duty exhaust[1], heavy-duty exhaust[2], and evaporative[26] emission rate report from which each of the other organic emissions are estimated using the calculations documented in the following section. Gas-phase organic air toxics are calculated from VOC emissions as discussed in the MOVES air toxics report.[7]

3.1 Total Organic Gaseous Calculations

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

$$CH_4 = THC \times \frac{CH_4}{THC} \quad \textbf{Equation 1}$$

$$NMHC = THC \times \left(1 - \frac{CH_4}{THC}\right) \quad \textbf{Equation 2}$$

Following the calculation of NMHC, the MOVES algorithm calculates NMOG, VOC and TOG as shown in Equation 3 through Equation 5.

$$NMOG = NMHC \times \frac{NMOG}{NMHC} \quad \textbf{Equation 3}$$

$$VOC = NMHC \times \frac{VOC}{NMHC} \quad \textbf{Equation 4}$$

$$TOG = NMOG + CH_4 \quad \textbf{Equation 5}$$

In previous versions of MOVES, the data used to calculate CH_4/THC was not consistent with the data used to calculate ratios of organic aggregates.[27] In MOVES3, for many of the vehicles and emission processes, we determined CH_4/THC ratios from the SPECIATE profiles that are currently used in the model. The CH_4/THC ratios stored in the *MethaneTHCRatio* table in MOVES3 vary by emission process, regulatory class, fuel subtype, and model year. The methodology to calculate CH_4/THC ratios from SPECIATE data is presented in Section 3.2 and the calculated ratios for each profile are presented in Table 3-2.

Within MOVES, the NMOG/NMHC and VOC/NMHC ratios shown in Equation 3 and Equation 4 are called "speciation constants." In MOVES3, speciation constants were calculated for each SPECIATE profile used in MOVES in order to be consistent with the updated CH_4/THC ratios included in this release and with the TOG calculation chain.[e] These ratios continue to be stored in the *HCSpeciation* table which now also includes the key fields regulatory class and fuel subtype . The new speciation constant parameters are also presented in Table 3-2.

The calculation of NMOG and VOC in previous MOVES versions included additional terms that represented adjustments to correct for the oxygenated volume in the fuel (oxySpeciation, volToWtPercentOxy and oxyVolume parameters). In this latest release, different speciation

[e] Previous to MOVES3, the speciation constant parameters were calculated using either of two methods. The first method was based on the relative carbon fraction of each species and was first developed for MOBILE4.1. The second method was based on Equation 1066.635-1 of the CFR. For further details, the reader is directed to the MOVES2014 speciation report.[11]

constants are provided for fuel subtypes for different fractions of ethanol in gasoline (E0, E5, E8, E10, E15, E85), and the previous adjustments made to correct for oxygenated volume in the fuel were removed, simplifying the equations as shown in Equation 3 and Equation 4. The new methodology removes the capability of MOVES to adjust NMOG and VOC according to other oxygenated compounds such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME). However, fuel market projections indicate that additives other than ethanol are unlikely to return to the market, supporting the removal of these parameters from the model.

3.2 Ratios for Evaporative Emissions and Most Exhaust Emissions

We use SPECIATE profiles to derive CH_4/THC, NMOG/NMHC and VOC/NMHC for all emissions processes and vehicle classes except exhaust emissions from 2001-and-later light-duty gasoline vehicles, exhaust emissions from flex-fuel vehicles using E85 fuel, CNG exhaust, and the CH_4/THC fractions for 2010-and-later heavy-duty diesel exhaust, as discussed in the following subsections.

The speciation profiles in MOVES3 were obtained from the SPECIATE database.[8] Each profile has a detailed list of measured compounds and reports their weight as percentage of TOG. The calculation of NMOG for each profile was done by simply subtracting CH_4 from TOG as shown in Equation 6.

$$NMOG = TOG - CH_4 \qquad \textbf{Equation 6}$$

The calculation of NMHC is based on Equation 1066.635-1 in the Code of Federal Regulations. The equation provided in the CFR was rearranged as shown in Equation 7 to solve for NMHC using NMOG calculated in the previous step as an input.

$$m_{NMHC} = m_{NMOG} + \rho_{NMHC} \times \sum_{i=1}^{N} \frac{m_{OHCi}}{\rho_{OHCi}} \times RF_{OHCi_{[THC-FID]}} - \sum_{i=1}^{N} m_{OCHi} \qquad \textbf{Equation 7}$$

Where:

m_{NMOG} = mass of NMOG in the exhaust.
m_{NHMC} = mass of NMHC in the exhaust.
ρ_{NMHC} = 576.816 g/m3 which is the effective C1-equivalent density of NMHC as specified in §1066.1005(f).
m_{OHCi} = mass of oxygenated species i in the exhaust.
ρ_{OHCi} = C1-equivalent density of oxygenated species i as specified in 40 CFR 1066.605-1. For methanol, the density is 1332.02 g/m^3; for ethanol, the density is 957.559 g/m^3; for acetaldehyde,

the density is 915.658 g/m^3; for formaldehyde, the density is 1248.21 g/m^3; and for propanol, the density is 832.74 g/m^3.
$RF_{OHCi[THC\text{-}FID]}$ = response factor of a THC-FID to oxygenated species i relative to propane on a C1-equivalent basis as determined in 40 CFR 1065.845. The RF for acetaldehyde is 0.5; for formaldehyde is 0; for ethanol is 0.75; for methanol is 0.63 and for propanol is 0.85.

After NMHC and NMOG are calculated, the calculation of THC is done as shown in Equation 8. Once THC is calculated, the CH_4/THC can then be determined.

$$THC = NMOG \times \frac{NMHC}{NMOG} + CH_4 \qquad \textbf{Equation 8}$$

Finally, VOC is calculated following the definition used in MOVES, where methane (CH_4), ethane (C_2H_2) and acetone (C_3H_6O) are subtracted from TOG emissions as shown in Equation 9.

$$VOC = TOG - CH_4 - C_2H_2 - C_3H_6O \qquad \textbf{Equation 9}$$

Table 3-2 presents the ratios determined for each SPECIATE composite profile. Information on the data behind each SPECIATE profile is provided in more detail in Appendix A.

Table 3-2 notes the assignment of the derived speciation ratios to different model years, processes, fuel subtypes, and regulatory classes. For gasoline exhaust, we use profiles 8750a and 8751a to represent gasoline exhaust for 2000 and earlier light-duty vehicles. For other gasoline regulatory classes (motorcycles and heavy-duty vehicles), the same profiles were used for all model years.

Table 3-2 Updated CH_4/THC and Speciation Constant Parameters from SPECIATE Profiles for MOVES3

Profile Number	Profile Description	Emission Process	Fuel Subtype	Vehicles	CH_4/THC Ratio	NMOG/NMHC Ratio	VOC/NMHC Ratio
95120[f]	Liquid diesel	Evaporative Permeation	Diesel, biodiesel	All diesel	0	1	1
8750a	Pre-Tier 2 E0 exhaust	Running, starts exhaust and crankcase	Conventional Gasoline	Pre-2001 LD gasoline	0.142	1.024	0.996
				All MC and non-LD gasoline			
8751a	Pre-Tier 2 E10 exhaust	Running, starts exhaust and crankcase	RFG, E10, E8, E5	Pre-2001 LD gasoline	0.146	1.037	1.008
				All MC and non-LD gasoline			
8753	E0 Evap	Evaporative (vapors, leaks, refueling spillage)	Conventional Gasoline	All gasoline	0	1	1
8754	E10 Evap	Evaporative (vapors, leaks, refueling spillage)	E10, E8, E5	All gasoline	0	1.071	1.071
8766	E0 Evap perm	Evaporative Permeation	Conventional Gasoline	All gasoline	0	1	1
8769	E10 Evap perm	Evaporative Permeation	E10, E8, E5	All gasoline	0	1.129	1.129
8770	E15 Evap perm	Evaporative Permeation	E15	All gasoline	0	1.175	1.175
8774	Pre-2007 MY HDD exhaust	Running, starts, extended idle exhaust and crankcase	Diesel, Biodiesel	Pre-2007 diesel	0	1.145	1.124
		APU		Pre-2024 APU			
		Running, starts exhaust and crankcase		Pre-2007 LD diesel			
8775	2007-2009 HDD exhaust	Running, starts exhaust and crankcase	Diesel, Biodiesel	2007+ LD diesel	0.589	1.343	1.285
		APU		2024+ APU			
		Running, starts, extended idle exhaust and crankcase		2007+ HD diesel			
95335a	2010+ HDD exhaust	Running, starts exhaust and crankcase	Diesel, Biodiesel	2010+ LD diesel	0, Not Used[g]	1.085	0.965
		Running, starts, extended idle exhaust and crankcase		2010+ HD diesel			

Table 3-2 (continued)

Profile Number	Profile Description	Emission Process	Fuel Subtype	vehicles	CH_4/THC Ratio	NMOG/NMHC Ratio	VOC/NMHC Ratio
8869	E0 Headspace	Refueling displacement vapor loss	Conventional Gasoline	All gasoline	0	1	1
8870	E10 Headspace	Refueling displacement vapor loss	E10, E8, E5	All gasoline	0	1.037	1.037
8871	E15 Headspace	Refueling displacement vapor loss	E15	All gasoline	0	1.175	1.175
8872	E15 Evap	Evaporative (vapors, leaks, refueling spillage)	E15	All gasoline	0	1.118	1.118
8934	E85 Evap	Evaporative permeation	E85, E70	All gasoline vehicles running on high ethanol blends	0	1.501	1.501
		Evaporative (vapors, leaks), refueling displacement and spillage losses		All gasoline vehicles running on high ethanol blends			

[f] Profile 95120 is based on NMOG and we assume that there is no methane in liquid diesel fuel. In addition, no oxygenated species are measured in the profile (formaldehyde, acetaldehyde, or ethanol), nor any non-volatile organic compounds (ethane, and acetone), thus the CH4/THC, NMOG/NMHC and VOC/NMHC values are 0, 1, and 1, respectively.

[g] MOVES uses a 0.38 CH_4/THC ratio based on a literature review discussed in Section 3.6

For vapor venting, fuel leaks, and fuel spillage loss emissions from E0 and E10, the speciation constants are based on SPECIATE profiles from the Auto/Oil Air Quality Improvement Research Program (profiles 8753 and 8754).[h] The speciation profiles for refueling displacement vapor loss (profiles 8869, 8870, and 8871) for E0, E10, and E15 fuels were based on measurements conducted by EPA.[28]) Profile 8872 used for vapor venting, leaks, and refueling spillage for E15 fuels is based on SPECIATE profile 8754 (a composite profile developed from the Auto/Oil Air Quality Improvement Research Program) and data collected in the EPAct/V2/E-89 program on E10 and E15 fuels. For evaporative permeation emissions, MOVES uses speciation constants developed from three ethanol blend levels (E0, E10, E15) from the CRC E-77 program (profiles 8766, 8769, 8770).[29] In the CRC E-77 programs the test procedure specifically separated the evaporative emissions mechanisms, therefore there was an apparent ethanol effect on permeation but not a clear RVP effect.

The speciation constants for all evaporative emission processes from E85-fueled vehicles are calculated from SPECIATE profile 8934 developed from the CRC E-80 report.[30] The speciation profile used for diesel refueling emissions, (which only include liquid diesel spillage loss in MOVES[26]) was updated in MOVES3 to be based on a liquid diesel SPECIATE profile 95120.[f]

For pre-2007 diesel emissions (both light-duty and heavy-duty), MOVES uses speciation profile 8774, which is based on a review of speciated diesel emissions on pre-2007 model year engine technologies. MOVES uses the pre-2007 NMOG/NMHC value for diesel auxiliary power units (APUs; processID 91) for all model years prior to 2024 because they are not subject to the same control as on-highway diesel engines. For 2007 to 2009 model year light-duty and heavy-duty diesel vehicles, MOVES uses speciation profile (8775) based on data from Phase 1 of the Advanced Collaborative Emissions Study (ACES)[31], which includes diesel engines equipped with diesel particulate filter, and is the technology used to meet the heavy-duty 2007 diesel standards.[32] MOVES also applies the ACES Phase 1 speciation profile to 2024 and later auxiliary power units because it is anticipated they would use diesel particulate filters to meet the APU PM standards promulgated as part of the Phase 2 medium and heavy-duty greenhouse gas regulation.[33]

In MOVES3 we incorporated a new speciation profile (95335a) to 2010 and later diesel vehicles based the ACES Phase 2 test program.[34] This program tested three heavy heavy-duty 2011 model year engines equipped with diesel particulate filters and selective catalytic reduction systems that are representative of current diesel technologies used to achieve the 2010 heavy-duty emission standards. The engines and aftertreatments were tested new, and the emissions of NMHC were over 99% below the 2010 emission standards. Furthermore, emissions of the majority of individual organic compounds were below the levels measured from the ACES Phase 1 program, including methane emissions, which were below the detection limit in ACES Phase 2, but which contributed over 50% of the TOG emissions in the ACES Phase 1 program.[35]

[h] The CRC E-77 program[29] observed a significant effect for both RVP and ethanol in the diurnal emissions data largely due to the vapor venting breakthrough emissions which were vented outside of the SHED using special procedures as defined in the individual study reports. As noted in the 2017 peer-review[12], there is likely an accompanying effect of RVP on vapor venting emissions (from both vapor venting and fuel displacement venting) , and both RVP and ethanol content should be considered as factors when developing updated vapor venting speciation profiles in future test programs.

Due to the low level of TOG emissions, the relative error of the speciation fractions of TOG is high in the ACES Phase 2 program. We have developed methane fractions from a literature review of emission studies on MY 2010-and-later heavy-duty diesel engines as discussed in Section 3.6. In addition, we removed alcohol species from the original profile (95335) that are likely measurement artifacts as documented in Appendix D. In addition, many of the measurements were near detection limits, and individual species measurements showed inconsistencies when compared to the emission trends of groups of gaseous hydrocarbons from ACES Phase 1 (see Appendix D). Given the limited number of tests and low emission levels measured, it is not possible to determine whether these inconsistencies represent real differences, test to test variability, or measurement uncertainties.

Despite the uncertainties regarding the Phase 2 speciation profile, we have incorporated it into MOVES (including the NMOG/NMHC and VOV/NMHC ratios) because it is the most comprehensive chemical sampling program available for exhaust from MY 2010 and later heavy-duty diesel technology. We recommend further speciated measurements of modern heavy-duty diesel engine exhaust, including vehicles with aged and deteriorated aftertreatment systems that likely emit higher concentrations of organic gas and particulate matter emissions.

3.3 Ratios for 2001-and-Later Light-Duty Gasoline Exhaust

We determined ratios of CH_4/THC, NMOG/NMHC and VOC/NMHC for exhaust emissions from Tier 2 (model year 2001-and-later) vehicles running on gasoline-ethanol blends (0 percent - 15 percent ethanol) using bag-specific data from the EPAct Phase 1 program[36] In contrast, the SPECIATE profiles (8756, 8757, and 8758) developed from the EPACT/V2/E-89 program combined the start and running emissions (Table 4-1). As presented in this section, the speciation constants varied significantly by bag, and we determined that it was preferable to use the resolved speciation constants based on the bag data from the same data set used to derive the SPECIATE profiles.

EPAct Phase 1 was designed to collect data from light-duty vehicles running on low-level ethanol blends. Three vehicles (MY 2008) were tested to generate data for the three bags required to create speciated composite profiles. The tests involved 9 runs using fuel with 0 percent ethanol, 6 runs using fuel with 10 percent ethanol and 7 runs using fuel with 15 percent ethanol. Further information on vehicles, fuels and testing is detailed in the EPAct Phase I report.[36] The data corresponding to the runs used for this analysis is listed in Appendix A.

For ethanol levels between 0-15 percent, the average CH_4 and THC emissions were calculated and subsequently a ratio of means was determined (i.e., CH_4avg/THCavg). To verify if there was a statistically significant trend with ethanol composition, a linear regression between these ratios and ethanol composition was performed (Figure 3-1). The regression analysis indicated that the slope was statistically significant (significance level < 0.05) for start emissions but not for running emissions. Therefore, CH_4/THC for starts are specific for each ethanol composition, but for running an average CH_4/THC across all low-level ethanol blends is used. The linear fit for starts was used to interpolate CH_4/THC values for E5 and E8 fuel compositions used in MOVES3 for which no SPECIATE profiles are available.

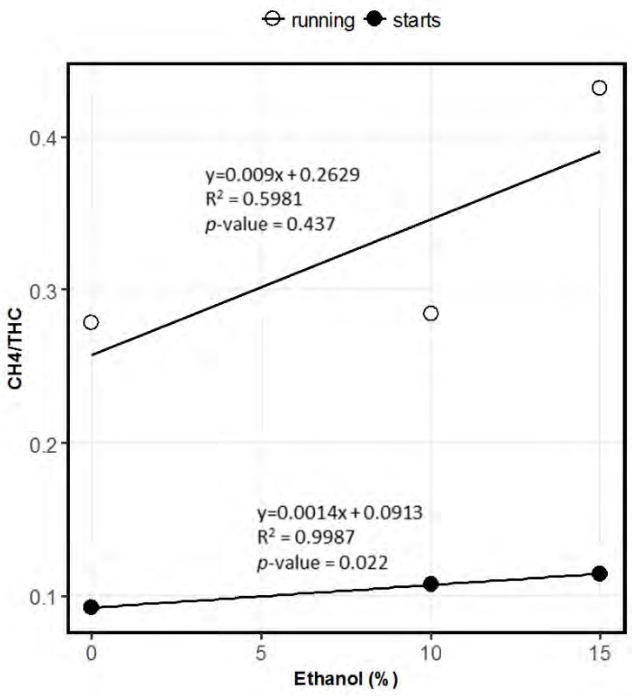

Figure 3-1 Relationship between CH_4/THC Ratios and Ethanol Composition for Tier 2 Vehicles using Low-Level Ethanol Blends

The speciated data used to determine NMOG/NMHC and VOC/NMHC for Tier 2 vehicles corresponds to the same EPAct Phase 1 runs referred to in the determination of CH_4/THC ratios for these vehicles. Data from Bag 3 was subtracted from Bag 1 to determine cold start emissions. NMOG, VOC and NMHC were calculated for each test following the methodology described in Section 3.1. The reported speciation constant parameters were determined as a ratio of means (i.e., NMOGavg/NMHCavg or VOCavg/NMHCavg) for each ethanol composition. The linear relationship between speciation constant parameters and ethanol composition was statistically significant for starts ($\alpha < 0.05$), but not for running emissions (Figure 3-2). Therefore, like the CH_4/THC ratios, we report speciation constant parameters for start emissions (Table 3-3) at each ethanol composition analyzed, whereas for running emissions (Table 3-4) we report an average across the ethanol compositions. This approach is supported by a previous study performed by the Oak Ridge National Laboratory (ORNL)[37] which focused on the estimation of NMOG emissions from 68 vehicles using mid-level ethanol blends. The ORNL study found that given very low emissions normally measured in bag 2 and the level of scatter associated with them, the recommended approach was to use a constant NMOG/NMHC ratio across ethanol compositions.

We apply the resulting EPAct Phase 1 speciation constant values for all light-duty gasoline vehicles in model year 2001 and later. As we note in the discussion of the light-duty $PM_{2.5}$ speciation profile (Appendix E.1), modern gasoline direct injection vehicles have significantly different composition of particulate matter emissions. We anticipate that there are also significant differences in the organic gas speciation. We plan to incorporate light-duty gasoline organic gas speciation profiles and constants in MOVES and SPECIATE as such data on representative, in-use vehicles become available.

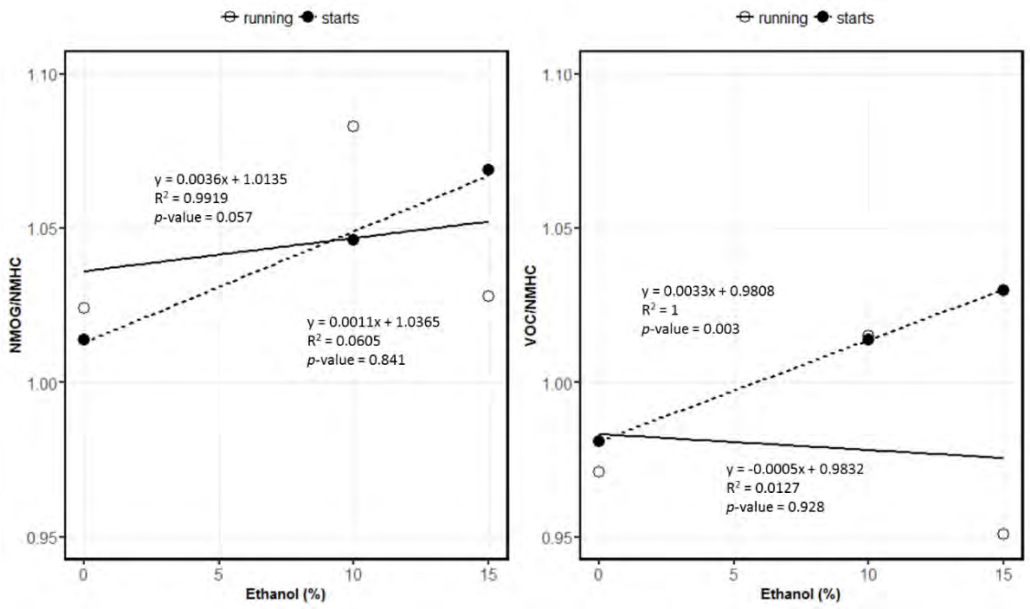

Figure 3-2 Relationship between Speciation Constant Parameters and Ethanol Composition for Tier 2 Vehicles using Low-Level Ethanol Blends

Furthermore, the reported NMOG/NMHC ratio for 0 percent ethanol level in the ORNL study was 1.0302 which corresponds to the intercept of the best-fit line for the current analysis. For comparison purposes, we also determined the NMOG/NMHC ratio for the SPECIATE running profile 8756 (Tier 2 E0 exhaust) using the methodology described in this report. The NMOG/NMHC ratio we estimated was 1.038, showing reasonable agreement with the value determined by the ORNL study.

Table 3-3 CH_4/THC and Speciation Constant Parameters for Start Emissions from Tier 2 Vehicles

Bag data from profile	Profile description	Emission process	Fuel Subtype	Affected vehicles	CH_4/THC Ratio	NMOG/NMHCRatio	VOC/NMHC Ratio
8756	Tier 2 E0 exhaust	Start exhaust and crankcase	Conventional Gasoline	2001+ LD gasoline	0.091	1.014	0.981
N/A	Tier 2 E5 exhaust	Start exhaust and crankcase	E5	2001+ LD gasoline	0.098	1.031	0.997
N/A	Tier 2 E8 exhaust	Start exhaust and crankcase	E8	2001+ LD gasoline	0.102	1.042	1.007
8757	Tier 2 E10 exhaust	Start exhaust and crankcase	E10	2001+ LD gasoline	0.105	1.046	1.014
8758	Tier 2 E15 exhaust	Start exhaust and crankcase	E15	2001+ LD gasoline	0.112	1.069	1.030
8855	Tier 2 E85 exhaust	Start exhaust and crankcase	E85, E70	Pre-2001 MY flex-fuel vehicles running on high ethanol blends	0.273	1.511	1.454
8855	Tier 2 E85 exhaust	Start exhaust and crankcase	E85, E70	MY 2001+ flex-fuel vehicles running on high ethanol blends	0.273	Not Used [a]	Not Used [a]

[a] MY 2001 and later E85 fueled vehicles use the Tier 2 E10 NMOG/NMHC and VOC/NMHC ratios as discussed in Section 3.4

Table 3-4 CH_4/THC and Speciation Constant Parameters for Running Emissions from Tier 2 Vehicles

Bag data from profile	Profile description	Emission Process	Fuel Subtype	Affected vehicles	CH_4/THC Ratio	NMOG/NMHC Ratio	VOC/NMHC Ratio
8756	Tier 2 E0 exhaust	Running exhaust and crankcase	Conventional Gasoline	2001+ LD gasoline	0.338	1.038	0.974
N/A	Tier 2 E5 exhaust	Running exhaust and crankcase	E5	2001+ LD gasoline	0.338	1.038	0.974
N/A	Tier 2 E8 exhaust	Running exhaust and crankcase	E8	2001+ LD gasoline	0.338	1.038	0.974
8757	Tier 2 E10 exhaust	Running exhaust and crankcase	E10	2001+ LD gasoline	0.338	1.038	0.974
8758	Tier 2 E15 exhaust	Running exhaust and crankcase	E15	2001+ LD gasoline	0.338	1.038	0.974
8855	Tier 2 E85 exhaust	Running exhaust and crankcase	E85, E70	Pre-2001 MY flex-fuel vehicles running on high ethanol blends	0.822	1.234	0.934
8855	Tier 2 E85 exhaust	Running exhaust and crankcase	E85, E70	MY 2001+ vehicles running on high ethanol blends	0.822	Not Used[b]	Not Used[b]

[b] MY 2001 and later E85 fueled vehicles use the Tier 2 E10 NMOG/NMHC and VOC/NMHC ratios as discussed in Section 3.4

3.4 Ratios for Flex Fuel Vehicles using High Ethanol Blends (E85)

The CH_4/THC ratios and speciation constants used for high-level ethanol blends (E70 and E85), shown in Table 3-3, were developed from three high-level ethanol fueled vehicles tested as part of the EPAct/V2/E-89 program.[38] The CH_4/THC, NMOG/NMHC and VOC/NMHC ratios are used to estimate CH_4, NMHC, NMOG, VOC, and TOG emissions for pre-2001 model year E85 vehicles. The CH_4/THC ratios are also used to estimate CH_4 and NMHC emissions for 2001 and later model year vehicles.

The NMOG and VOC emissions from high-level ethanol fueled vehicles for 2001 and later model year vehicles in MOVES are calculated differently. As discussed in the fuel effects report[51], NMOG and VOC emission rates for high-level ethanol exhaust emissions are based on the EPAct/V2/E-89 data, plus data from three other testing programs with a total of 19 Tier 2 FFV vehicles tested on both E10 gasoline and E85 fuels. No significant differences were observed in the NMOG emissions between the Tier 2 vehicles tested on E10 and E85 fuels. As such, MOVES calculates NMOG and VOC emissions from NMHC emissions calculated using

E10 CH4/NMHC ratios, and fuel effects primarily using E10 fuel properties.[i] NMOG and VOC emissions for E85-fueled vehicles are then calculated using the NMOG/NMHC and VOC/NMHC ratios from the Tier 2 E10 Profile (8757). We recognize this approach can result in discrepancies between NMHC and VOC emissions from E85-fueled vehicles particularly if the methane ratios are significantly different between ratios between the EPAct/V2/E-89 study (3 vehicles), and the larger 19-vehicle dataset.[j] One of the reasons this approach was taken was due to the limited data on E85 emissions; it reflects the need for further research on E85 emissions. A more detailed discussion of NMOG and VOC emissions from high ethanol blend fueled vehicles is included in the MOVES Fuel Effects Report.[51]

3.5 Ratios for CNG Vehicles

The speciation values for compressed natural gas (CNG) exhaust are derived from a study conducted by the California Air Resources Board on a CNG lean-burn transit bus with and without an oxidation catalyst (Ayala et al. 2003[43]). The derivation of the CNG methane and speciation constants are documented in Appendix B. In MOVES, we apply the speciation values from the "without control" tests to pre-2002 model year CNG vehicles, and the values "with the oxidation catalyst" to 2002 and later vehicles as shown in Table 3-5. The data used to develop the speciation constants was not complete enough to develop full speciation profiles. In the absence of mobile-source CNG speciation profile, we use SPECIATE profile 1001[k] to speciate the residual TOG (Table 4-1).

Table 3-5 CH_4/THC and Speciation Constant Parameters for CNG Exhaust

Profile Description	Model Years affected	Emission process	CH_4/THC Ratio	NMOG/NMHC Ratio	VOC/NMHC Ratio
CNG lean-burn	1960-2001	Starts and running exhaust and crankcase	0.886	1.9	1.68
CNG lean-burn oxidation catalyst	2002-2060	Starts and running exhaust and crankcase	0.959	1.24	0.93

The peer-reviewers of the MOVES2014 Speciation report[11] recommended we consider using more recent studies of CNG vehicles. In response, we compared the CH_4/THC, NMOG/NMHC, and VOC/NMHC developed from Ayala et al. (2003)[43], to more recent studies including data on stoichiometric three-way catalyst (TWC) technology engines as shown in Table 3-6. The MOVES CH_4/THC value falls within the range of recent studies. Larger differences between

[i] With the exception of sulfur level, see the discussion in the MOVES3 fuel effects report[51]

[j] Only a fraction of the vehicles tested in the 19 vehicle-test sample reported methane measurements. If the methane fraction is significantly different in the EPAct/V2/E-89 program compared to the 19 vehicle-test sample compared to the EPAct/V2/E-89 program used to derive the NMOG rates, this could create the observed inconsistency in the NMOG/NMHC and VOC/NMHC ratios.

[k] As shown in Table A-4, Speciate profile 1001 is based on a measurements from a stationary CNG engine

studies are observed for the NMOG/NMHC and VOC/NMHC ratios, particularly for the uncontrolled lean-burn values. The differences can be explained by the fact that the CNG exhaust from Ayala et al. (2003)[43] used in MOVES contain high formaldehyde emissions, particularly for uncontrolled lean-burn buses, which causes high NMOG/NMHC ratios. The large variation in these values may also be due to differences in measurement methods, particularly because non-methane hydrocarbons constitute a small fraction of the total organic gas emissions from CNG buses.

The MOVES speciation value for the catalyst -equipped engines used for MY 2001 and later, are slightly outside the range of values obtained in other studies, but still compare relatively well considering the variability among the different studies. As such, we have maintained the use of them in MOVES. The variation among the different values could be used to assess the relative uncertainty of the methane, NMOG, and VOC emissions estimated in MOVES.

Table 3-6 Comparison of CH_4/THC and Speciation Constant Parameters for CNG Engines from several studies

Study	Technology	Model year	Cycles tested	CH_4/THC Ratio	NMOG/NMHC Ratio	VOC/NMHC Ratio
CEC-2015[39]	Lean-burn	2005	CBD[a]	0.853	1.062	1.062
	Stoichiometric TWC	2011-2013	CBD	0.881	1.183	1.183
Thiruvengadam et al.[40,41]	Stoichiometric TWC	2008-2009, 2011	UDDS[b]	0.982	1.096	1.096
	Dual-Fuel High-Pressure Direct Injection (HPDI)	2011	UDDS	0.683	1.031	1.031
CE-CERT[42]	Stoichiometric TWC[c]	2014	UDDS	0.941	ND[d]	ND
	Stoichiometric TWC	2014	CBD	0.719	ND	ND
Ayala et al.[43] (MOVES)	Lean-burn, no control	2000	CBD	0.886	1.9	1.68
	Lean-burn, Oxidation catalyst	2000	CBD	0.959	1.24	0.93

Notes:
[a] Central Business District
[b] Urban Dynamometer Driving Schedule
[c] TWC= Three-way catalyst
[d] ND: Not Determined

Currently, we do not estimate evaporative or refueling emissions from CNG vehicles in MOVES and thus, have no CH_4/THC, NMOG/NMHC, and VOC/NMHC ratios for these processes. This is an area for future research.

3.6 CH_4 Ratios for 2010-and-Later Heavy-Duty Diesel Vehicles

The pre-2007, 2007-2009, and 2010-and-later model years, CH_4/THC ratios for heavy-duty diesel based on the assigned speciation profiles in Table 3-2 are 0%, 58%, and 0%. The 2010-and-later speciation profiles (95335a) is developed from the ACES Phase 2 program, where methane emissions were below the detection limit.[35] Methane and NMHC emissions below the detection limit has also been reported in other studies that measured emissions from MY 2010 and later heavy-duty vehicles.[44,87]

However, due to the large inconsistency in the methane fractions between the 2007-2009 and 2010-and-later model years, and our relative uncertainty regarding the methane fraction from the Phase 2 profiles (See Appendix D), we conducted a literature review on methane emissions from MY 2010 and later heavy-duty diesel trucks. Three different studies from the literature and EPA certification data reported significant CH_4/THC ratios from MY 2010+ heavy-duty exhaust as shown in Table 3-7. From the reported values, we calculated an average CH_4/THC ratio of 38%, which we use in MOVES3 for all MY 2010 and later diesel-fueled vehicles.

We recognize there is uncertainty regarding representative driving conditions and vehicles. Quiros *et al.*(2016,2017)[45,46] showed that methane fractions varied by driving cycle, but there was not a consistent trend in the methane ratios from low to higher load operation. Due to the wide variety of results, we decided to take an average of each of the cycle-average values from each of the studies shown in Table 3-7, except for the local drayage value from Quiros *et al.*[45,46] which was deemed an outlier value (90% methane). This approach was deemed the most reasonable to yield a representative methane fraction for in-use driving.

The vehicles sampled also tended to be vehicles with low mileage accumulation. The reported odometer readings that were available were relatively low for heavy-duty diesel trucks (less than 200,000 miles). The EPA certification data are obtained from test-engines with fully functioning aftertreatment systems that have not been applied in-use. In theory, the CH_4/THC ratios are likely to decrease as vehicles age, as the aftertreatment system becomes less efficient at oxidizing NMHC. However, we don't have the data nor the MOVES structure to support this, and we are using the methane fraction to represent all vehicle ages for MY 2010-and-later diesel vehicles.

As discussed in Section 3.2, we are continuing to use the ACES Phase 2 speciation program for the speciation factors for NMHC from 2010-and-later exhaust (i.e. NMOG/NMHC and VOC/NMHC ratios, and the speciation profile to estimate the chemical mechanism species from the integrated species and NONHAPTOG). Most of the studies evaluated did not provide sufficient speciation measurements from which to develop speciation profiles or even speciation factors beyond the methane ratios. Future work could develop updated speciation ratios and profiles from Hays *et al.*(2017)[47] and other relevant studies.

Table 3-7 CH_4/THC Ratios for MY 2010+ Heavy-Duty Diesel Trucks

Source	Vehicle #	Reg Class	Model Year	Technology	Odometer	Cycle	CH_4/THC (%)
Quiros *et al* 2016[45] Quiros *et al* 2017[46]	4	HHD	2013-2014	DOC+DPF+SCR	40K to 186K	Hill Climb	18%
						Interstate	25%
						Regional	20%
						Local Drayage	90%
						Near Dock	22%
						Urban	33%
Hays *et al* 2017[47]	3	LHD2b3, LHD45, MHD	2011	LHD2b3: DOC+NAC+DPF LHD45 & MHD: DOC+SCR+DPF	4K to 35K	CARB MHD UDDS and HD-UDDS	42%
Karavalakis *et al* 2016[48]	1	HHD	2014	DOC+DPF+SCR	NA	UDDS	68%
						HHDDT Transient	55%
EPA Certification Data[49,a]	9 engine families	LHD	2016-2019	DOC+DPF+SCR	NA	Transient (TR) Comb Adj	47%
	16 engine families	MHD					39%
	10 engine families	HHD					46%
						Average = (excluding the Local Drayage from Quiros *et al.*)	38%

Note: DOC-Diesel Oxidation Catalyst, DPF-Diesel Particulate Filter, NAC-NOx Adsorber Catalyst, SCR-Selective Catalytic Reduction

[a] The methane fractions from the EPA certification data were calculated as average of ratios from each engine family, rather than a ratio of averages, which would yield lower methane fractions

4 TOG Chemical Mechanism (CM) Speciation

4.1 Overview

TOG speciation required for air quality models is different than PM speciation, due to the concept of chemical mechanisms. Chemical mechanisms (see Section 2.3) are used to simplify the thousands of individual organic compounds into a manageable set of CM species used for air quality modeling. 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 (See Section 5).

As defined in Section 2.3, “integrated species” are pollutants from which MOVES directly calculates chemical mechanism emissions. MOVES maps the gaseous integrated species (e.g. benzene) and the remaining TOG (referred to as Residual TOG or NONHAPTOG) to the CM species used by each chemical mechanism, in units of moles, for use by air quality models. In

this report, this mapping process of the Residual TOG to chemical is referred to as TOG speciation. The calculation of Residual TOG is shown in Equation 10 below.

Residual TOG = TOG - MOVES gaseous integrated species **Equation 10**

Currently, we integrate 15 individual MOVES gaseous species, listed in Table 2-2. While a select list of PAHs, dioxins, and furans are also computed by MOVES, they are not integrated (with the exception of one PAH species, naphthalene). The other PAHs, dioxins and furans are not included in the integrated species in part because they compose a small percentage of the Residual TOG emissions; incorporating them into the integrated species would require additional data processing without a significant impact on the chemical mechanism estimates.

The profiles used in this process, and the mapping of real species into CM species are discussed in the following sections.

4.2 Real TOG 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. However, 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, based on SPECIATE, that we are using in MOVES, together with the fuels, affected vehicles, and MOVES emission processes to which they apply. SPECIATE is the EPA's repository of volatile organic gas and particulate matter (PM) speciation profiles from air pollution sources.[8] 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 A-4. lists the referenced sources of the real speciation profiles used in MOVES.

MOVES applies the speciation profile by model year, fuel subtype, regulatory class and emission process; Appendix C provides the assignment at this level. Fuel subtype refers to fuel groupings within the larger fuel types of gasoline, diesel, CNG and E85 as detailed in Table C-3. Regulatory class refers to vehicle type as defined in Table C-2. Emission process refers to the emission's physical mechanism. As listed in Table C-1, MOVES has twelve emission processes that are relevant for TOG speciation. 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 light-duty[1] and heavy-duty exhaust[2] emission rate report and the evaporative report.[26] In MOVES, different TOG and PM speciation profiles can be applied to different processes, but not to individual operating modes.

Table 4-1 Speciation Profiles Used for Onroad TOG Emissions[l]

Profile	Profile Description	Fuel	Affected Vehicles	Emission Process
1001	CNG Exhaust	CNG	All CNG Transit Buses	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
95120[m]	Liquid Diesel	Diesel	All Diesel	Evap Permeation, Evap Fuel Vapor Venting, Evap Fuel Leaks, Refueling Displacement Vapor Loss, Refueling Spillage Loss
8753	E0 Evap	E0	All Gas	Evap Fuel Vapor Venting, Evap Fuel Leaks, Refueling Spillage Loss
8754	E10 Evap	E10	All Gas	Evap Fuel Vapor Venting, Evap Fuel Leaks, Refueling Spillage Loss
8756	Tier 2 E0 Exhaust	E0	2001+ LD Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8757	Tier 2 E10 Exhaust	E10	2001+ LD Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8758	Tier 2 E15 Exhaust	E15	All Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8766	E0 Evap Permeation	E0	All Gas	Evap Permeation
8769	E10 Evap Permeation	E10	All Gas	Evap Permeation
8770	E15 Evap Permeation	E15	All Gas	Evap Permeation
8774	Pre-2007 MY HDD Exhaust	Diesel	Pre-2007 HD Diesel	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust, Crankcase Extended Idle Exhaust, Extended Idle Exhaust
8774	Pre-2007 MY HDD Exhaust	Diesel	Pre-2024 APU	Auxiliary Power Exhaust
8774	Pre-2007 MY HDD Exhaust	Diesel	Pre-2007 LD Diesel	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8775	2007-2009 HDD Exhaust	Diesel	2007-2009 LD Diesel	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8775	2007-2009 HDD Exhaust	Diesel	2007-2009 HD Diesel	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust, Crankcase Extended Idle Exhaust, Extended Idle Exhaust

[l] Appendix C provides a complete mapping of the TOG speciation profiles to modelYearGroupID, processID, fuelSubTypeID, and regClassID.

[m] While MOVES maps the liquid diesel profile to several processes, MOVES only estimates emissions from refueling spillage loss. The other evaporative and refueling processes from diesel vehicles have zero emissions.

Table 4-1 (continued)

Profile	Profile Description	Fuel	Affected Vehicles	Emission Process
8775	2007-2009 HDD Exhaust	Diesel	2024+ APU	Auxiliary Power Exhaust
95335a	2011 HDD Exhaust	Diesel	2010+ LD Diesel	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
95335a	2011 HDD Exhaust	Diesel	2010+ HD Diesel	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust, Crankcase Extended Idle Exhaust, Extended Idle Exhaust
8855	Tier 2 E85 Exhaust	E70, E85	E70, E85	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8869	E0 Headspace	E0	All Gas	Refueling Displacement Vapor Loss
8870	E10 Headspace	E10	All Gas	Refueling Displacement Vapor Loss
8871	E15 Headspace	E15	All Gas	Refueling Displacement Vapor Loss
8872	E15 Evap	E15	All Gas	Evap Fuel Vapor Venting, Evap Fuel Leaks, Refueling Spillage Loss
8934	E85 Evap	E70, E85	E70, E85	Evap Permeation, Evap Fuel Vapor Venting, Evap Fuel Leaks, Refueling Displacement Vapor Loss, Refueling Spillage Loss
8750a	Pre-Tier 2 E0 Exhaust	E0	Pre-2001 LD Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8750a	Pre-Tier 2 E0 Exhaust	E0	All MC and non-LD Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8751a	Pre-Tier 2 E10 Exhaust	RFG, E10	Pre-2001 LD Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust
8751a	Pre-Tier 2 E10 Exhaust	RFG, E10	All MC and Non-LD Gas	Running Exhaust, Start Exhaust, Crankcase Running Exhaust, Crankcase Start Exhaust

4.3 TOG Chemical Mechanism Species

The mapping of real species to CM species is mechanism-specific. Each chemical mechanism is based on a mapping of real organic gas species to one or more CM species. The atmospheric chemistry is then modeled using these CM species. As outlined in Table 2-1, MOVES3 can output chemical mechanisms using following four mechanisms: CB05, CB6CMAQ, SAPRC07T, and CB6AE7. All the species in each real speciation profile of TOG are mapped to the chemical mechanism species associated with each chemical mechanism. Then all the occurrences of each CM species for each mechanism are added up to give molar quantities of chemical mechanism species (lumped species) for each chemical mechanism.

While the original "real speciation profiles" include the "integrated species," the MOVES estimates for the 15 integrated species listed in Table 2-2 are based on as much or more detailed and accurate information than available from applying the real speciation profiles. Therefore, we independently calculate and subtract these species from the real speciation profiles and then develop CM speciation for the residual TOG (referred to as NONHAPTOG). For example, the benzene fraction estimated by MOVES for light-duty gasoline vehicles accounts for the benzene content in the gasoline fuel, whereas the benzene fraction estimated in the TOG speciation profiles is based on the benzene level in the tests conducted for the speciation measurements.

The CM speciate profiles are generated outside MOVES using the Speciation Tool.[24] After separately mapping the integrated species and the residual TOG to CM species, MOVES adds all CM species together to produce CM species output. All chemical mechanism species output is in units of moles. MOVES emission rates are combined with activity in the SMOKE-MOVES process (Section 2.5), and emissions are subsequently spatially gridded and allocated to the hourly level in SMOKE[n], to then be used by an air quality model, such as CMAQ. Figure 4-3 is a diagram of the process of TOG speciation conducted by MOVES for air quality modeling.

[n] Defined in Section 2.5

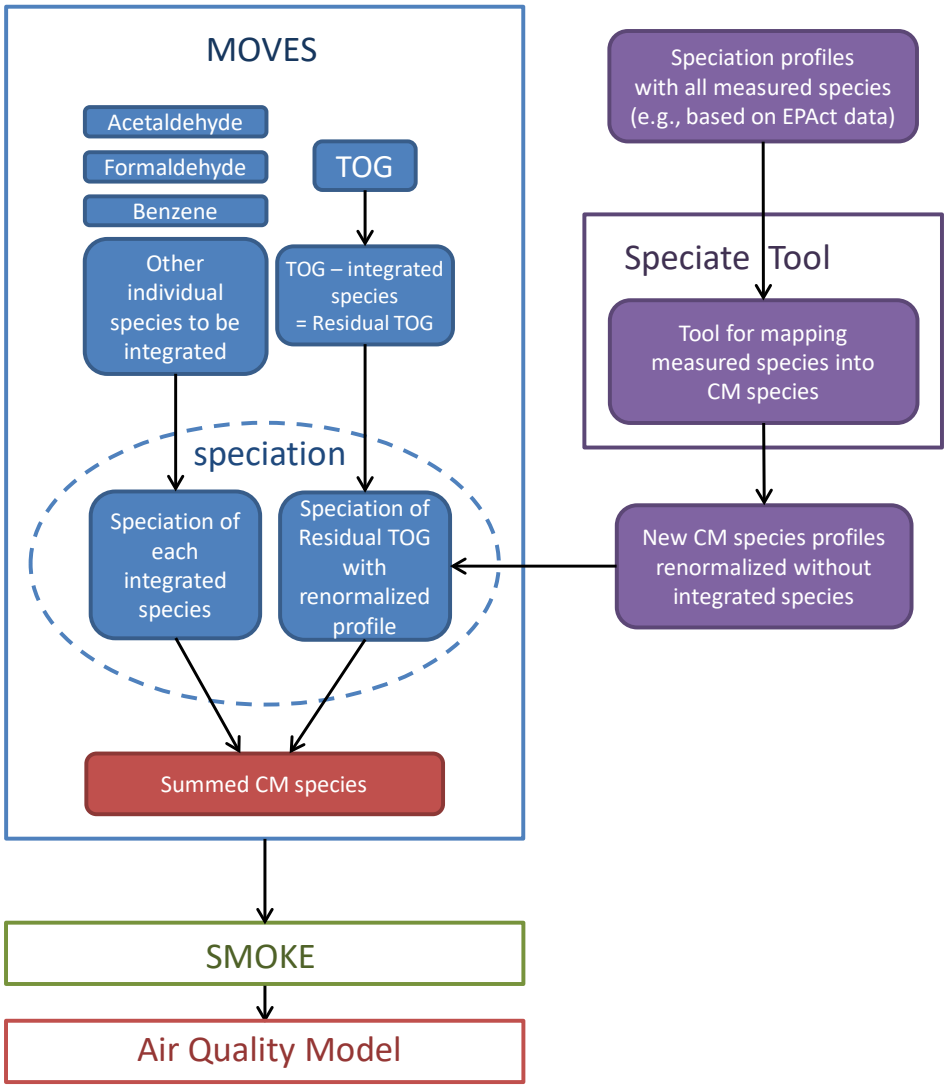

Figure 4-3. Diagram of the Process of TOG Speciation for Air Quality Modeling as it occurs with MOVES

5 $PM_{2.5}$ Speciation

5.1 MOVES $PM_{2.5}$ Species

MOVES estimates the 18 $PM_{2.5}$ species outlined in Table 5-1.

Table 5-1 AE6 Chemical Mechanism $PM_{2.5}$ Species

$PM_{2.5}$ Species	AE6 Species Name
Primary organic carbon	POC
Elemental carbon	PEC
Sulfate	PSO4
Nitrate	PNO3
Ammonium	PNH4
Non-carbon organic matter	PNCOM
Iron	PFE
Aluminum	PAL
Silicon	PSI
Titanium	PTI
Calcium	PCA
Magnesium	PMG
Potassium	PK
Manganese	PMN
Sodium	PNA
Chloride	PCL
Particulate water	PH2O
Primary unspeciated $PM_{2.5}$[o]	PMOTHR

Similar to the methods used to speciate total organic gases, MOVES uses speciation profiles to estimate individual $PM_{2.5}$ species. The $PM_{2.5}$ Speciation profiles were developed to directly estimate the species used for the CMAQ Aerosol Module, version 6, or "AE6;"[24] all other measured $PM_{2.5}$ species are aggregated into PMOTHER.[o] If needed, post-processing can be used to aggregate the AE6 species into the PM2.5 species used with the Comprehensive Air Quality Model with Extensions (CAMx).[24]

[o] Primary unspeciated $PM_{2.5}$ (PMOTHR) is calculated as 1- sum(AE6 species fractions) and can include both unspeciated $PM_{2.5}$ mass as well as measurements of other $PM_{2.5}$ species that are not included in the AE6 chemical mechanism species..

5.2 $PM_{2.5}$ Speciation Calculations

Figure 5-1 and Figure 5-2 provide an overview of the algorithm used to calculate speciated and total exhaust PM emission rates in MOVES. The steps used to calculate $PM_{2.5}$ emissions and $PM_{2.5}$ speciation are outlined in nine steps below. Steps 1 – 4 are outlined in Figure 5-1.

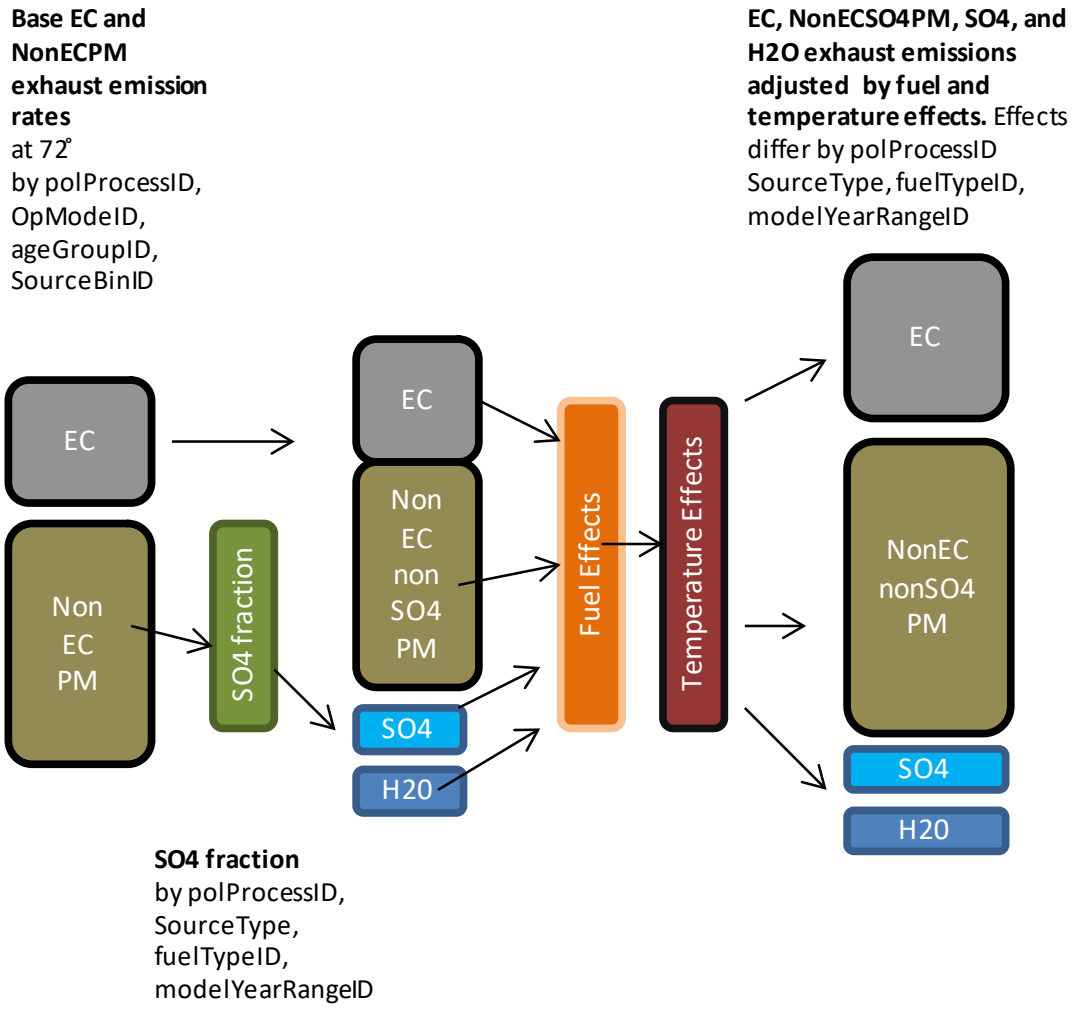

Figure 5-1 Flow Chart of Calculation of the Intermediate $PM_{2.5}$ Emission Rates

Step 1. MOVES stores $PM_{2.5}$ exhaust emission rates in the emissionRateByAge table by pollutant process (start, running, extended idle), operating mode, sourcebin (fuelType, engine technology, regulatory class, model year), and vehicle age. MOVES stores the base exhaust rates for $PM_{2.5}$ in two primary components (EC and nonECPM), so that the EC/$PM_{2.5}$ ratio can vary across operating modes.[p,2]

[p] Within MOVES, modal EC/PM ratios are developed for conventional diesel vehicles (pre-2007) as documented in the MOVES3 heavy-duty exhaust report.[2] Modal EC/$PM_{2.5}$ ratios have not been developed for other vehicle types (gasoline, CNG, ethanol, and 2007+ diesel), and the EC and NonECPM emission rates for these sourcetypes and fuels have a constant ratio across operating modes.

Step 2. MOVES calculates sulfate (SO_4) and particulate water (H_2O) emissions as a fraction of nonECPM. The sulfate to nonECPM fraction (SulfatenonECPMFraction) used in MOVES is derived from the $PM_{2.5}$ speciation profiles documented in Table 5-5. MOVES stores this value in the sulfateFraction MOVES table. The sulfate calculator, documented in the MOVES fuel effects report,[51] adjusts the sulfate fraction based on the default or user-supplied fuel sulfur level. The remaining nonECPM is renamed nonECnonSO_4PM. 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 ambient 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, nonECnonSO_4PM, SO_4, and H_2O emissions are each adjusted using the same temperature adjustments, because our data does not support individual temperature adjustments.[61] The temperature effects are documented in the Emission Adjustments report.[50]

Step 4. MOVES adjusts the intermediate species (EC and NonECnonSO_4PM) according to the fuel properties and the applicable fuel effects (e.g., EPAct fuel effects model for 2001 and later light-duty gasoline). The fuel adjustments and calculators are described in the Fuel Effects Report.[51]

Steps 5 – 8 are outlined in Figure 5-2.

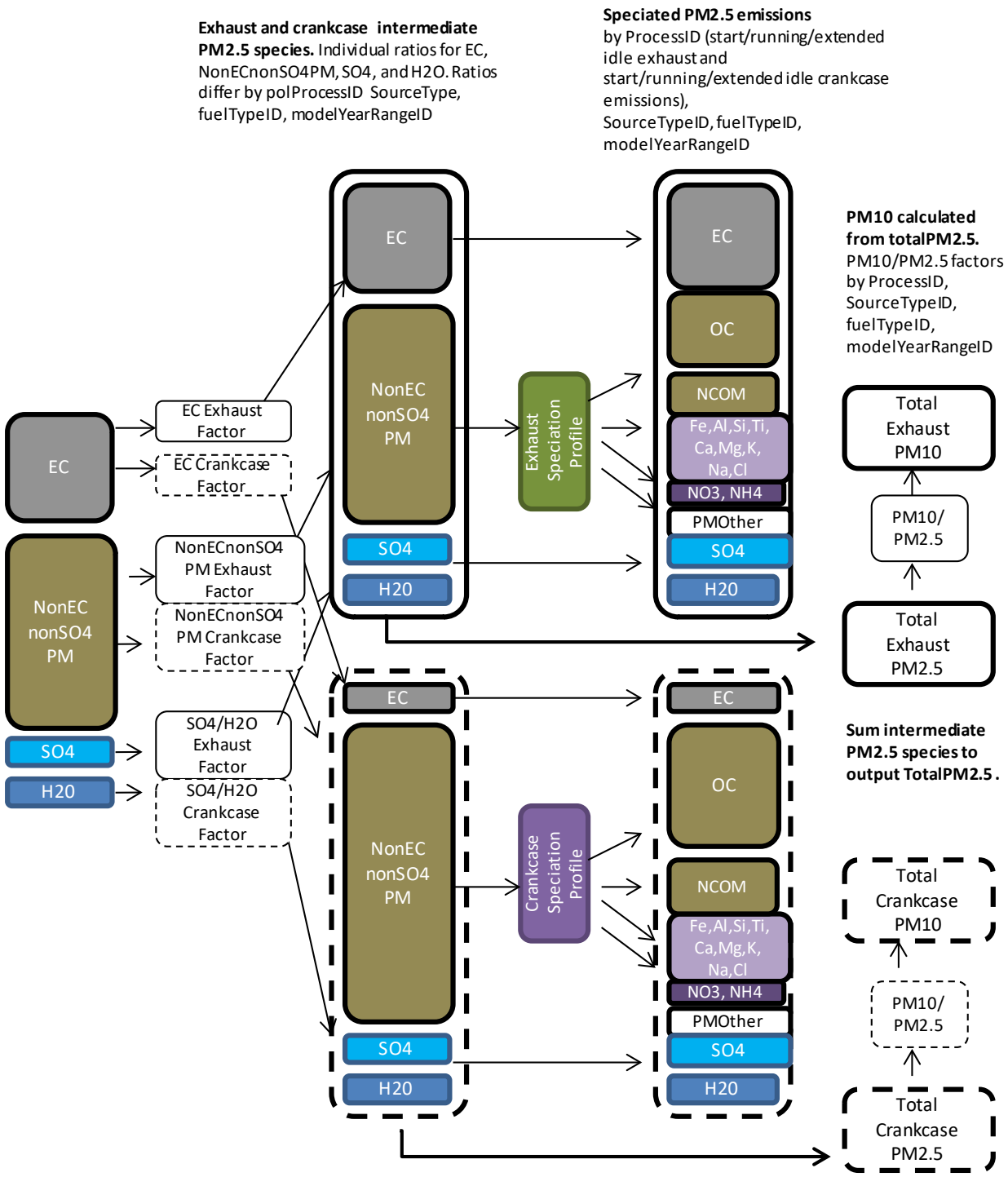

Figure 5-2 Flow Chart of Calculation of Exhaust and Crankcase $PM_{2.5}$ and PM_{10} Emission Rates, and $PM_{2.5}$ Exhaust and Crankcase Speciation

Step 5. Exhaust and crankcase emissions are calculated from the intermediate exhaust $PM_{2.5}$ species (EC, NonECnonSO4PM, SO_4, and H_2O), 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. Example crankcase ratios for heavy-duty diesel vehicle are shown in Table 5-2.

For most vehicles types (including pre-2007 and 2010_+ heavy-duty diesel, gasoline, and 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.

For 2007-2009 MY heavy-duty diesel engines, crankcase emissions are assumed to be included in the tailpipe 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 2007-2009heavy-duty diesel, the exhaust and crankcase ratios sum to one for each PM subspecies.

The exhaust and crankcase ratios are applied by intermediate subspecies, to account for differences in $PM_{2.5}$ speciation between crankcase and tailpipe particulate matter emissions. For example, MOVES models higher EC/PM composition for exhaust than for crankcase emissions for pre-2007 conventional[q] diesel, using the exhaust and crankcase ratios as shown in Table 5-2. For MY 2007-2009 heavy-duty diesel vehicles, the exhaust and crankcase ratios are the same across intermediate $PM_{2.5}$ species, yielding the same $PM_{2.5}$ composition for exhaust and crankcase emissions. This is intended because the PM2.5 speciation profile is estimated from measurements that contained both tailpipe exhaust and crankcase exhaust emissions.[2]

The sources of the crankcase emission factors are documented in the light-duty exhaust [1] and heavy-duty exhaust emissions rates reports.[2]

[q] We use the term “conventional diesel” to refer to diesel trucks which lack exhaust aftertreatment systems such as diesel particulate filters (DPF), diesel oxidation catalysts (DOC), and selective catalytic reduction systems (SCR) that modern diesel trucks use to meet the EPA 2007/2010 heavy-duty emission standards.

Table 5-2 Example Heavy-duty Diesel Exhaust and Crankcase Ratios by Pollutant, Process, Model Year Group, and Source Type

		1960-2006 Heavy-duty diesel (all heavy-duty source types)			2007-2009 Heavy-Duty diesel (all heavy-duty source types except single unit trucks)[a]		
Pollutant		Start	Running	Extended Idle	Start	Running	Extended Idle
EC	Exhaust	1	1	1	1	0.971	0.707
nonEC nonSO4-PM		1	1	1	1	0.971	0.707
SO4		1	1	1	1	0.971	0.707
H2O		1	1	1	1	0.971	0.707
EC	Crankcase	0.007	0.004	0.007	0	0.0290	0.293
nonEC nonSO4-PM		0.367	0.937	0.367	0	0.0290	0.293
SO4		0.367	0.937	0.367	0	0.0290	0.293
H2O		0.367	0.937	0.367	0	0.0290	0.293

[a]The single-unit truck source types have varying crankcase ratios by model year to account for vehicles with closed-crankcase systems as discussed in the MOVES3 Heavy-duty Exhaust Report.[2]

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. MOVES calculates primary exhaust and crankcase PM_{10} emissions from the primary $PM_{2.5}$ emissions using $PM_{10}/PM_{2.5}$ ratios. The $PM_{10}/PM_{2.5}$ ratio used for primary exhaust and crankcase emissions are listed in Table 5-3. MOVES 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 MOVES for PM_{10} emissions, because it is not needed for air quality modeling purposes.[r,52] The derivation of the $PM_{10}/PM_{2.5}$ ratio is presented in Appendix F.

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. MOVES calculates the remaining $PM_{2.5}$ species, by applying speciation profiles to the adjusted nonECnonSO4 fraction. The nonECnonSO4 speciation profiles are calculated from the

[r] Within CMAQ, the US EPA assumes a single speciation profile for all anthropogenic coarse PM.[52]

$PM_{2.5}$ profiles in Table 5-5, by removing EC, SO_4, and H_2O and then renormalizing the remaining species. These values are stored in the MOVES pmSpeciation tables, with a column key 'inputPollutantID' specifying that the PM speciation profile is based on nonECnonSO4 (pollutantID 120). The data sources and derivation for the $PM_{2.5}$ profiles are documented in Appendix E.

Step 9. Although not shown in Figure 5-1 or Figure 5-2, MOVES can calculate additional particulate-phase species, required for the National Emission Inventory (NEI) and National Air Toxics Assessment (NATA). Listed in Table 5-4, these include: manganese, nickel, chromium, arsenic, and particulate mercury. The metals are emitted in exhaust as $PM_{2.5}$, but they are calculated with a separate calculator than the other $PM_{2.5}$ species. The emission rates for these metals are not chained from NonECSO_4PM, but are independent mass/distance rates as documented in the Air Toxic Emissions Report.[7] 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, CMAQv5.1 only requires manganese as a required $PM_{2.5}$ species. By default, MOVES 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 5-4 Metal Particulate Air Toxics Produced by MOVES

Pollutant
Chromium 6+
Manganese
Nickel
Particulate Hg
Arsenic

5.3 $PM_{2.5}$ Exhaust Speciation Profiles

Table 5-5 lists the $PM_{2.5}$ speciation profiles used in MOVES with the SPECIATE database profileID. As discussed earlier, these profiles only estimate the AE6 Chemical Mechanism $PM_{2.5}$ species, with the other measured species and unspeciated mass being considered as part of the unspeciated $PM_{2.5}$ species (PMOTHR).

Table 5-5 MOVES $PM_{2.5}$ Exhaust Speciation Profiles

Profile ID	Profile Name	Source Data
8992	Light-duty Gasoline Exhaust - Start	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	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	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	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	Khalek, I. A.; Bougher, T. L; Merrit, P. M.; Phase 1 of the Advanced Collaborative Emissions Study. CRC Report: ACES Phase 1, June 2009.
95219a	CNG transit bus exhaust from a lean-burn engine - no aftertreatment	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.
95220a	CNG transit bus exhaust from a lean-burn engine – oxidation catalyst	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.

The $PM_{2.5}$ profiles used for the applicable source type, fuel, pollutant process, and model year ranges are described in Table 5-6 and detailed in Table D-1.

Table 5-6 Application of MOVES $PM_{2.5}$ Speciation Profiles

Profile ID	Description	Fuel	Affected Vehicles	Emission Process
8992	Light-duty Gasoline Exhaust - Start	All gasoline vehicles (E0 to E85)	All model years	Running exhaust; crankcase running exhaust.
8993	Light-duty Gasoline Exhaust- Hot Stabilized Running	All gasoline vehicles (E0 to E85)	All model years	Start exhaust; crankcase start exhaust.
8994	Conventional HDD - Idle	Diesel	Pre-2007 and all MY auxiliary power units	Running exhaust; crankcase running and extended idle exhaust; auxiliary power unit
8995	Conventional HDD – Hot Stabilized Running	Diesel	Pre-2007	Start exhaust; crankcase start exhaust.
8996	2007 and Newer Diesel Exhaust Composite	Diesel	2007+	Start exhaust; crankcase start exhaust. Running exhaust; crankcase running and extended idle exhaust; auxiliary power unit
95219a	CNG transit bus exhaust from a lean-burn engine - no aftertreatment	CNG	pre-2002 model year	Start exhaust; crankcase start exhaust. Running exhaust; crankcase running and extended idle exhaust; auxiliary power unit
95220a	CNG transit bus exhaust from a lean-burn engine – oxidation catalyst	CNG	2002+ model year	Start exhaust; crankcase start exhaust. Running exhaust; crankcase running and extended idle exhaust; auxiliary power unit

MOVES 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 nonECnonSO_4 emissions emitted during extended idle and start are speciated using the Idle Profile (8994). Tailpipe exhaust and crankcase nonECnonSO_4 emissions emitted during running operation are speciated using the running profile (8995). In addition, the idle profile (8994) is used to characterize nonECnonSO_4 emissions 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. It should be noted that while PM speciation data for 2010 and later diesel engines is available from the ACES Phase 2 test program, we did not update PM speciation to incorporate these data because the ACES Phase 2 emissions data did not collect any active regeneration events, and thus, had minimal sulfate emissions. Testing done by California Air Resources Board[53] has shown active regeneration events occur on 2010+ technology on-highway diesel trucks, but at a lower frequency than 2007-2009 model year trucks. During active regeneration, fuel is injected into the aftertreatment system to raise the temperature to burn off the soot collected in the diesel particulate filter, which increases emissions of particulate matter (mostly sulfate). Thus it is important that sulfate emissions be represented in the $PM_{2.5}$ profile to represent real-world regeneration events.[54]

The CNG compression ignition profile is applied to the pre-2002 model CNG heavy-duty vehicles, and the CNG profile with oxidation catalyst profile is applied to the 2002+ model year CNG heavy-duty vehicles.

5.4 Brake and Tire Wear Speciation

Brake and tire wear $PM_{2.5}$ are not speciated within MOVES. For developing the emissions modeling platform, SPECIATE Profiles 95462 and profile 95460 developed from Schauer et al. 2006[67] are applied to brake wear and tire wear $PM_{2.5}$ emissions in the moves2smk postprocessor that prepares the emission factors for processing in SMOKE.[55]

Appendix A Supporting Information for TOG calculations

Table A-1 and Table A-2 summarize the data[56] used to generate CH4/THC ratios for Tier 2 vehicles running on low-level ethanol blends as described in Section 3.3. In Table A-2, "cold start" refers to the difference between Bags 1 and 3. Running data corresponds to stabilized emissions from Bag 2. In the particular case of running emissions, seven tests (shown in grey in Table A-1 and Table A-2) were not considered in the analysis because the reported CH_4 emissions were higher than the reported THC emissions, possibly because measurements were close to the detection limit of the instrument.

Table A-1 Data[56] Used to Generate CH4/THC Ratios for Tier 2 Vehicles Running on Low-Level Ethanol Blends

Bag data from profile	Run Number EPAct Phase 1	Ethanol (%)	Bag1 – Bag 3		Bag 2	
			CH_4 (g/mi)	THC (g/mi)	CH_4 (g/mi)	THC (g/mi)
8756	3162	0	0.048	0.427	0.006	0.016
	3169	0	0.050	0.570	0.006	0.017
	3179	0	0.024	0.299	0.001	0.000
	3190	0	0.027	0.355	0.001	0.000
	3205	0	0.042	0.369	0.006	0.024
	3215	0	0.043	0.430	0.006	0.026
	3223	0	0.019	0.236	0.001	0.002
	3231	0	0.017	0.211	0.001	0.004
	3239	0	0.030	0.382	0.001	0.000
8757	3280	10	0.031	0.351	0.001	0.000
	3291	10	0.029	0.343	0.001	0.001
	3302	10	0.045	0.362	0.005	0.014
	3313	10	0.049	0.382	0.006	0.021
	3326	10	0.016	0.163	0.001	0.004
	3339	10	0.016	0.165	0.001	0.003
8758	3480	15	0.058	0.448	0.007	0.018
	3492	15	0.053	0.424	0.007	0.014
	3508	15	0.017	0.141	0.001	0.002
	3516	15	0.017	0.209	0.001	0.002
	3542	15	0.052	0.494	0.001	0.000
	3553	15	0.043	0.379	0.001	0.000
	3568	15	0.022	0.248	0.001	0.000

Table A-2. Data[56] Used to Generate Speciation Constant Parameters for Tier 2 Vehicles Running on Low-Level Ethanol Blends

Bag data from profile	Run Number EPAct Phase 1	Ethanol (%)	Cold Start NMOG (g/mi)	Cold Start VOC (g/mi)	Cold Start NMHC (g/mi)	Running NMOG (g/mi)	Running VOC (g/mi)	Running NMHC (g/mi)
8756	3162	0	0.345	0.332	0.338	0.009	0.008	0.008
	3169	0	0.468	0.453	0.458	0.010	0.010	0.010
	3179	0	0.256	0.250	0.255	0.001	0.001	0.001
	3190	0	0.284	0.276	0.282	0.001	0.001	0.001
	3205	0	0.314	0.301	0.306	0.013	0.012	0.013
	3215	0	0.360	0.346	0.353	0.013	0.012	0.013
	3223	0	0.197	0.190	0.196	0.001	0.001	0.001
	3231	0	0.168	0.162	0.165	0.004	0.004	0.004
	3239	0	0.295	0.287	0.294	0.001	0.001	0.001
8757	3280	10	0.312	0.305	0.301	0.001	0.001	0.001
	3291	10	0.315	0.306	0.301	0.000	0.000	0.000
	3302	10	0.331	0.320	0.317	0.007	0.006	0.006
	3313	10	0.345	0.332	0.327	0.008	0.007	0.007
	3326	10	0.144	0.139	0.137	0.000	0.000	0.000
	3339	10	0.159	0.154	0.151	0.000	0.000	0.000
8758	3480	15	0.390	0.372	0.363	0.012	0.011	0.012
	3492	15	0.371	0.354	0.348	0.012	0.011	0.012
	3508	15	0.143	0.137	0.133	0.001	0.001	0.001
	3516	15	0.188	0.182	0.172	0.000	0.000	0.000
	3542	15	0.433	0.420	0.410	0.000	0.000	0.000
	3553	15	0.328	0.317	0.310	0.000	0.000	0.000
	3568	15	0.239	0.232	0.221	0.000	0.000	0.000

Table A-3. documents the CH_4/THC and speciation constant parameters for all the sources in MOVES (by including the data from Table 3-2, Table 3-3, Table 3-4, and Table 3-5). In addition, it specifies the MOVES variables that are used to define the CH4/THC and speciationConstants within the MethaneTHCRatio and HcSpeciation tables, respectively.

Table A-3 CH_4/THC and Speciation Constant Parameters and Their Relationship to MOVES Variables

Profile number	Profile description	modelYear-GroupID	processID	fuelSubTypeID	regClassID	CH_4/THC	NMOG/NMHC	VOC/NMHC
95120	Liquid Diesel	1960-2060	11	20,21,22	0	0	1	1
			12,13,18,19	20,21,22	10,20,30,40,41, 42,46,47,48	0		
8750a	Pre-Tier 2 E0 exhaust	1960-2000	1,2,15,16	10	20,30	0.142	1.024	0.996
		1960-2060			10,40,41,42,46, 47,48			
8751a	Pre-Tier 2 E10 exhaust	1960-2000	1,2,15,16	11,12,13,14	20,30	0.146	1.037	1.008
		1960-2060			10,40,41,42,46, 47,48			
8753	E0 Evap	1960-2060	12,13,19	10	10,20,30,40,41, 42,46,47,48	0	1	1
8754	E10 Evap	1960-2060	12,13,19	12,13,14	10,20,30,40,41, 42,46,47,48	0	1.071	1.071
8766	E0 Evap perm	1960-2060	11	10	0	0	1	1
8769	E10 Evap perm	1960-2060	11	12,13,14	0	0	1.129	1.129
8770	E15 Evap perm	1960-2060	11	15,18	0	0	1.175	1.175
8774	Pre-2007 MY HDD exhaust	1960-2006	1,2,15,16,17,90	20,21,22	40,41,42,46,47, 48	0	1.145	1.124
		1960-2023	91		46,47			
		1960-2006	1,2,15,16		20,30			
8775	2007-2009 HDD exhaust	2007-2009	1,2,15,16	20,21,22	20,30	0.589	1.343	1.285
		2024-2060	91		46,47			
		2007-2009	1,2,15,16,17,90		40,41,42,46,47, 48			
95335a	2010+ HDD exhaust	2010-2060	1,2,15,16	20,21,22	20, 30	0	1.085	0.965
			1,2,15,16,17,90		40,41,42,46,47, 48			

Table A-3 (continued)

Profile number	Profile description	modelYear GroupID	processID	fuelSubTypeID	regClassID	CH_4/THC	NMOG/NMHC	VOC/NMHC
8869	E0 Headspace	1960-2060	18	10	10,20,30,40,41,42,46,47,48	0	1	1
8870	E10 Headspace	1960-2060	18	12,13,14	10,20,30,40,41,42,46,47,48	0	1.037	1.037
8871	E15 Headspace	1960-2060	18	15,18	10,20,30,40,41,42,46,47,48	0	1.175	1.175
8872	E15 Evap	1960-2060	12,13,19	15,18	10,20,30,40,41,42,46,47,48	0	1.118	1.118
8934	E85 Evap	1960-2060	11	50,51,52	10,20,30,40	0	1.501	1.501
			12,13,18,19		10,20,30,40			

Table A-4 Data Sources for the SPECIATE[8] Profiles used in MOVES

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.	
95120	Liquid Diesel - California composite	Gentner, Drew R, Gabriel Isaacman, David R Worton, Arthur WH Chan, Timothy R Dallmann, Laura Davis, Shang Liu, et al. "Elucidating Secondary Organic Aerosol from Diesel and Gasoline Vehicles through Detailed Characterization of Organic Carbon Emissions." Proceedings of the National Academy of Sciences 109, no. 45 (2012): 18318-23. DOI: 10.1073/pnas.1212272109	
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.

Table A-4 (continued)

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 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.	
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.

Table A-4 (continued)

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	
95335	Diesel Exhaust – Heavy-heavy duty truck – 2011 model year	Khalek, I., Blanks, M., and Merritt, P. M. (2013). Phase 2 of the Advanced Collaborative Emissions Study. Prepared by Southwest Research Institute for the Coordinating Research Council and the Health Effects Institute, November 2013. Available at www.crcao.org.	

Appendix B CNG CH_4/THC and Speciation Constant Parameters for CNG vehicles

SPECIATE 5.1[8] does not contain a TOG speciation profile from modern CNG exhaust emissions. We used hydrocarbon speciation data from Ayala et al. that measured a 2000 MY transit bus with a Detroit Diesel Series 50G engine with and without an oxidation catalyst collected on the CBD cycle.[43] This data allows us to isolate the impact of the oxidation catalyst. Studies have shown that the speciation of hydrocarbon can be drastically different between uncontrolled CNG buses and CNG buses with oxidation catalysts. For example, formaldehyde emissions can be quite large from uncontrolled CNG buses[57,58], but are significantly reduced with oxidation catalysts.[43] Large formaldehyde emissions have a large impact on the NMOG and VOC emissions estimated from THC emissions from CNG buses because THC-FID measurements have a small response to formaldehyde concentrations.[59]

We used the CBD test cycle to be consistent with our analysis of the criteria emission rates documented in the heavy-duty emission rate report.[2] NMOG and VOC conversion factors are listed in Table B-1. The NMOG values are calculated using Equation 7. The VOC emissions are calculated from subtracting the ethane and acetone from the NMOG values. The emissions of hazardous air pollutants, including formaldehyde and acetaldehyde, are also estimated from this study as documented in the MOVES3 Toxics Emissions Report.[7]

Table B-1 Hydrocarbon Speciation Values for CNG Transit Emissions with No Control and with Oxidation Catalyst from Ayala et al. (2003)[43]

Measured values (mg/mile)	No Control	Oxidation Catalyst
THC	8660	6150
CH4	7670	5900
C2H6	217	72.2
Formaldehyde	860	38.4
Acetaldehyde	50.7	32.6
Calculated values (mg/mile)		
NMHC	990	250
NMOG	1881.0	309.0
VOC	1658.5	232.1
Ratios		
NMOG/NMHC	1.90	1.24
VOC/NMHC	1.68	0.93

Appendix C TOG Speciation Map

Table C-4 provides a speciation map between MOVES TOG profiles and the distinguishing factors used in MOVES. To help interpret this table, we have also provided tables that describe the MOVES processes, fuel subtypes, and regulatory classes and list their id codes. ModelYearGroupID is simply the first model year of the group, followed by the last model year.

Table C-1 MOVES Processes Relevant for Speciation Profiles[s]

processID	Process Name	
1	Running Exhaust	Exhaust emissions from a running vehicle
2	Start Exhaust	Exhaust emissions that occur at engine start
11	Evap Permeation	migration of hydrocarbons through materials in the fuel system
12	Evap Fuel Vapor Venting	Escape of vapors that are generated through heating of gasoline fuel system
13	Evap Fuel Leaks	Fuels escaping gasoline fuel system in a non-vapor form
15	Crankcase Running Exhaust	Combustion products and oil droplets from compression ignition engines that are vented to the atmosphere rather than routed through the exhaust
16	Crankcase Start Exhaust	
17	Crankcase Extended Idle Exhaust	
18	Refueling Displacement Vapor Loss	Displaced fuel vapors when liquid fuel is added to the vehicle tank
19	Refueling Spillage Loss	Vapor emissions from any liquid fuel that is spilled during refueling
90	Extended Idle Exhaust	Idle emissions during “hotelling” of long-haul combination trucks
91	Auxiliary Power Exhaust	Auxiliary power unit emissions during hotelling of long-haul combination trucks

[s] Not a complete list of MOVES emission processes.

Table C-2 Regulatory Classes in MOVES3

regClassID	Regulatory Class Name	Description
0	Doesn't Matter	Doesn't Matter
10	MC	Motorcycles
20	LDV	Light-Duty Vehicles
30	LDT	Light-Duty Trucks
41	LHD2b3	Class 2b and 3 Trucks (8,500 lbs < GVWR <= 14,000 lbs)
42	LHD45	Class 4 and 5 Trucks (14,00 lbs. < GVWR <= 19,500 lbs.)
46	MHD	Class 6 and 7 Trucks (19,500 lbs. < GVWR < =33,000 lbs.)
47	HHD	Class 8a and 8b Trucks (GVWR > 33,000 lbs.)
48	Urban Bus	Urban Bus (see CFR Sec. 86.091_2)
49	Gliders	Glider Vehicles[60]

Table C-3 Fuel Subtypes in MOVES3

fuelSubtypeID	fuelTypeID	fuelSubtypeDesc
10	1	Conventional Gasoline
11	1	Reformulated Gasoline (RFG)
12	1	Gasohol (E10)
13	1	Gasohol (E8)
14	1	Gasohol (E5)
15	1	Gasohol (E15)
20	2	Conventional Diesel Fuel
21	2	Biodiesel (BD20)
22	2	Fischer-Tropsch Diesel (FTD100)
30	3	Compressed Natural Gas (CNG)
40	4	Liquefied Petroleum Gas (LPG)
50	5	Ethanol
51	5	Ethanol (E85)
52	5	Ethanol (E70)
90	9	Electricity

Table C-4 TOG Speciation Map

Profile	Profile Description	modelYear-GroupID	processID	fuelSubTypeID	regClassID
1001	CNG Exhaust	19602060	1,2,15,16	30	48
95120[m]	Liquid Diesel	19602060	11	20,21,22	0
95120[m]	Liquid Diesel	19602060	12,13,18,19	20,21,22	10,20,30,40,41,42,46,47,48
8753	E0 Evap	19602060	12,13,19	10	10,20,30,40,41,42,46,47,48
8754	E10 Evap	19602060	12,13,19	12,13,14	10,20,30,40,41,42,46,47,48
8756	Tier 2 E0 Exhaust	20012060	1,2,15,16	10	20,30
8757	Tier 2 E10 Exhaust	20012060	1,2,15,16	12,13,14	20,30
8758	Tier 2 E15 Exhaust	19602060	1,2,15,16	15,18	10,20,30,40,41,42,46,47,48
8766	E0 evap permeation	19602060	11	10	0
8769	E10 evap permeation	19602060	11	12,13,14	0
8770	E15 evap permeation	19602060	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	19602060	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	20072009	1,2,15,16	20,21,22	20,30
8775	2007+ MY HDD exhaust	20072009	1,2,15,16,17,90	20,21,22	40,41,42,46,47,48
95335a	2010+ MY HDD exhaust	20102060	1,2,15,16	20,21,22	20,30
95335a	2010+ MY HDD exhaust	20102060	1,2,15,16,17,90	20,21,22	40,41,42,46,47,48
8855	Tier 2 E85 Exhaust	19602060	1,2,15,16	50,51,52	10,20,30,40,41,42,46,47,48
8869	E0 Headspace	19602060	18	10	10,20,30,40,41,42,46,47,48
8870	E10 Headspace	19602060	18	12,13,14	10,20,30,40,41,42,46,47,48
8871	E15 Headspace	19602060	18	15,18	10,20,30,40,41,42,46,47,48
8872	E15 Evap	19602060	12,13,19	15,18	10,20,30,40,41,42,46,47,48
8934	E85 Evap	19602060	11	50,51,52	0
8934	E85 Evap	19602060	12,13,18,19	50,51,52	20,30,40
8750a	Pre-Tier 2 E0 exhaust	19602000	1,2,15,16	10	20,30
8750a	Pre-Tier 2 E0 exhaust	19602060	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	19602060	1,2,15,16	11,12,13,14	10,40,41,42,46,47,48

Appendix D Comparison of ACES Phase 1 and Phase 2 SPECIATE Profiles

We initially developed profile 95335 from the ACES Phase 2 profile as recommended by the MOVES2014 peer-reviewers.[11] However, there are inconsistencies between the ACES Phase 1 and 2 profiles. For example, ACES Phase 1 is composed of over 50% percent methane, while the ACES Phase 2 profile has zero percent methane (Updated in Section 3.6). Other anomalies in the ACES Phase II profile included benzene is not detected (ND) in the ACES Phase II profile (from which we then assumed benzene=0), while ethanol comprises over 3% of the TOG emissions. As suggested by one of the 2017 peer-reviews[12], to better understand the consistency of these changes, we compared emission trends among different groups of gaseous hydrocarbons (Tables D-5) and individual compounds (Table D-6 through D-10) between the ACES Phase 1 and Phase 2 profiles.

While relative amounts of olefins and aromatics substantially increased in the Phase 2 profile relative to Phase 1, paraffins, aldehydes and ketones decreased. However, there was inconsistency in emission changes among individual compounds in all chemical groups. For example, propane increased by more than a factor of four from ACES Phase 1 to ACES Phase 2, but hexane decreased by 69%. Similarly, while the total weight percentage of olefins decreased, both ethene and propene increased as a proportion of total organic emissions. Carbonyl compounds consistently decreased with the exception of acetaldehyde which increased by 3%.

We did not attempt to impute minimum values in the cases where the species were not detected in one of the profiles. Our speciation profiles consist of the weight percentage of total organic emissions for each detected species as opposed to an absolute emissions value (in mg/mi or similar unit); therefore, it is not straightforward to apply a below detection limit value to not measured species

Within SPECIATE profile 95335, the mass fraction of three alcohol species, ethyl alcohol (ethanol), isopropyl alcohol (2-propanol), methyl alcohol (methanol), sum to 7% of the total TOG emissions. We do not believe these alcohol species are produced in modern heavy-duty exhaust; instead they are likely an artifact of measurement during sampling or analysis in the laboratory. With agreement from one of the 2017 peer-reviewers[12], we created a new profile (95335a) from 95335 where the mass fractions for the alcohol species are set to zero and we re-weighted the remaining non-alcohol species.

While it is difficult to predict how complex emission control systems may affect individual compounds, the inconsistent pattern of hydrocarbon measurements suggests that there are potential significant uncertainties in the measurements. Additional sources of uncertainty in the ACES phase 2 profile are due to the small number of engines tested (three), the low concentrations of organic gas emitted with new 2010-compliant engines and aftertreatment systems causing many measurements to be near the detection limits. Although ACES Phase 2 is currently our best data source for the speciation of advanced technology diesels, the data should still be interpreted with caution. As we discussed in the main text, we recommend further work

to improve the confidence of speciation of exhaust from modern heavy-duty diesel engines, including from engines with aged and deteriorated aftertreatment systems.

Table D-5 Comparison of Groups of Compounds from diesel exhaust speciation from ACES Phase 1 and ACES Phase 2).

Compound Group	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
Paraffins (total)	67.09	33.07	-51%
Olefins (total)	6.13	33.09	440%
Aromatics (total)	5.77	17.37	201%
Aldehydes/Ketones (total)	16.66	7.83	-53%
Unknown	4.35	1.56	-64%
Other		7.07	

Table D-6 Comparison of Individual Compounds from diesel exhaust speciation from ACES Phase 1 and ACES Phase 2): Parafins

CAS	Name	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
74-82-8	methane	51.64[t]		
74-84-0	Ethane	1.34	10.11	655%
96-37-7	methylcyclopentane	0.02		
112-40-3	dodecane	2.34	0.36	-84%
1120-21-4	undecane	1.75		
106-97-8	N-butane	1.10	0.17	-85%
109-66-0	N-pentane	1.01	3.06	201%
78-78-4	Isopentane (2-Methylbutane)		0.88	
124-18-5	decane	0.38	0.12	-68%
111-84-2	nonane	0.28	2.72	873%
74-98-6	Propane	0.51	2.75	441%
75-28-5	Isobutane	0.50	1.03	108%
3522-94-9	2,2,5-trimethylhexane	0.04		
590-73-8	2,2-dimethylhexane	0.66		
589-43-5	2,4-dimethylhexane	0.42		
589-34-4	3-methylhexane	0.15	0.26	76%
108-87-2	methylcyclohexane	0.89	0.77	-13%
619-99-8	3-ethylhexane	0.08		
110-54-3	n-hexane	0.24	0.07	-69%
96-14-0	3-methylpentane	0.14		
107-83-5	2-methylpentane	0.13	0.59	336%
79-29-8	2,3-dimethylbutane	0.09		
15869-87-1	2,2-dimethyloctane	0.00	0.30	26037%
111-65-9	octane	0.20	0.36	80%
565-75-3	2,3,4-trimethylpentane	0.54		
560-21-4	2,3,3-trimethylpentane	0.52		
540-84-1	2,2,4-trimethylpentane	0.37	0.37	-1%
565-59-3	2,3-dimethylpentane	0.35		
562-49-2	3,3-dimethylpentane	0.00		
590-35-2	2,2-dimethylpentane	0.02		
1068-19-5	4,4-dimethylheptane	0.16		
1072-05-5	2,6-dimethylheptane	0.20	0.82	303%
589-81-1	3-methylheptane	0.07		
592-27-8	2-methylheptane			
142-82-5	heptane	0.28	0.09	-66%
463-82-1	2,2-dimethylpropane	0.68		
75-83-2	2,2-dimethylbutane		2.40	

[t] This differs from the 58% CH4/THC reported in Table 3-2 because the 51% reports the fraction of methane/TOG. We calculated THC from TOG using the methods described in Section 3.2

Table D-6 (Continued)

CAS	Name	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
767-58-8	1-methylindane			
2216-33-3	3-methyloctane		0.16	
584-94-1	2,3-dimethylhexane			
108-08-7	2,4-dimethylpentane		1.45	
591-76-4	2-methylhexane		0.41	
124-11-8	1-nonene		0.06	
2213-23-2	2,4-dimethylheptane		0.61	
4032-94-4	2,4-dimethyloctane		0.63	
3221-61-2	2-methyloctane		0.19	
583-48-2	3,4-dimethylhexane		0.22	
90622-57-4	C9-c12 isoalkanes		1.51	
2532-58-3	Cis-1,3-dimethylcyclopentane		0.46	
16883-48-0	Cis-1,trans-2,4-trimethylcyclopentane		0.06	
1759-58-6	Trans-1,3-dimethylcyclopentane		0.07	

Table D-7 Comparison of Individual Compounds from diesel exhaust speciation from ACES Phase 1 and ACES Phase 2): Olefins

CAS	Name	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
74-85-1	ethene	3.07	9.55	212%
763-29-1	2-methyl-1-pentene	0.01		
115-07-1	propene	0.94	4.31	359%
74-86-2	acetylene	0.58	0.82	42%
115-11-7	2-methylpropene	0.97	13.33	1268%
106-99-0	1,3-butadiene	0.04		
590-19-2	1,2-butadiene			
592-41-6	1-hexene	0.01		
7688-21-3	Cis-2-hexene			
4050-45-7	Trans-2-hexene			
106-98-9	1-butene	0.03		
590-18-1	cis-2-butene		0.53	
624-64-6	trans-2-butene			
513-35-9	2-methyl-2-butene		3.01	
691-37-2	4-methyl-1-pentene	0.06		
625-27-4	2-methyl-2-pentene	0.03		
7385-78-6	3,4-dimethyl-1-pentene	0.07		
107-40-4	2,2,4-trimethyl-2-pentene	0.04		
142-29-0	cyclopentene	0.01		
816-79-5	3-ethyl-2-pentene	0.01	0.50	4963%
107-00-6	1-butyne	0.25		
542-92-7	cyclopentadiene	0.02		
627-20-3	Cis-2-pentene		0.17	
110-83-8	Cyclohexene		0.87	

Table D-8 Comparison of Individual Compounds from diesel exhaust speciation from ACES Phase 1 and ACES Phase 2): Aromatics

CAS	Name	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
71-43-2	benzene	0.61		
108-88-3	toluene	1.24	1.52	22%
95-47-6	o-xylene	0.65	0.37	-44%
108-38-3; 106-42-3	m/p-xylenes	1.04	6.65	539%
527-53-7	1,2,3,5-tetramethylbenzene	0.16		
95-93-2	1,2,4,5-tetramethylbenzene	0.08	1.25	1526%
95-63-6	1,2,4-trimethylbenzene	0.75	0.18	-76%
25551-13-7	trimethylbenzene			
526-73-8	1,2,3-trimethylbenzene	0.06	4.54	7737%
108-67-8	1,3,5-trimethylbenzene			
1758-88-9	1,4-dimethyl-2-ethylbenzene	0.12		
620-14-4	1-Methyl-3-ethylbenzene	0.08		
622-96-8	1-Methyl-4-ethylbenzene			
611-14-3	1-methyl-2-ethylbenzene	0.05	0.02	-56%
103-65-1	Propylbenzene		0.72	
100-41-4	ethylbenzene	0.31	0.92	194%
98-19-1	tert-butyl-m-xylene	0.13		
100-42-5	styrene			
98-82-8	isopropylbenzene		0.52	
538-93-2	(2-methylpropyl)benzene	0.20	0.12	-43%
535-77-3	1-Methyl-3-isopropylbenzene	0.05		
527-84-4	1-methyl-2-isopropylbenzene	0.06		
1074-43-7	1-Methyl-3-propylbenzene	0.02		
03968-85-2	2-methyl-butyl-benzene	0.05		
1074-92-6	t-1-Butyl-2-Methylbenzene	0.03		
91-20-3	Naphthalene	0.07		
141-93-5	1,3-diethylbenzene (meta)			
105-05-5	1,4-diethylbenzene (para)			
0	Isomers of diethylbenzene			
104-51-8	butylbenzene			
	1,2,4-trimethylbenzene			
25155-15-1	Isopropyltoluene			
28729-54-6	Propyltoluene			
7364-19-4	1-tert-butyl-4-ethylbenzene		0.56	

Table D-9 Comparison of Individual Compounds from diesel exhaust speciation from ACES Phase 1 and ACES Phase 2): Aldehydes/Ketones

CAS	Name	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
50-00-0	formaldehyde	10.05	2.20	-78%
75-07-0	acetaldehyde	3.36	3.45	3%
107-02-8	acrolein	0.50	0.30	-41%
67-64-1	acetone	0.76	1.01	34%
100-52-7	benzaldehyde	0.79	0.03	-96%
123-38-6	propionaldehyde	0.15	0.24	58%
78-93-3	Methyl ethyl ketone (2-butanone)	0.16	0.08	-50%
123-72-8	butyraldehyde	0.16	0.11	-30%
66-25-1	hexanaldehyde	0.11	0.04	-64%
590-86-3	isovaleraldehyde	0.08	0.03	-69%
104-27-0	M- & p-tolualdehyde	0.49	0.13	-75%
110-62-3	valeraldehyde	0.05	0.14	208%
4170-30-3	Crotonaldehyde		0.02	
28351-09-9	Dimethylbenzaldehyde		0.02	
529-20-4	o-Tolualdehyde		0.04	

Table D-10 Comparison of Individual Compounds from diesel exhaust speciation from ACES Phase 1 and ACES Phase 2): Other/Unknown

CAS	Name	ACES Phase 1 (Weight %)	ACES Phase II (Weight %)	% Change: Phase I to Phase II
64-17-5	Ethyl alcohol (ethanol)		3.19	
67-63-0	Isopropyl alcohol (2-Propanol)		1.74	
67-56-1	Methyl alcohol (methanol)		2.14	
N/A	C-6 Compounds		1.42	
N/A	C-8 Compounds		0.14	
N/A	Unknown	4.35		

Appendix E Development of $PM_{2.5}$ speciation profiles in MOVES

This report includes the derivation of each $PM_{2.5}$ profiles used in MOVES to estimate AE6 chemical mechanism $PM_{2.5}$ species.

For comparison purposes, the seven $PM_{2.5}$ profiles developed for MOVES are presented in Table E-1. The remainder of this appendix explains how each profile was derived.

Table E-1 $PM_{2.5}$ Profiles developed for MOVES

	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 (95219a)	CNG transit bus exhaust from a lean-burn engine - aftertreatment (95220a)
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%		
unspeciated (PMOTHR)	2.09%	4.58%	1.28%	1.09%	0.78%	43.90%	40.74%

E.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 MOVES.[1] 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 this "chemical subset" is included in Table E-2.

Table E-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 MOVES is documented in Sonntag *et al.* (2013).[61] A summary of the speciation derivation is included in this report, as well as a discussion on implementing the profile into the MOVES 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 analysis 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 MOVES to account for the silicone contamination.[1] 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 to develop single start and running $PM_{2.5}$ speciation profiles for all light-duty gasoline vehicles.

While differences in the $PM_{2.5}$ compositions were detected among model year groups, the speciation sample size was deemed too limited to accurately capture the impact of deterioration and high-emitting vehicles within each model-year group. Instead 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.[62,63,64,65] 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.[66] Other test programs have confirmed that high emitting gasoline vehicles also occur in vehicle fleets such as 1990-era vehicles with electronic fuel injection.[62,63,64] 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.[67] 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 E-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 MOVES, 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,[61] 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[62,68,69,70] and gasoline-direct injection (GDI) vehicles.[71,72,73] We plan on incorporating light-duty gasoline PM profiles to MOVES and SPECIATE as such data on representative, in-use vehicles become available.

The developed $PM_{2.5}$ profiles used in MOVES for gasoline exhaust are included in Table E-3.. The number of samples for each $PM_{2.5}$ species are also shown. 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 MOVES are consistent with the EC fractions listed here.

For application in MOVES, only the $PM_{2.5}$ species required by CMAQv5.1 are reported. Metal emission rates for Mn, Cr, and Ni for gasoline vehicles based on the KCVES are provided in the Air Toxics Report.[7] 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 much lower after implementation of the Tier 2[74] and Tier 3[75] Gasoline Sulfur Standards (30 ppm beginning 2006-2008, and 10 ppm in 2020). In MOVES, the baseline sulfate emissions estimated from the $PM_{2.5}$ profile are adjusted according to the fuel sulfur content as discussed in the fuel effects report.[51]

Details on the data, quality control measures, and statistical methods used to develop the profile are documented in the Sonntag *et al.* (2013).[61] 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 MOVES are also presented.

Table E-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%
Unspeciated (PMOTHR)	66	2.09%	+/-	1.75%	99	4.56%	+/-	1.10%

E.2 Development of E55/59 Profile for Pre-2007 Conventional Diesel

An $PM_{2.5}$ profile for pre-2007 conventional[q] diesel trucks was developed from the CRC E55/59 Study: Heavy-Duty Vehicle Chassis Dyno Testing for Emissions Inventory.[76] The E55/59 program is the current source for $PM_{2.5}$ emission rates for medium- and heavy-duty pre-2007 model year conventional diesel trucks in MOVES, and is the source of the conventional pre-2007 diesel TOG speciation profiles. By using the E55/59 study for $PM_{2.5}$ speciation profiles, we are using consistent data with both the $PM_{2.5}$ emission rates and the TOG speciation profiles in MOVES.

The E55/59 $PM_{2.5}$ profile includes measurements from eight heavy-duty trucks, ranging from 1985 to 2004 model year as shown in Table D-4. The E55/59 average sulfur content is 172 ppm. 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 E-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 (HHDDTs) 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 diesel truck (MHDDT). In Phase 2, the HHDDTs were also tested on the UDDS, as well as a high-speed cruise mode added after Phase 1. The MHDDT was tested on MHDDT 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.[76]

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[77] and from Table 17 of the E55/59 Phase 1 report.[78] The data reduction steps used to develop a $PM_{2.5}$ speciation profile from the E55/59 speciated data are outlined in the following Steps: 1-4.

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.[76] 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 D-1. Thirty average speciation profiles were calculated from the 65 tests as shown in Figure D-1. Typically, each truck/cycle average contains two tests.

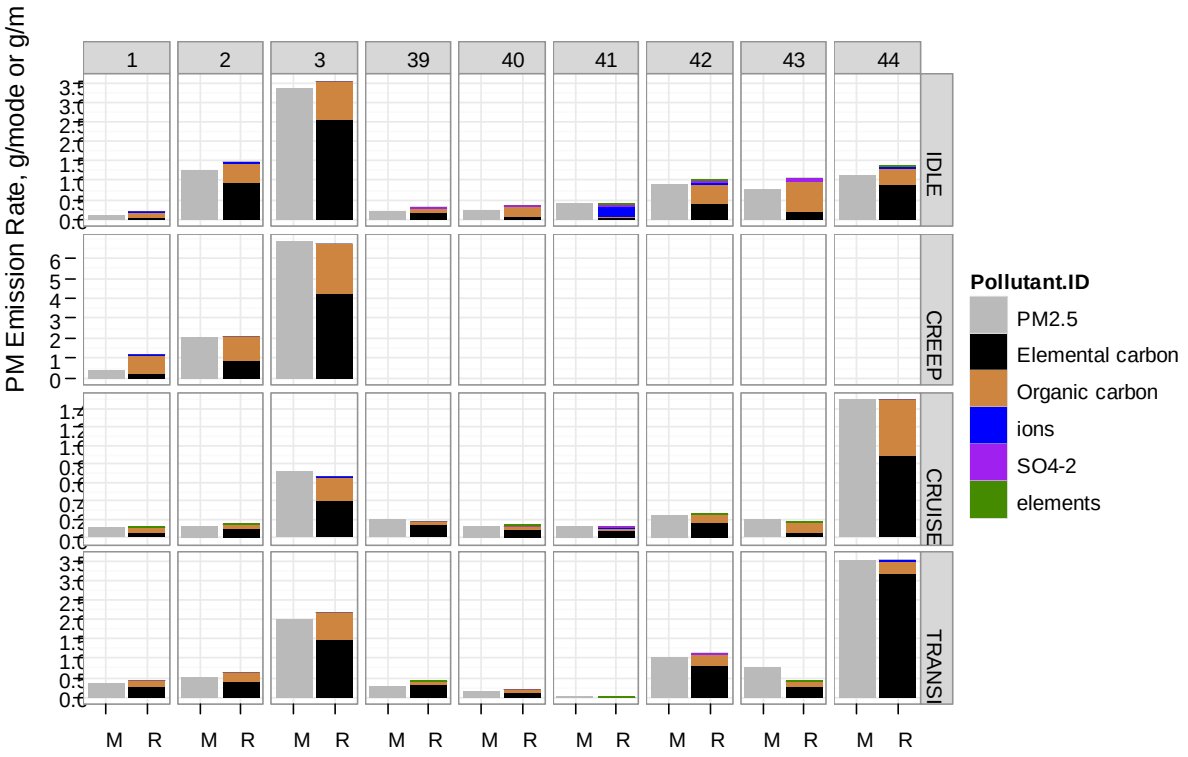

Figure D-1 Average $PM_{2.5}$ Speciation Profiles by Truck and Test Cycle from the E55/59 Program. M = Measured total $PM_{2.5}$, R = Reconstructed Total $PM_{2.5}$ from the Speciated Measurements

Step 2. We removed the average $PM_{2.5}$ profiles with suspect data. As shown in Figure D-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[79], 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)[61] reproduced in Table E-5.

Table E-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[61] and analysis of emissions from other combustion sources.[80] We calculated the organic matter (OM) as the remainder of the $PM_{2.5}$ using Equation 11.

$$OM\% = 100 - EC\% - elements\% - metal\ bound\ oxygen\% - ions\% \quad \textbf{Equation 11}$$

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)[81] and developed from work conducted on medium-duty diesel emissions[79], as shown in Equation 12 and Equation 13.

$$OC\% = \left(\frac{5}{6}\right) OM\% \quad \textbf{Equation 12}$$

$$NCOM\% = \left(\frac{1}{6}\right) OM\% \quad \textbf{Equation 13}$$

The initial and corrected OC/PM factors are shown in Table E-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.[82]

Table E-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 E-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 E-7 $PM_{2.5}$ Profiles for Pre-2007 Diesel Exhaust Developed for MOVES2014

	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%

In MOVES, the EC/PM fraction from the Idle profile (8994) is used for idle emissions from running (opModeID 1, processID 1) and extended idle (processID 90). It is also used to speciate the PM from start emissions (processID 2) and auxiliary power emissions (processID 91). The running profile is used to speciate the PM from all other operating modes from running emissions (processID 1).

Table E-8 compares the profiles developed from the E-55/59 study to measurements made at CE-CERT (Shah et al. (2004)[83]), a composite profile developed by Schauer *et al.* (2006)[67] from the DOE Gasoline/Diesel PM Split Study, and the NFRAQS heavy-duty diesel profile (SPECIATE Profile 91106). The EC/PM fraction from the E55/59 transient cycle compares well to both the composite profiles. The E55/59 idle profile has a substantially lower EC/PM fraction than the composite profiles, with a corresponding higher fraction of organic matter. The cold/start idle profile from CE-CERT (Shah et al. (2004)) also shows an even lower EC/PM fraction during idle than high load conditions. The MOVES sulfate fractions appear to be 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.

Table E-8 Comparison of MOVES Conventional Pre-2007 Diesel Profiles with other $PM_{2.5}$ Conventional Diesel Profiles

	MOVES E-55/59		CE-CERT 2004[a]		DOE Gasoline/ Diesel PM Split Study	Northern Front Range Air Quality Study
	Idle (8994)	Running (8995)	Cold start/Idle	Running (Transient)	Composite	Composite (91106)
Elemental carbon	46.4%	79.0%	13.3%	68.0%	72.7%	77.1%
Organic matter	41.7%	17.4%	81.4%	33.5%	24.1%	17.6%
SO_4-2	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%

Note:
a. Organic matter estimated using the 1.2 * OC, other components not measured.

E.3 Development of the ACES PM2.5 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.[31] 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.[84] 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.[85] 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-and-later 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.[31] In the absence of these species, the sulfate is expected to exist as hydrated sulfuric acid. Khalek *et al.* 2011[84] 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)[84], 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.[86]

The ACES Profile is included in the SPECIATE database as profile #5680. This profile is the basis of SPECIATE profile 8996 used in MOVES with one adjustment. MOVES 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 (Equation 12) as used for pre-2007 diesel and light-duty gasoline. The species not needed by MOVES from the ACES Phase 1 profile are summed into the unspeciated fraction. The speciation values are presented in Table D-9. Metal emission rates for manganese, chromium, and nickel from MOVES are derived from the ACES Phase 1 data.[7] They are estimated using the metals calculator with mass/distance emission rates, and are not reported in the SPECIATE profiles.

Table E-9 SPECIATE $PM_{2.5}$ Profile 8996 Developed from the 16-hour Cycle from Four Heavy-duty Diesel Engines with Catalyzed-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%
Unspeciated	0.78%

The ACES Phase 1 derived EC fraction of 9.9% falls within the range of EC fraction of total carbon emissions (2 to 20%) reported from Thiruvengadam et al. 2016.[87]

E.4 Development of the Compressed Natural Gas (CNG) Profile

The California Air Resource Board (CARB) conducted several emission characterization studies on compressed natural gas vehicles. In our profile development, we used only the data reported by CARB for a CNG New Flyer bus with a 2000 MY Detroit Diesel (DDC) Series 50G engine, equipped with and without an oxidation catalyst. 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. CARB also conducted tests on a CNG bus with a 2001 Cummins Westport engine. Other studies that reported EC/OC did not measure emission rates for elements.[88]

We developed the profiles shown in Table E-10 with and without catalyst to estimate the impact of oxidation catalyst control. 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 heavy-duty emissions report[2] and was considered more

representative of typical transit bus behavior.[u,89] The PAH/OC ratios documented in the MOVES3 toxics report[7] were also developed from the CARB measurements on the DDC 50G.

Table E-10 $PM_{2.5}$ 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.[90,91] 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.[92] 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 E-10, the composition of the $PM_{2.5}$ stayed fairly constant. The EC and OC fractions between the two control conditions are not statistically different. 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.

[u] The CNG profile was developed for MOVES2014, where transit buses were the only source type that were run on CNG fuels. In MOVES3, CNG is modeled in all of the heavy-duty source types except combination trucks as documented in the population and activity report.[89]

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)[88] reported that the OC/PM fraction on three CNG transit buses with DDC Series 50G engines ranged from 29 percent to 74 percent of the $PM_{2.5}$. The EC emissions measured by Lanni *et al.* (2003)[88] 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 compares well with the sulfate fraction reported for the 2001 Cummins Westport by CARB[91] (2.8 percent), and by Lanni *et al.* (2003)[88] (1.5 percent to 2.4 percent).

Appendix F $PM_{10}/PM_{2.5}$ 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).[93] 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).[94]

The diesel $PM_{10}/PM_{2.5}$ factor is based on a 1985 EPA report[95], 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)[96], who states that the coarse mode contains 5-20 percent of the total aerosol mass. Unfiltered crankcase emissions published by Donaldson Company Inc. (2011)[97] 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)[98] 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.[97,99] 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 $PM_{10}/PM_{2.5}$ ratios for CNG emissions, and the gasoline ratio is used for CNG emissions. Table F-1 contains the selected exhaust $PM_{10}/PM_{2.5}$ ratios used in MOVES.

Table F-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 G Speciating emissions outside of MOVES

Post-processing of onroad emissions to speciate residual TOG and PM requires the selection of these pollutants when designing the MOVES RunSpec. As defined in section 2.3, residual TOG (NONHAPTOG, pollutantID = 88) corresponds to the remaining TOG mass after MOVES has applied fuel and temperature effects to calculate gaseous integrated species. Similarly, the new Residual PM (nonECnonSO4nonOM, pollutantID = 124) corresponds to the remaining PM mass after MOVES has applied fuel and temperature adjustments, and has calculated particulate integrated species: EC, SO_4 and the newly defined total organic matter (TOM, pollutantID = 123). TOM is simply the sum of two existing MOVES pollutants: NCOM and OC. We have opted to aggregate these species into the new TOM pollutant to facilitate the speciation of organic matter under the Reactive Organic Carbon framework[100] during post-processing downstream from MOVES.

During the speciation step within MOVES, residual TOG and PM are matched to specific speciation profiles by fuel subtype, emission process, regulatory class and model year (see Figures 4-3 and 5-2). To mimic this step during postprocessing outside of MOVES, we have added a new table (*rocSpeciation* table) to the MOVES default database that records the latest mapping of emissions to traditional speciation profiles, as well as new parameters for the speciation of organic matter within the ROC framework. The rocSpeciation table contains the following columns: fuelSubtypeID, regClassID, processID, minModelYearID, maxModelYearID, pmSpeciationProfileID, CROCCode, CROCOMratio, togSpeciationProfileID, GROCCode and GROCNMOGratio. The first five columns characterize the vehicle emission source; togSpeciationProfileID and pmSpeciationProfileID indicate the traditional speciation profiles[8] associated with each vehicle emission source as discussed in previous sections of this document; the "Code" columns specify the ROC speciation profiles[101] (listed in EPA's SPECIATE5.2 [8]) associated with a given vehicle emission source and the "Ratio" columns contain adjustment factors applied within the post-processing script to generate Condensable Reactive Organic Carbon (CROC) mass and Gaseous Reactive Organic Carbon (GROC) mass.

The new rocSpeciation table is not used by MOVES and it is only intended to be used by the post-processing script. For modelers planning to speciate onroad emissions outside of MOVES, in addition to selecting the appropriate pollutants, they must also specify output by SCC, regulatory class, fuel type, emission process and model year for the postprocessing script to run.

The post-processing script generates a SQL database with NONHAPTOG, Residual PM and TOM speciated emissions. The speciated emissions are grouped into SMOKE SCCs to facilitate the combination with vehicle activity within SMOKE-MOVES. A diagram of the new workflow for the post-process is shown in Figure G-1. Further details on how to run the script and how to use the output are provided in the instructions associated with the post-processing speciation script included in the MOVES GUI.

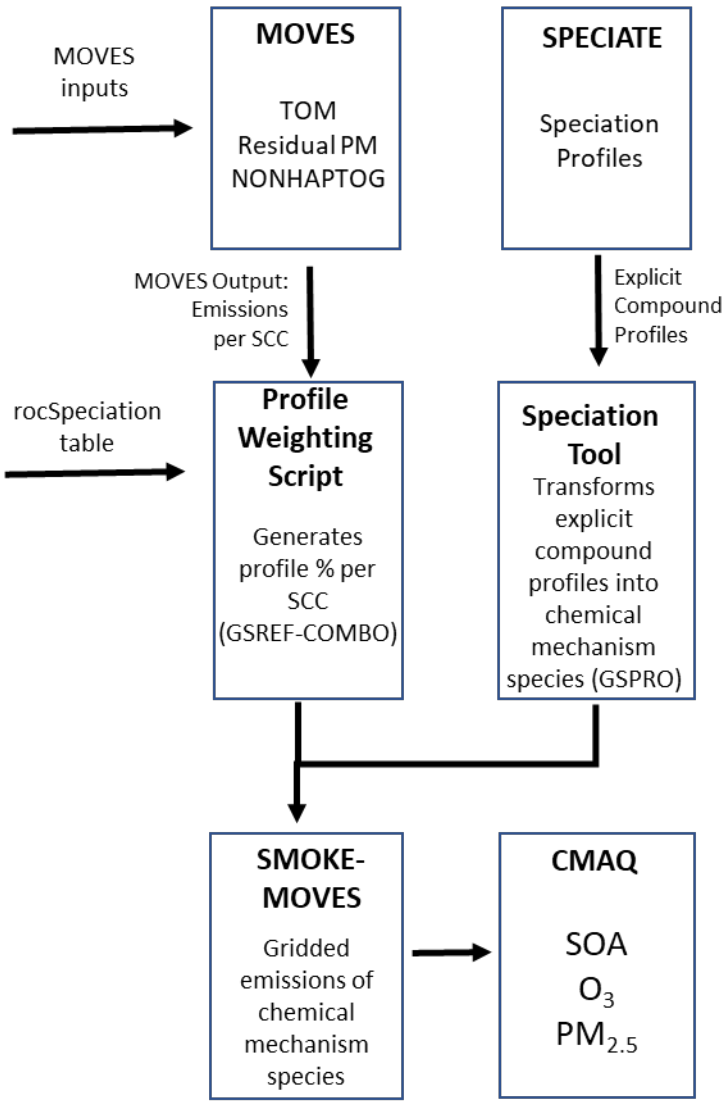

Figure G-1. Diagram showing the new workflow to post-process the speciation of onroad emissions into chemical mechanism species and how it interacts with other modeling platform tools.

6 References

[1] USEPA (2020). *Exhaust Emission Rates for Light-Duty Onroad Vehicles in MOVES3*. EPA-420-R-20-019. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.

[2] USEPA (2020). *Exhaust Emission Rates of Heavy-Duty Onroad Vehicles in MOVES3*. EPA-420-R-20-018. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.

[3] USEPA (2018). *Speciation Profiles and Toxic Emission Factors for Nonroad Engines in MOVES2014b*. EPA-420-R-18-011. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. July 2018. https://www.epa.gov/moves/moves-technical-reports.

[4] USEPA (2003). Conversion Factors for Hydrocarbon Emission Components. EPA420-P-03-002. May 2003

[5] 40 CFR 1065 "Engine-Testing Procedures." Code of Federal Regulations.

[6] 40 CFR 1066 "Vehicle-Testing Procedures." Code of Federal Regulations.

[7] USEPA (2020). *Air Toxic Emissions from Onroad Vehicles in MOVES3*. EPA-420-R-20-022. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.

[8] USEPA (2022). SPECIATE5.2. https://www.epa.gov/air-emissions-modeling/speciate

[9] Johnson, T. and A. Joshi (2018). Review of Vehicle Engine Efficiency and Emissions, SAE International.

[10] Osman, A. I., et al. (2016). A bimetallic catalyst on a dual component support for low temperature total methane oxidation. *Applied Catalysis B: Environmental*, 187, 408-418. DOI: https://doi.org/10.1016/j.apcatb.2016.01.017.

[11] USEPA (2015). *Speciation of Total Organic Gas and Particulate Matter Emissions from On-road Vehicles in MOVES2014*. EPA-420-R-15-022. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2015. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100NOJG.txt.

[12] USEPA (2017). *Speciation and Toxic Emissions from Onroad Vehicles, and Particulate Matter Emissions from Light-Duty Gasoline Vehicles in MOVES201X - Draft Report*. Draft report and peer-review documents. Record ID 328810. EPA Science Inventory. September 2017. https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=328810.

[13] Hydrocarbon (2020). In Encyclopaedia Britannica. https://www.britannica.com/science/hydrocarbon

[14] 40 CFR 51.100 (s) "Volatile Organic Compounds", Code of Federal Regulations

[15] Yarwood, G., S. Rao, M. Yocke, and G. Z. Whitten (2005). *Updates to the Carbon Bond Chemical Mechanism: CB05*. Final Report to the US EPA, RT-0400675. Available at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf.

[16] Greg Yarwood, Jaegun Jung, Gary Z. Whitten, Gookyoung Heo, Jocelyn Mellberg and Mark Estes (2010). *Updates to the Carbon Bond Mechanism for Version 6 (CB6)*. Presented at the 9th Annual CMAS Conference, Chapel Hill, NC, October 11-13, 2010

[17] USEPA (2019). *Technical Support Document (TSD) Preparation of Emissions Inventories for the Version 7.2 2016 North American Emissions Modeling Platform*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Air Quality Assessment Division. Emissions Inventory and Analysis Group. Research Triangle Park, North Carolina. September 2019. https://www.epa.gov/sites/production/files/2019-09/documents/2016v7.2_regionalhaze_emismod_tsd_508.pdf.

[18] Hutzell. B. (2012). CMAQv6.0 Chemistry Notes- SAPRC07T. https://www.airqualitymodeling.org/index.php/CMAQv5.0_Chemistry_Notes

[19] Beardsley, R., T. Shah and G. Yarwood (2020). *Speciation Tool v5.0 Mechanism Mappings for CMAQ (AE7 and AE8) and CAMx (cf2) - MEMO*. Ramboll. March 24, 2020. https://github.com/CMASCenter/Speciation-Tool/blob/master/docs/Ramboll_sptool_mapping_updates_AE7_AE8_24Mar2020_final_full.pdf.

[20] USEPA (2012). *Black Carbon Report to Congress*. EPA-450/R-12-001. March 2012. http://www.epa.gov/blackcarbon/2012report/fullreport.pdf.

[21] Chow, J. C., et al. (2004). Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols. *Environ Sci Technol*, 38 (16), 4414-4422. DOI: 10.1021/es034936u.

[22] Shah, S. D., D. R. Cocker, J. W. Miller and J. M. Norbeck (2004). Emission Rates of Particulate Matter and Elemental and Organic Carbon from In-Use Diesel Engines. *Environ Sci Technol,* 38 (9), 2544-2550. DOI: 10.1021/es0350583.
[23] Simon, H. and P. V. Bhave (2011). Simulating the Degree of Oxidation in Atmospheric Organic Particles. *Environ Sci Technol,* 46 (1), 331-339. DOI: 10.1021/es202361w.
[24] Shah, T., Y. Shi, R. Beardsley and G. Yarwood (2020). *Speciation Tool User's Guide Version 5.0*. Ramboll. June 2020. https://www.cmascenter.org/speciation_tool/documentation/5.0/Ramboll_sptool_users_guide_V5.pdf.
[25] CMAS Center (2015). SMOKE-MOVES and the Emissions Modeling Framework. Updated 12/30/2015. https://www.cmascenter.org/emf/internal/smoke_moves/
[26] USEPA (2020). *Evaporative Emissions from Onroad Vehicles in MOVES3*. EPA-420-R-20-012. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.
[27] USEPA (2020). *Greenhouse Gas and Energy Consumption Rates for Onroad Vehicles in MOVES3*. EPA-420-R-20-015. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.
[28] USEPA (2010). *Hydrocarbon Composition of Gasoline Vapor Emissions from Enclosed Fuel Tanks*. EPA-420-D-10-001. Office of Transportation and Air Quality and Office of Research and Development. US Environmental Protection Agency. Ann Arbor, MI. January 2010. https://nepis.epa.gov/Exe/ZyPDF.cgi/P100FI6K.PDF?Dockey=P100FI6K.PDF.
[29] Coordinating Research Council, "*Vehicle Evaporative Emission Mechanisms: A Pilot Study*". CRC E-77. June 2008
[30] Coordinating Research Council, "*Exhaust and Evaporative Emissions Testing of Flexible-Fuel Vehicles*". CRC-E80. August 2011.
[31] Khalek, I., T. Bougher and P. Merrit (2009). *Phase 1 of the Advanced Collaborative Emissions Study*. CRC Report: ACES Phase 1.
[32] Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements, 66 FR 5002, January 18, 2001.
[33] Greenhouse Gas Emissions and Fuel Efficiency Standards for Medium- and Heavy-Duty Engines and Vehicles—Phase 2, 81 FR 73478, October 25, 2016
[34] Khalek, I. A., M. G. Blanks and P. M. Merritt (2013). *PHASE 2 OF THE ADVANCED COLLABORATIVE EMISSIONS STUDY*. CRC Report: ACES Phase 2. Coordinating Research Council, Inc. & Health Effects Institute. November 2013.
[35] Khalek, I. A., M. G. Blanks, P. M. Merritt and B. Zielinska (2015). Regulated and unregulated emissions from modern 2010 emissions-compliant heavy-duty on-highway diesel engines. *Journal of the Air & Waste Management Association,* 65 (8), 987-1001. DOI: 10.1080/10962247.2015.1051606.
[36] USEPA (2013). *Data Collected in EPAct Fuel Effects Study Pilot Phases*. Memorandum EPA-HQ-OAR-2011-0135-2180 to the Tier 3 Docket. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135. April 2013.
[37] Sluder C. Scott, W. B. H. (2011). *NMOG Emissions Characterizations and Estimation for Vehicles Using Ethanol-Blended Fuels*. ORNL/TM-2011/461. Oak Ridge National Laboratory.
[38] USEPA (2013). *Assessing the Effect of Five Gasoline Properties on Exhaust Emissions from Light-Duty Vehicles Certified to Tier 2 Standards*. EPA-420-R-13-004. April 2013
[39] Karavalakis, G., T. Durbin, K. Johnson and M. Hajbabaei (2015). *Evaluation of the performance and air pollutant emissions of heavy-duty vehicles operating on various natural gas blends*. CEC-2015-2016-029. CE-CERT, University of California, Riverside.
[40]Thiruvengadam, A., et al. (2015). Emission Rates of Regulated Pollutants from Current Technology Heavy-Duty Diesel and Natural Gas Goods Movement Vehicles. *Environ Sci Technol,* 49 (8), 5236-5244. DOI: 10.1021/acs.est.5b00943.
[41]Thiruvengadam, A., et al. (2016). Unregulated greenhouse gas and ammonia emissions from current technology heavy-duty vehicles. *Journal of the Air & Waste Management Association,* 66 (11), 1045-1060. DOI: 10.1080/10962247.2016.1158751.
[42] Johnson, K. (2016). *Ultra-Low NOx Natural Gas Vehicle Evaluation ISL G NZ*. CE-CERT. November 2016.

[43] Ayala, A., et al. (2003). Oxidation Catalyst Effect on CNG Transit Bus Emissions. *Society of Automotive Engineers*,(SAE Technical Paper 2003-01-1900).
[44] May, A. A., et al. (2014). Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. *Atmospheric Environment*, 88 (0), 247-260. DOI: http://dx.doi.org/10.1016/j.atmosenv.2014.01.046.
[45] Quiros, D. C., et al. (2016). Real-World Emissions from Modern Heavy-Duty Diesel, Natural Gas, and Hybrid Diesel Trucks Operating Along Major California Freight Corridors. *Emission Control Science and Technology,* 2 (3), 156-172. DOI: 10.1007/s40825-016-0044-0.
[46] Quiros, D. C., J. Smith, A. Thiruvengadam, T. Huai and S. Hu (2017). Greenhouse gas emissions from heavy-duty natural gas, hybrid, and conventional diesel on-road trucks during freight transport. *Atmospheric Environment*, 168 (Supplement C), 36-45. DOI: https://doi.org/10.1016/j.atmosenv.2017.08.066.
[47] Hays, M. D., et al. (2017). Temperature and Driving Cycle Significantly Affect Carbonaceous Gas and Particle Matter Emissions from Diesel Trucks. *Energy & Fuels*. DOI: 10.1021/acs.energyfuels.7b01446.
[48] Karavalakis, G., et al. (2016). Emissions and fuel economy evaluation from two current technology heavy-duty trucks operated on HVO and FAME blends. *SAE International Journal of Fuels and Lubricants,* 9 (1), 177-190.
[49] USEPA (2020) "Annual Certification Data for Vehicles, Engines, and Equipment." Heavy-Duty Highway Gasoline and Diesel Certification Data Retrieved November, 25, 2020, from https://www.epa.gov/compliance-and-fuel-economy-data/annual-certification-data-vehicles-engines-and-equipment.
[50] USEPA (2020). *Emission Adjustments for Temperature, Humidity, Air Conditioning, and Inspection and Maintenance for Onroad Vehicles in MOVES3*. EPA-420-R-20-013. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.
[51] USEPA (2020). *Fuel Effects on Exhaust Emissions from Onroad Vehicles in MOVES3*. EPA-420-R-20-016. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI. November 2020. https://www.epa.gov/moves/moves-technical-reports.
[52] Bhave, P., et al. (2011). *Impact of ISORROPIA II on air quality model predictions*. CMAS Conference, Chapel Hill, NC. October 24-26, 2011.
http://www.cmascenter.org/conference/2011/slides/bhave_impact_isorropia_2011.ppt.
[53] Quiros, D., et al. (2016). *Characterization of chemical composition of particulate matter from modern heavy-duty vehicles under real-world driving conditions.* CRC Real-World Emissions Workshop, Newport Beach, CA, CRC. March 13-16, 2016.
[54] Ruehl, C., et al. (2016). *Mass Balance and Emissions from both active and passive regenerations of heavy duty diesel particulate filters*. CRC Real-World Emissions Workshop, Newport Beach, CA, CRC. March 13-16, 2016.
[55] USEPA (2018). *Technical Support Document (TSD) Preparation of Emissions Inventories for the Version 7.1 2014 Emissions Modeling Platform for the National Air Toxics Assessment*. page 68. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Air Quality Assessment Division. Emissions Inventory and Analysis Group. Research Triangle Park, North Carolina. August 2018.
[56] USEPA (2013). *EPAct Pilot data summary April 2013*. Memorandum EPA-HQ-OAR-2011-0135-2181 to the Tier 3 Docket. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135. April 2013.
[57] Hesterberg, T. W., C. A. Lapin and W. B. Bunn (2008). A Comparison of Emissions from Vehicles Fueled with Diesel or Compressed Natural Gas. *Environ Sci Technol*, 42 (17), 6437-6445. DOI: 10.1021/es071718i.
[58] Kado, N. Y.; Okamoto, R. A.; Kuzmicky,, P. A.; Kobayashi, R.; Ayala,A.; Gebel, M. E.; Rieger, P. L.;Maddox, C.; Zafonte, L.; Emissions of Toxic Pollutants from Compressed Natural Gas and Low Sulfur Diesel-Fueled Heavy-Duty Transit Buses Tested over Multiple Driving Cycles. Environmental Science & Technology 2005 39 (19), 7638-7649.
[59] 40 CFR 1065.845 "Vehicle-Testing Procedures. Response Factor Determination" Code of Federal Regulations.
[60] US EPA, *Frequently Asked Questions about Heavy-Duty "Glider Vehicles" and "Glider Kits"*, EPA-420-F-15-904, Ann Arbor, MI: July 2015, https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100MUVI.PDF.
[61] Sonntag, D. B., R. W. Baldauf, C. A. Yanca and C. R. Fulper (2013). Particulate matter speciation profiles for light-duty gasoline vehicles in the United States. *Journal of the Air & Waste Management Association,* 64 (5), 529-545. DOI: 10.1080/10962247.2013.870096.
[62] Robert, M. A., S. VanBergen, M. J. Kleeman and C. A. Jakober (2007). Size and composition distributions of particulate matter emissions: Part 1—Light-duty gasoline vehicles. *Journal of the Air & Waste Management Association,* 57 (12), 1414-1428.

[63] Carrol, J., I. Khalek, L. Smith, E. Fujita and B. Zielinska (2011). *Collaborative Lubricating Oil Study on Emissions*. NREL/SR-5400-52668. October, 2011. http://www.nrel.gov/docs/fy12osti/52668.pdf.
[64] Lough, G. C., et al. (2007). Development of molecular marker source profiles for emissions from on-road gasoline and diesel vehicle fleets. *Journal of the Air & Waste Management Association,* 57 (10), 1190-1199.
[65] Cadle, S. H., et al. (1999). Composition of Light-Duty Motor Vehicle Exhaust Particulate Matter in the Denver, Colorado Area. *Environ Sci Technol,* 33 (14), 2328-2339. DOI: 10.1021/es9810843.
[66] Sonntag, D. B., C. R. Bailey, C. R. Fulper and R. W. Baldauf (2012). Contribution of Lubricating Oil to Particulate Matter Emissions from Light-Duty Gasoline Vehicles in Kansas City. *Environ Sci Technol,* 46 (7), 4191-4199. DOI: 10.1021/es203747f.
[67] Schauer, J., et al. (2006). *Characterization of Metals Emitted from Motor Vehicles*. Health Effects Institute Research Report Number 133 Health Effects Institute Research Report Number 133. http://pubs.healtheffects.org/.
[68] Kleeman, M. J., S. G. Riddle, M. A. Robert and C. A. Jakober (2007). Lubricating Oil and Fuel Contributions To Particulate Matter Emissions from Light-Duty Gasoline and Heavy-Duty Diesel Vehicles. *Environ Sci Technol,* 42 (1), 235-242. DOI: 10.1021/es071054c.
[69] Ayala, A., et al. (2011). *Prospects for low PM and low climate impacts in future advanced clean cars for California. Presented at the 21st CRC Real World Emissions Workshop, March*. CRC Real-World Emissions Workshop, San Diego, CA, CRC. March 20-23, 2011.
[70] May, A. A., et al. (2014). Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. *Atmospheric Environment,* 88 (0), 247-260. DOI: http://dx.doi.org/10.1016/j.atmosenv.2014.01.046.
[71] Andersson, J., M. Keenan and K. Akerman (2009). *GDI particles—Legislation, current levels and control*. 2009 Cambridge Particle Meeting. March 16, 2009
[72] Storey, J., T. Barone, J. Thomas and S. Huff (2012). Exhaust particle characterization for lean and stoichiometric DI vehicles operating on ethanol–gasoline blends. *Society of Automotive Engineers,*(SAE Technical Paper 2012-01-0437). DOI: doi:10.4271/2012-01-0437.
[73] Forestieri, S. D., et al. (2013). Real-Time Black Carbon Emission Factor Measurements from Light Duty Vehicles. *Environ Sci Technol,* 47 (22), 13104-13112. DOI: 10.1021/es401415a.
[74] USEPA (2000). "Control of Air Pollution From New Motor Vehicles: Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control Requirements", 65 FR 6698, February 10, 2000.
[75] USEPA (2014). "Control of Air Pollution From Motor Vehicles: Tier 3 Motor Vehicle Emission and Fuel Standards", 79 FR 23414, April 28, 2014.
[76] Clark, N. and M. Gautam (2007). *HEAVY-DUTY Vehicle Chassis Dynamometer Testing for Emissions Inventory, Air Quality Modeling, Source Apportionment and Air Toxics Emissions Inventory*. CRC Report. No. E55/59. Aug-07.
[77] Mullen, M. (2010). *Diesel Unregulated Emissions Characterization*. CRC Report No. E-75-2. Jul-10.
[78] Clark, N. and M. Gautam (2003). *HEAVY-DUTY Vehicle Chassis Dynamometer Testing for Emissions Inventory, Air Quality Modeling, Source Apportionment and Air Toxics Emissions Inventory: Phase 1 Report*. CRC Report. No. E55/59. Apr-03.
[79] Schauer, J. J., M. J. Kleeman, G. R. Cass and B. R. T. Simoneit (1999). Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks. *Environ Sci Technol,* 33 (10), 1578-1587. DOI: 10.1021/es980081n.
[80] Reff, A., et al. (2009). Emissions Inventory of PM2.5 Trace Elements across the United States. *Environ Sci Technol,* 43 (15), 5790-5796. DOI: 10.1021/es802930x.
[81] Kleeman, M., J. Schauer and G. Cass (2000). Size and composition of fine particulate matter emitted from motor vehicles. *Environ Sci Technol,* 34 (7), 1132-1142.
[82] Noll, J. and M. E. Birch (2008). Effects of Sampling Artifacts on Occupational Samples of Diesel Particulate Matter. *Environ Sci Technol,* 42 (14), 5223-5228. DOI: 10.1021/es702883k.
[83] Shah, S. D., D. R. Cocker, J. W. Miller and J. M. Norbeck (2004). Emission Rates of Particulate Matter and Elemental and Organic Carbon from In-Use Diesel Engines. *Environ Sci Technol,* 38 (9), 2544-2550. DOI: 10.1021/es0350583.
[84] Khalek, I. A., T. L. Bougher, P. M. Merritt and B. Zielinska (2011). Regulated and Unregulated Emissions from Highway Heavy-Duty Diesel Engines Complying with U.S. Environmental Protection Agency 2007 Emissions Standards. *Journal of the Air & Waste Management Association,* 61 (4), 427-442. DOI: 10.3155/1047-3289.61.4.427.

[85] Subramanian, R., et al. (2009). Climate-Relevant Properties of Diesel Particulate Emissions: Results from a Piggyback Study in Bangkok, Thailand. *Environ Sci Technol,* 43 (11), 4213-4218. DOI: 10.1021/es8032296.
[86] USEPA, (2009). SPECIATE 4.2 SPECIATION DATABASE DEVELOPMENT DOCUMENTATION. EPA/600-R-09/038. Available at: http://nepis.epa.gov/
[87] Thiruvengadam, A., et al. (2016). Unregulated greenhouse gas and ammonia emissions from current technology heavy-duty vehicles. *Journal of the Air & Waste Management Association,* 66 (11), 1045-1060. DOI: 10.1080/10962247.2016.1158751.
[88] Lanni, T., B. Frank, S. Tang, D. Rosenblatt and D. Lowell (2003). Performance and Emissions Evaluation of Compressed Natural Gas and Clean Diesel Buses at New York City's Metropolitan Transit Authority. *Society of Automotive Engineers*,(SAE Technical Paper 2003-01-0300).
[89] USEPA (2020). *Population and Activity of On-road Vehicles in MOVES CTI NPRM*. Office of Transportation and Air Quality. US Environmental Protection Agency. Ann Arbor, MI.
[90] Ayala, A., et al. (2003). Oxidation Catalyst Effect on CNG Transit Bus Emissions. *Society of Automotive Engineers*,(SAE Technical Paper 2003-01-1900).
[91] Okamoto, R. A., N. Y. Kado, P. A. Kuzmicky, A. Ayala and R. Kobayashi (2006). Unregulated Emissions from Compressed Natural Gas (CNG) Transit Buses Configured with and without Oxidation Catalyst. *Environ Sci Technol,* 40 (1), 332-341. DOI: 10.1021/es0479742.
[92] Gautam, M., et al. (2011). *Testing of Volatile and Nonvolatile Emissions from Advanced Technology Natural Gas Vehicles*. Contract No. 07-340. July, 2011. http://www.arb.ca.gov/research/apr/past/07-340.pdf.
[93] Norbeck, J., T. Durbin and T. Truex (1988). *Measurement of Primary Particulate Matter Emissions from Light Duty Motor Vehicles*. Prepared by College of Engineering, Center for Environmental Research and Technology, University of California, for Coordinating Research Council and South Coast Air Quality Management District.
[94] Schauer, J. J., C. G. Christensen, D. B. Kittelson, J. P. Johnson and W. F. Watts (2008). Impact of Ambient Temperatures and Driving Conditions on the Chemical Composition of Particulate Matter Emissions from Non-Smoking Gasoline-Powered Motor Vehicles. *Aerosol Science and Technology,* 42 (3), 210-223. DOI: 10.1080/02786820801958742.
[95] USEPA (1985). *Size Specific Total Particulate Emission Factors for Mobile Sources*. EPA 460/3-85-005. August, 1985.
[96] Kittelson, D. B. (1998). Engines and nanoparticles: a review. *Journal of Aerosol Science,* 29 (5–6), 575-588. DOI: http://dx.doi.org/10.1016/S0021-8502(97)10037-4.
[97] Kalayci, V. (2011). *Spiracle™ Crankcase Filtration Systems: Technical Article*. Donaldson Company, Inc.
[98] Tatli, E. and N. Clark (2009). Crankcase Particulate Emissions from Diesel Engines. *SAE Int. J. Fuels Lubr.,* 1, 1334-1344. DOI: doi:10.4271/2008-01-1751.
[99] Dollmeyer, T. A., et al. (2007). Meeting the US heavy-duty diesel emission standards - designing for the customer. *Society of Automotive Engineers*,(SAE Technical Paper 2007-01-4170). DOI: doi:10.4271/2007-01-4170.
[100] Heald, C. L. and Kroll, J. H. (2020). The fuel of atmospheric chemistry: Toward a complete description of reactive organic carbon, *Science Advances*, 6, eaay8967, DOI:10.1126/sciadv.aay8967.
[101] Murphy B. et al. (2022), Reactive Organic Carbon Air Emissions from Mobile Sources in the United States (*in prep*.)