# MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling

# Table of Contents

# 1 Introduction

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

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

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

The reason for bringing the speciation capability inside MOVES is improved accuracy and flexibility. Because the speciation of TOG and $PM_{2.5}$ depends on technology, fuels, and emission processes, speciation is approximate and difficult to implement outside MOVES. Pre-MOVES2014, speciation profiles were applied outside the model primarily by source classification code (SCC) or aggregate emission process (evaporation, exhaust, refueling, brakewear, tirewear), although county was also used to allow speciation to account for combinations of ethanol fuel blends in different areas. This outside-of-MOVES speciation is limited as it is difficult to apply speciation profiles by model-year group, regulatory class, fuel subtype (e.g., gasolines with different ethanol content), or specific emission process (e.g., exhaust start, exhaust extended idle, exhaust running). For example, TOG and $PM_{2.5}$ speciation differs for pre- and post-2007 model year heavy-duty diesel vehicles. Since the input to air

quality models is by calendar year, and the mix of pre- and post-2007 model year vehicles changes by calendar year, a custom profile for each calendar year must be prepared to speciate diesel emissions. The pre-MOVES2014 approach used a national run to approximate the fractions of VOC and $PM_{2.5}$ from pre- and post-2007 model year vehicles, applying these fractions to pre- and post-2007 model year heavy-duty diesel vehicle speciation profiles to create a single weighted profile for each calendar year. Inside MOVES, speciation (like all calculations) is done on a model-year, fuel, and emission-process basis, giving it the ability to reflect distinctions in different TOG and $PM_{2.5}$ profiles. In addition, since it is done inside MOVES, the time-consuming, approximate, and error-prone process of preparing and applying speciation profiles in emission processing for air quality models is eliminated. Also, putting speciation into MOVES removes the pressure to include regulatory class and emission process in SCC.

# 2 Speciation Glossary

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

- Aggregate species: collections of real species. For example, THC, TOG and VOC are aggregate gaseous species. NonEC and NonECnonSO4PM are aggregate particulate matter species.

- Elemental Carbon (EC): "A descriptive term for carbonaceous particles based on chemical composition rather than light-absorbing characteristics. Often used as a synonym for black carbon." [5] Also defined as graphitic carbon formed through pyrolysis through combustion[6]. Elemental carbon is routinely measured through thermal optical techniques as particle-phase carbon that does not volatize at high temperatures in an oxygen-free environment.

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

- Chemical mechanism: In air-quality models, chemical mechanisms are simplified representations of the full panoply of atmospheric chemical reactions. They have been developed by air-quality modelers to speed 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. The only mechanism that we are including in MOVES2014 is the "carbon-bond chemical mechanism" (CB05).[7] However, since the mapping is table-driven, MOVES2014 has the structure in place to generate CM species for any chemical mechanism. OTAQ expects to add others over time.

- Integrated species: real species for which MOVES produces emissions that are subtracted from TOG, leaving residual TOG. They are referred to as "integrated" because they are integrated with the TOG speciation. The way they are integrated is to subtract them from TOG and then CM-speciate the residual TOG. At present, MOVES2014 integrates the 16 species shown in Table 1. MOVES is designed to accept different sets of integrated species, if desired.

**Table 1. Integrated MOVES pollutants**

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

- Intermediate $PM_{2.5}$ species: Subspecies of $PM_{2.5}$ species used to improve computational time, and reduce the size of the emission rate tables. They include aggregate species including non-elemental carbon particulate matter (NonECPM) and the non-elemental carbon, non-sulfate particulate matter (NonECnonSO4PM), and real species, including 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 real species are reported as MOVES outputs.

- Chemical mechanism species (CM species): the species used by chemical mechanisms. CM species include both artificial constructs (sometimes referred to as "lumped species") and real species. CM species are unique to particular chemical mechanisms (e.g., CB05, SAPRC07). All real TOG species are mapped to CM species. For a particular chemical mechanism, the CM species can be referred to by the name of the mechanism, for example, CB05 species.

- CM speciation profile: the mapping of either a real species (e.g., hexane) or 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.[7] The mapping of real species is independent of process and fuel. The mapping of aggregate species (e.g., residual TOG) is simply the sum of the mappings of the individual real species from the real speciation profiles. The mapping of aggregate species depends on process and fuel.

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

- Organic Carbon (OC): "The mix of compounds containing carbon bound with other elements; e.g., hydrogen and oxygen. Organic carbon may be a product of incomplete combustion, or formed through the oxidation of VOCs in the atmosphere." (EPA, 2012). From a measurement perspective, organic carbon is the particle-phase carbon collected on a filter that volatizes at high temperatures in an oxygen-free environment.

- Non-carbon organic mass (NCOM): the mass of the oxygen, hydrogen, nitrogen and other elements present in particle-phase organic mass. OC and NCOM are modeled separately in air quality models in order to model the degree of oxidation of organic matter, which depends on the emission source and the chemical transformation in the atmosphere[8].

- 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, from elemental carbon measurements made using thermal optical measurements, or surrogate elemental carbon measurements such as photoacoustic sensors.

- Non-elemental carbon, non-sulfate particulate matter (nonECnonSO4PM): A MOVES intermediate species used to represent the $PM_{2.5}$ mass other than elemental carbon, sulfate, and associated water. NonECnonSO4PM includes organic matter, elements, and ions. NonECnonSO4PM is adjusted for fuel and temperature effects, prior to speciation due to limited data on temperature and fuel effects on individual $PM_{2.5}$ species in the exhaust, and to improve computational time.

- Non-methane hydrocarbons (NMHC): Defined as THC minus methane emissions.

- Non-methane organic gases (NMOG): Defined as TOG minus methane emissions.

- Real species means "species" in the normal chemical sense: a pure chemical substance. The word "real" helps distinguish these species from lumped species or $PM_{2.5}$ aggregated species.

- Real speciation profile: a complete listing of the real species and their quantities for TOG. 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 and fuel, since the mix of real species in TOG is different for different processes (e.g. evaporative and exhaust) and for different fuels. The SPECIATE database is the EPA repository for these profiles. (http://www.epa.gov/ttn/chief/software/speciate/index.html)

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

- Process: MOVES2014 has twelve emission processes that are relevant for TOG speciation. The Process IDs and names are included in Table 2.

**Table 2. MOVES processes relevant to speciation profiles**

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

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

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

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

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

- Volatile Organic Compounds (VOC): TOG emissions minus less-ozone forming hydrocarbons including methane and ethane[1]. EPA may over time exclude additional organic compounds from the definition of VOC which have negligible photochemical reactivity. See http://www.epa.gov/ttn/naaqs/ozone/ozonetech/def_voc.htm for the current list.

# 3 Hydrocarbon Speciation Calculations

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

**Table 3. Relationships among Hydrocarbon Aggregate Species in MOVES**

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

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

## *3.1 Non-Methane Hydrocarbon Calculation*

Exhaust regulations for hydrocarbons, are often expressed in terms of non-methane hydrocarbons (NMHC). MOVES calculates both methane and NMHC from the THC emissions using methane/total hydrocarbon ratios (CH4THCRatio in the MethaneTHCRatio Table). The development of the methane/total hydrocarbon ratios is documented in the MOVES2014 Greenhouse Gas and Energy Consumption Rates Report[9].

## *3.2 Non-Methane Organic Gases Calculation*

Non-Methane Organic Gases (NMOG) is defined as the all non-methane organic gases, including oxygenated hydrocarbons such as alcohols and aldehydes. To calculate NMOG from NMHC requires accounting for the FID response factor for the oxygenated hydrocarbons. For example, formaldehyde has an FID response of 0, so formaldehyde measurements need to be fully added to the NMHC value. Acetaldehyde has a FID response factor of 0.5, which means that only ½ of the measured acetaldehyde emissions need to be added to the FID measurements.

To compute NMHC to NMOG factors as a ratio, the following equation is used:

$$\text{Speciation - Factor}_{\text{NMOG}} = \frac{NMOG}{NMHC_{\text{FID}}} = \frac{(CF_{\text{HCHO}}\, MPC_{\text{HCHO}}) + (CF_{\text{acetald}}\, MPC_{\text{acetald}}) + (CF_{\text{EtOH}}\, MPC_{\text{EtOH}}) + (CF_{\text{NMHC}} MPC_{\text{NMHC}})}{[(CF_{\text{acetald}}\, FID_{\text{acetald}}) + (CF_{\text{EtOH}}\, FID_{\text{EtOH}}) + (CF_{\text{NMHC}} FID_{\text{NMHC}})] \times MPC_{\text{NMHC}}}$$

**Equation 1**

*Where:*

*CF = carbon fraction*

*MPC = mass per carbon*

*$FID_X$ = FID response factor*

Within MOVES, the following equations are used to calculate NMOG.

For fuels containing ethanol:

$$NMOG = NMHC \cdot (speciationConstant + oxySpeciation \cdot volToWtPercentOxy \cdot ETOHVolume)$$

For fuels containing Methyl tert-butyl ether (MTBE):

$$NMOG = NMHC \cdot (speciationConstant + oxySpeciation \cdot volToWtPercentOxy \cdot MTBEVolume)$$

For fuels containing Ethyl tert-butyl ether (ETBE):

$$NMOG = NMHC \cdot (speciationConstant + oxySpeciation \cdot volToWtPercentOxy \cdot ETBEVolume)$$

For fuels containing tert-Amyl methyl ether (TAME):

$$NMOG = NMHC \cdot (speciationConstant + oxySpeciation \cdot volToWtPercentOxy \cdot TAMEVolume)$$

**Table 4. Volume to Weight Percent Oxygen for Gasoline Oxygenates**

| Oxygenate Name | Volume to Weight Percent Oxygen (volToWtPercentOxy) |
|---|---|
| Ethanol | 0.3488 |
| MTBE | 0.1786 |
| ETBE | 0.1533 |
| TAME | 0.1636 |

Exhaust speciation factors for pre-Tier 2 gasoline vehicles remain unchanged from MOVES2010. The pre-Tier 2 gasoline HC factors in MOVES were taken from MOBILE6.2 materials and were originally produced for MOBILE4.1 and MOBILE5. These values are displayed in Table 5.

**Table 5. Parameters used to calculate NMOG/NMHC Ratios for Pre-Tier 2 gasoline**

| Model Year Group | Fuel Subtype | Process | SpeciationConstant | OxySpeciation |
|---|---|---|---|---|
| pre-1974 | <5% oxygenates | Start and Running Exhaust | 1.0352 | 0.0074 |
| 1975-1986 | | | 1.02113 | 0.0074 |
| 1987-1989 | | | 1.0179 | 0.0074 |
| 1990-1996 | | | 1.0167 | 0.0074 |
| 1997-2003 | | | 1.0163 | 0.0074 |
| pre-1974 | E5 to E10 | Start and Running Exhaust | 1.0352 | 0.0062 |
| 1975-1986 | | | 1.02113 | 0.0062 |
| 1987-1989 | | | 1.0179 | 0.0062 |
| 1990-1996 | | | 1.0167 | 0.0062 |
| 1997-2003 | | | 1.0163 | 0.0062 |
| pre-2004 | E20 | Start | 1.0703 | 0 |
| pre-2004 | E20 | Running | 1.0367 | 0 |
| pre-2004 | E70 to E100 | Start and Running Exhaust | 1.4858 | 0 |

For MOVES2014, we updated the hydrocarbon speciation factors for Tier 2 gasoline, E15, E70-E100, diesel, and CNG fueled vehicles. The exhaust hydrocarbon emissions from Tier 2-and-later vehicles are substantially different in composition from pre-Tier 2 vehicles. The new gasoline speciation factors are based on EPAct Phase 3 data.[10] The EPAct data was used to derive new E15 and E70-E100 NMOG/NMHC parameters. MOVES2014 uses the same HC speciation factors for E20 as previous versions; they are included in Table 6 for comparison.

More recent and extensive data were available for pre-2007 diesel engines than those used in earlier versions of MOVES[11,], and for 2007-and-later diesel engines data were available from the Advanced Collaborative Emissions Study (ACES).[12] MOVES2014 also includes updated NMOG speciation factors for compressed-natural-gas transit buses. Two speciation values are provided based on two model groups (pre-2002 and 2002 and later groups), which correspond to no control, and oxidation catalyst. CNG exhaust contains high formaldehyde emissions, particularly on uncontrolled compression ignition buses, which causes high NMOG/NMHC ratios. The derivation of the NMOG/NMHC and VOC/NMHC rates are documented in the 2014 Heavy-Duty Emissions Report. The new 'speciationConstant' and 'oxySpeciation' coefficients for Tier 2 gasoline, E15, E70-E100 blends, diesel vehicles, and compressed natural gas vehicles are summarized in Table 5.

**Table 6. Parameters used to calculate NMOG/NMHC Ratios**

| Engine Type | Fuel Subtype | Process | SpeciationConstant | OxySpeciation |
|---|---|---|---|---|
| Gasoline Tier 2 | E0 to E10 | Start | 1.0078 | 0.0082 |
| Gasoline Tier 2 | E0 to E10 | Running | 1.0149 | 0.0028 |
| Gasoline | E15 | Start | 1.0495 | 0 |
| Gasoline | E15 | Running | 1.0318 | 0 |
| Gasoline | E20 | Start | 1.0703 | 0 |
| Gasoline | E20 | Running | 1.0367 | 0 |
| Gasoline | E70 to E100 | Start and Running | 1.4858 | 0 |
| Diesel – pre-2007 | All | Start and Running | 1.1455 | 0 |
| Diesel – 2007+ | All | Start and Running | 1.3431 | 0 |
| CNG - pre-2002 | All | Start and Running | 1.90 | 0 |
| CNG – 2002 + | All | Start and Running | 1.24 | 0 |

## *3.3 Volatile Organic Compound Calculation*

Volatile Organic Compounds (VOC) are defined as the TOG compounds minus methane and ethane. In MOVES, VOCs are calculated as NMOG minus ethane.

To calculate VOC as a ratio from NMHC the following equation is used:

$$\text{Speciation Factor}_{VOC} = \frac{VOC}{NMHC_{\text{FID}}}$$

$$= \frac{(CF_{\text{HCHO}}\, MPC_{\text{HCHO}}) + (CF_{\text{acetald}}\, MPC_{\text{acetald}}) + (CF_{\text{EtOH}}\, MPC_{\text{EtOH}}) + (CF_{\text{NMHC}} MPC_{\text{NMHC}}) - (CF_{\text{ethane}}\, MPC_{\text{ethane}})}{[(CF_{\text{acetald}}\, FID_{\text{acetald}}) + (CF_{\text{EtOH}}\, FID_{\text{EtOH}}) + (CF_{\text{NMHC}} FID_{\text{NMHC}})] \times MPC_{\text{NMHC}}} \quad \textbf{Equation 2}$$

*Where:*

*CF = carbon fraction*

*MPC = mass per carbon*

*$FID_X$ = FID response factor*

MOVES uses the same calculator and table to calculate VOC emissions as NMOG emissions. However, the parameters are different to account for the exclusion of ethane emissions. The same data sources are used to derive the VOC/NMHC ratios as the NMOG/NMHC ratios presented earlier. The pre-Tier 2 gasoline values are displayed in Table 7.

**Table 7. Parameters used to calculate VOC/NMHC Ratios for Pre-Tier 2 gasoline vehicles**

| Model Year Group | Fuel Subtype | Process | SpeciationConstant | OxySpeciation |
|---|---|---|---|---|
| pre-1974 | <5% | Start and Running Exhaust | 1.0239 | 0.0159 |
| 1975-1986 | <5% | | 0.9799 | 0.0159 |
| 1987-1989 | <5% | | 0.976 | 0.0159 |
| 1990-1996 | <5% | | 0.9787 | 0.0159 |
| 1997-2003 | <5% | | 0.9797 | 0.0159 |
| Pre-2004 | E15 | Start | 0.9049 | 0 |
| Pre-2004 | E15 | Running | 1.0162 | 0 |
| Pre-2004 | E20 | Start | 0.9233 | 0 |
| Pre-2004 | E20 | Running | 1.0436 | 0 |
| Pre-2004 | E70 to E100 | Start and Running | 1.3981 | 0 |

The updated values in MOVES2014 for Tier 2 gasoline, E15, E70-E100, diesel, and CNG fueled-vehicles are displayed in in Table 6. The E20 values were not updated for MOVES2014, but are also included in Table 8 for comparison.

**Table 8. Parameters used to calculate VOC/NMHC Ratios**

| Engine Type | Fuel Subtype | Process | SpeciationConstant | OxySpeciation |
|---|---|---|---|---|
| Gasoline Tier 2 | E0 to E10 | Start | 0.9787 | 0.0068 |
| Gasoline Tier 2 | E0 to E10 | Running | 0.9148 | -0.0013 |
| Gasoline | E15 | Start | 1.0162 | 0 |
| Gasoline | E15 | Running | 0.9049 | 0 |
| Pre-2004 | E20 | Start | 0.9233 | 0 |
| Pre-2004 | E20 | Running | 1.0436 | 0 |
| Gasoline | E70 to E100 | Start and Running | 1.3981 | 0 |
| Diesel – pre-2007 | All | Start and Running | 1.1243 | 0 |
| Diesel – 2007+ | All | Start and Running | 1.3058 | 0 |
| CNG – Pre-2002 | All | Start and Running | 1.68 | 0 |
| CNG – 2002 + | All | Start and Running | 0.95 | 0 |

## *3.1 NMHC and VOC Calculations for Evaporative and Permeation Emissions*

Since no methane or ethane are found in evaporative or permeation emissions, THC is equivalent to NMHC, and VOC is equivalent to NMOG and TOG. Thus, speciation factors are only needed to convert THC to NMOG, to account for the mass of ethanol not measured by the FID:

$$\text{Speciation - Factor}_{\text{NMOG}} = \frac{NMOG}{NMHC_{\text{FID}}} = \frac{(CF_{\text{EtOH}}\ MPC_{\text{EtOH}}) + (CF_{\text{THC}} MPC_{\text{THC}})}{(CF_{\text{EtOH}}\ FID_{\text{EtOH}}) + (CF_{\text{THC}} FID_{\text{THC}})] \times MPC_{\text{THC}}} \qquad \textbf{Equation 3}$$

THC to NMOG factors for ethanol content at or below 20% are unchanged from earlier versions of MOVES for fuel vapor venting, fuel leaks, and refueling evaporative emissions. The speciation factors for E70/E85 were updated based on the analysis of the CRC E-80 program.[13] The values used by MOVES for these processes are reported in Table 7.

**Table 9. Gasoline Vehicle Evaporative THC to NMOG and VOC speciation factors**

| Engine Type | Fuel Subtype | Process | SpeciationConstant | OxySpeciation |
|---|---|---|---|---|
| Gasoline | <5% ethanol | Vapor Venting and Refueling Vapor Loss | 1 | 0.0243 |
| | E5 to E20 | | 1 | 0.0318 |
| | E70 to E100 | | 1.511 | 0 |

| | | | | |
|---|---|---|---|---|
| Gasoline | <5% ethanol | Fuel Leaks and Refueling Spillage Loss | 1 | 0.0455 |
| | E5 to E20 | | 1 | 0.025 |
| | E70 to E100 | | 1.511 | 0 |

New permeation factors were developed for MOVES2014 for E0 to E10, and for E15 based on data from the CRC E-77 program.[14,15] For E70 to E100, the speciation factor for permeation is identical to the factors for other evaporative processes (see Table 9), developed from CRC E-80 program. These factors are provided in Table 8. The permeation factor for E20 is unchanged with the MOVES2014 update and is also shown in Table 10.

**Table 10 Gasoline Vehicle Permeation hydrocarbon THC to NMOG and VOC speciation factors**

| Engine Type | Fuel Subtype | Process | SpeciationConstant | OxySpeciation |
|---|---|---|---|---|
| Gasoline | E0 to E10 | Permeation | 1 | 0.036 |
| Gasoline | E15 | Permeation | 1.1755 | |
| Gasoline | E20 | Permeation | 1.2235 | 0 |
| Gasoline | E70 to E100 | Permeation | 1.511 | 0 |

### *3.2 Total Organic Gases Calculation*

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

$$TOG = NMOG + Methane$$

# 4 TOG Speciation

### *4.1 Overview*

MOVES2014 produces output of the CM species of Total Organic Gases (TOG) in a form suitable for air-quality modeling. Prior to MOVES2014, the mapping of MOVES output of organic carbon species (e.g., benzene, 1,3-butadiene) and aggregates (e.g., TOG) into CM species was done outside MOVES by emission pre-processors to air-quality models. In this report, this mapping process is referred to as TOG speciation.

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

Residual TOG = TOG - MOVES gaseous organic carbon species

The MOVES organic carbon species that are subtracted are referred to as "integrated species." Currently, we are integrating 16 MOVES species, listed in Table 1. Those excluded are primarily the PAHs and the dioxins.

TOG speciation required for air quality models is different than PM speciation due to the concept of chemical mechanisms. Chemical mechanisms (defined in the glossary) are used to simplify

the thousands of individual organic compounds into a manageable set of CM species used for air quality modeling. The profiles used in this process, and the mapping of real species into CM species is discussed below. PM, on the other hand, is not mapped into CM species, but is split into various real species and some aggregated groups for use in air quality models.

MOVES 2014 does not produce the toxics output in molar units needed for CMAQ Toxics Versions, which track toxics as tracer species, separate from the chemical mechanism. MOVES2014 produces the toxics needed in mass units, just as the previous version did. As was done previously, the conversion into molar units for use by the various CMAQ Toxics Versions is done by SMOKE.

## *4.2 Real speciation profiles*

A real speciation profile is, in principle, a complete listing of all the species and their quantities for an aggregate species, such as TOG. Such a profile is produced by laboratory analysis of emissions. These are not CM speciation profiles and are independent of chemical mechanism. Of course, the hundred or so compounds in these profiles are not a complete listing, which would likely include thousands of species. But they are the major species by mass and reactivity. Table 8 summarizes the speciation profiles we are using in MOVES, together with the fuels, regulatory classes, and MOVES emission processes to which they apply. Table 9 indicates the source of these profiles, the source of the data, and the documentation. The emission processes relevant to the choice of speciation profile are identified in Table 8.

SPECIATE is the EPA's repository of volatile organic gas and particulate matter (PM) speciation profiles from air pollution sources.[16] The Speciate Database Project began at EPA in 1988; the current version, SPECIATE 4.3, was released in September, 2011. In 2005, an EPA SPECIATE Workgroup was formed to assure inclusion of the most current data and to quality-assure the content.[17] All the profiles listed in Table 3 are in SPECIATE 4.3 or will be in the next version, SPECIATE 4.4, scheduled to be completed within the coming year.

**Table 11. Speciation profiles used for onroad TOG emissions.**

| Profile | Description | Fuel | Affected Vehicles | MOVES ProcessID |
|---|---|---|---|---|
| 8766 | E0 evap permeation | E0 | All | 11 |
| 8769 | E10 evap permeation | E10 | All | 11 |
| 8770 | E15 evap permeation | E15 | All | 11 |
| 8753 | E0 Evap | E0 | All | 12,13,19 |
| 8754 | E10 Evap | E10 | All | 12,13,19 |
| 8872* | E15 Evap | E15 | All | 12,13,19 |
| 4547 | Diesel Headspace | Diesel | All | 12,13,19,11,18,19 |
| 8934* | E85 Evap | E85 | All | 12,13,19,11,18,19 |
| 8775 | 2007+ MY HDD exhaust | Diesel | 2007+ | 1,2,15,16,17,90 |
| 8774 | Pre-2007 MY HDD exhaust, | Diesel | Pre-2007 and all auxiliary power units | 1,2,15,16,17,90,91 |
| 8750a* | Pre-Tier 2 E0 exhaust | E0 | Pre-Tier 2 | 1,2,15,16,17,90 |
| 8756 | Tier 2 E0 Exhaust | E0 | Tier 2 | 1,2,15,16,17,90 |
| 8757 | Tier 2 E10 Exhaust | E10 | Tier 2 | 1,2,15,16,17,90 |
| 8758 | Tier 2 E15 Exhaust | E15 | Tier 2 | 1,2,15,16,17,90 |
| 8752 | Pre-Tier 2 E85 exhaust | E85 | Pre-Tier 2 | 1,2,15,16,17,90 |
| 8855 | Tier 2 E85 Exhaust | E85 | Tier 2 | 1,2,15,16,17,90 |
| 8751a* | Pre-Tier 2 E10 exhaust | RFG, E10, E15 | Pre-Tier 2 | 1,2,15,16,17,90 |
| 8869* | E0 Headspace | E0 | All | 18 |
| 8870* | E10 Headspace | E10 | All | 18 |
| 8871* | E15 Headspace | E15 | All | 18 |
| 1001 | CNG Exhaust | CNG | All | 1,2,15,16,17,90 |

*Inclusion in Speciate pending. (Not in Speciate 4.3)

**Table 12. Data sources for the MOVES profiles**

| Profile ID | Profile Name | Profile Source | Source Data | Additional Documentation |
|---|---|---|---|---|
| 8750a | Gasoline Exhaust - Reformulated gasoline (pre-Tier 2) | Next release of SPECIATE | 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) | Next release of SPECIATE | 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. |

| Profile ID | Profile Name | Profile Source | Source Data | Additional Documentation |
|---|---|---|---|---|
| 8752 | Gasoline Exhaust - E85 ethanol gasoline (pre-Tier ) | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | Characterization of Alternative Fuel Vehicle Emission Composition and Ozone Potential. EPA No. RW89936763. U.S. EPA 1995-1997. Annual Reports to the Department of Energy. Available at: http://www.epa.gov/nscep/index.html | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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. |
| 8855 | Gasoline Exhaust - Tier 2 light-duty vehicles using 85% Ethanol - Composite Profile | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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. | |
| 8753 | Gasoline Vehicle - Evaporative emission - Reformulated gasoline | S SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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. |

| Profile ID | Profile Name | Profile Source | Source Data | Additional Documentation |
|---|---|---|---|---|
| 8872 | Gasoline Vehicle - Evaporative emission - E15 ethanol gasoline - Calculated | Next release of SPECIATE | 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<br><br>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 | Next release of SPECIATE | 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 | |
| 8766 | Diurnal Permeation Evaporative Emissions from Gasoline Vehicles using 0% Ethanol - Combined - Composite Profile | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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/ | |
| 8869 | Gasoline Headspace Vapor - 0% Ethanol (E0) Combined - EPAct/V2/E-89 Program | Next release of SPECIATE | Hydrocarbon Composition of Gasoline Vapor Emissions from Enclosed Fuel Tanks, Report No. 420-R-11-018. U.S. EPA, December 2011. Available at: http://www.regulations.gov, Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0027. | Mobile Source Hydrocarbon Speciation Profiles for the Tier 3 Rule NPRM and Anti-backsliding Study Air Quality Modeling. Memorandum to the Docket. U.S. EPA, 2013. Available at: http://www.regulations.gov. Docket ID: EPA-HQ-OAR-2011-0135, Document ID: EPA-HQ-OAR-2011-0135-0089. |

| Profile ID | Profile Name | Profile Source | Source Data | Additional Documentation |
|---|---|---|---|---|
| 8870 | Gasoline Headspace Vapor - 10% Ethanol (E10) Combined - EPAct/V2/E-89 Program | Next release of SPECIATE | 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 | Next release of SPECIATE | 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. |
| 8774 | Diesel Exhaust Emissions from Pre-2007 Model Year Heavy-Duty Diesel Trucks | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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 | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | Phase 1 of the Advanced Collaborative Emissions Study. Coordinating Research Council, July 2009. Available at: http://www.crcao.com/publications/emissions/index.html | |
| 4547 | Gasoline Headspace Vapor - Circle K Diesel - adjusted for oxygenates | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | Internal data collection effort, Charles Lewis, U.S. EPA Office of Research and Development, with<br>Ying Hsu, E.H. Pechan & Associates, Inc., personal communication (t), June 29, 2004. | SPECIATE 4.2. Speciation Database Development Documentation. Report No. EPA/600-R-09/038, U.S. EPA, June 2009. Available at: http://www.epa.gov/ttn/chief/software/speciate/ |
| 1001 | Internal Combustion Engine - Natural Gas | SPECIATE Version 4.3. Available at: http://www.epa.gov/ttn/chief/software/speciate/ | 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. | |

## *4.3 Mapping of real species to chemical mechanism species and of residual TOG to chemical mechanism speciation profiles*

The mapping of real species to CM species is mechanism-specific. CB05 is a widely used chemical mechanism for air quality modeling and is the one OTAQ is incorporating into MOVES2014. Each chemical mechanism maps real organic gas species to one or more CM

species. The atmospheric chemistry is then modeled using these CM species. In the case of TOG, all the species in the real speciation profile are mapped in this way to the CB05 species. Then all the occurrences of each CM species are added up to produce a CB05 speciation profile for TOG. The CB05 speciation profiles that are used for real species and for all the TOG profiles will be generated outside of MOVES based on the TOG profiles in the Speciate Database and using the Speciation Tool, which generates the CB05 speciation profiles. [There soon will be a public release of the Speciation Tool, which we can reference.]

The "integration" process is based on the idea that certain species in TOG are estimated directly by MOVES, benzene for example, and are based on much more detailed and accurate information than the TOG speciation profile. Therefore, to map to CB05 species, it makes more sense to use the benzene estimated by MOVES rather than the benzene estimated in the TOG speciation profile. This is true for the 16 species listed in Table 1. To take advantage of this better data, the integration process removes the 16 pollutants from the TOG speciation profile to produce a residual-TOG speciation profile. Then, as described above for TOG, a chemical mechanism speciation profile is produced for residual-TOG.[18]

Finally, all the CB05 species mapped from both real species and from residual-TOG are added up by individual CB05 species to produce the MOVES output of CB05 species. Regular MOVES output is unchanged. As mentioned above, we are not including conversions to molar units of non-CB05 species for use by the various toxics versions of CMAQ. All chemical mechanism species are in units of moles. Because this process is table driven, MOVES2014 is capable of providing CM species for multiple chemical mechanisms. However, at present only the CB05 mechanism is implemented. Similarly, MOVES2014 is capable of integrating multiple species sets. However, as a start, we have implemented the 16 integrated species listed in Table 1. Figure 1 is a diagram of the process of TOG speciation for air quality modeling.

No new science is implied by TOG speciation in MOVES for air quality modeling. The only modification is that the process previously performed by SMOKE or other emissions pre-processors has been integrated into MOVES2014.

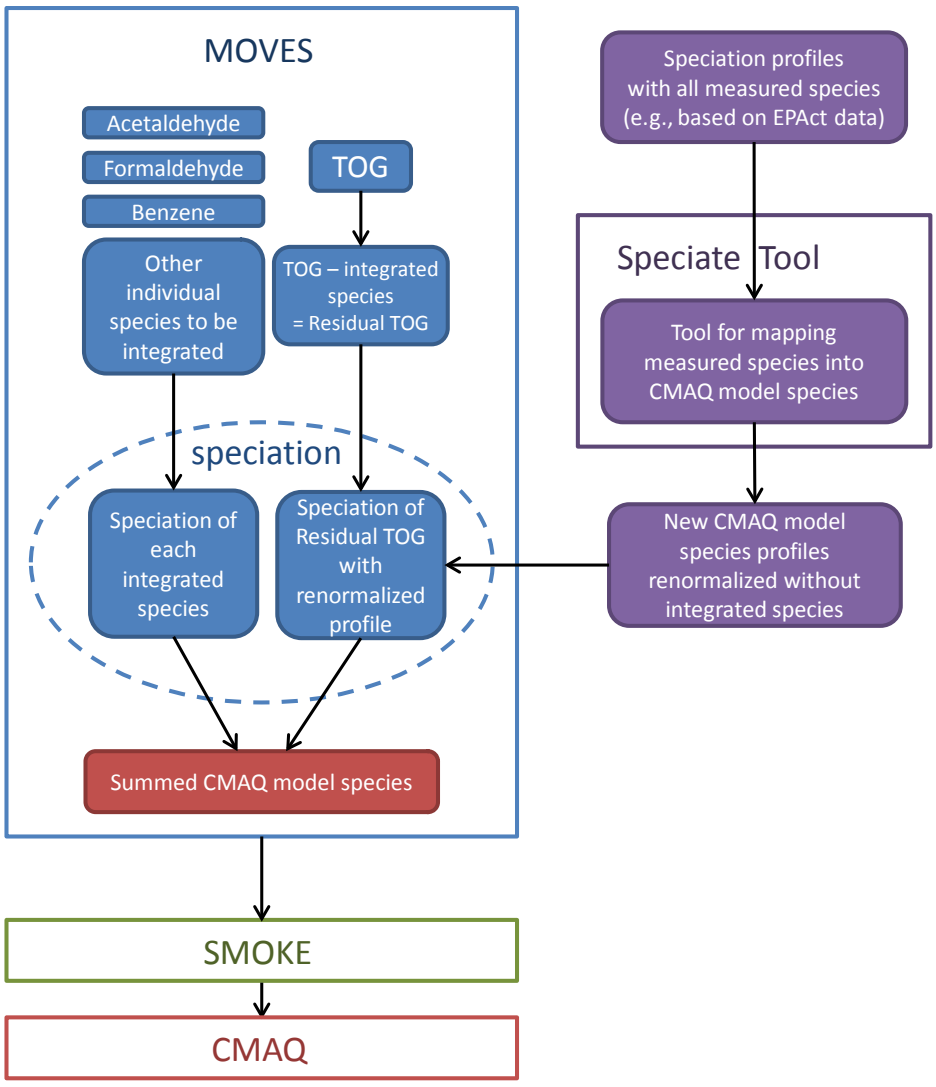


**Figure 1. Diagram of the process of TOG speciation for air quality modeling as it will occur in MOVES2014.**

# 5 $PM_{2.5}$ Speciation

## *5.1 Overview*

Modeling $PM_{2.5}$ in CMAQ does not use simplifying chemical mechanisms, and the real $PM_{2.5}$ species are input directly into the model. CMAQv5.0, which uses the CMAQ Aerosol Module, version 6, or "AE6", requires 18 $PM_{2.5}$ species as outlined in Table 10[19].The additional PM species required in CMAQv5.0 will be beneficial to air-quality agencies and researchers who use different air quality models. The additional PM species are compatible with previous versions of CMAQ and with the Comprehensive Air Quality Model with Extensions (CAMx) as shown in Table 10.

**Table 13. $PM_{2.5}$ species required in CMAQv5.0 (this version uses the CMAQ Aerosol Module, version 6, or "AE6")[19] , CMAQv4.7.1 (this version uses the CMAQ Aerosol Module, version 5, or "AE5"), and CAMx5.4[20].**

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

MOVES2014 is designed to produce all $PM_{2.5}$ species required by CMAQv5.0. Previous versions of MOVES (2010b and earlier) produced $PM_{2.5}$ in the form of three $PM_{2.5}$ species: Elemental Carbon (EC), Organic Carbon (OC) and sulfate ($SO_4$). Substantial post-processing of MOVES $PM_{2.5}$ outputs was needed to provide PM emissions inventories that could be

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

transformed by SMOKE into ready-inputs of speciated $PM_{2.5}$ for CMAQ. For example, MOVES2010b did not output nitrate, ammonium, and metals. These compounds were assumed to be included in the OC emission rates of $PM_{2.5}$. This division required post-processing the MOVES2010b OC emissions using $PM_{2.5}$ speciation profiles, and created differences between OC as defined by MOVES2010b and the post-processed OC used for air quality modeling. MOVES2014 removes the distinction by defining OC consistently with air quality models as defined in the glossary.

## *5.2 Steps*

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

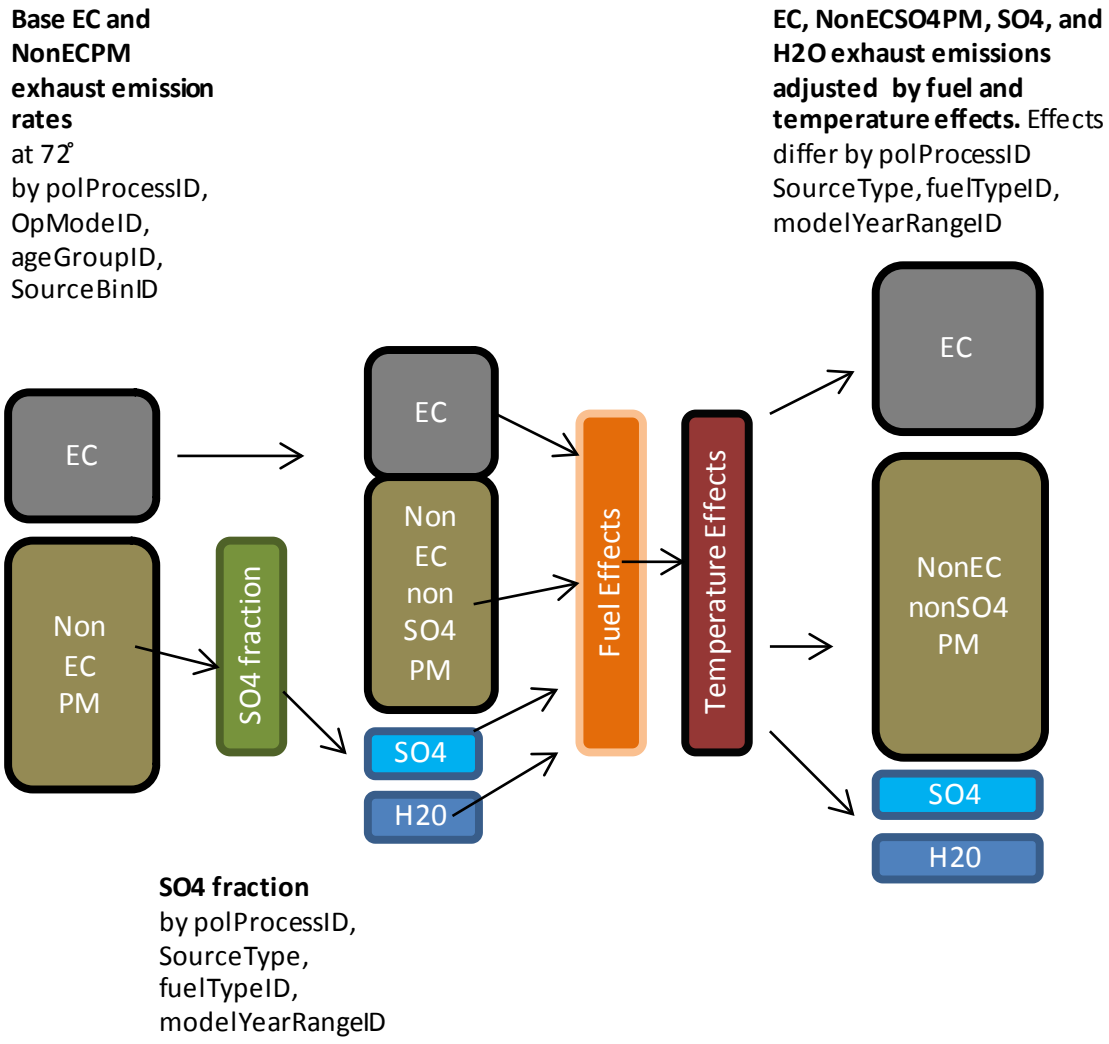


**Figure 2. Flow Chart of Calculation of the Intermediate $PM_{2.5}$ Emission Rates**

Step 1. MOVES2014 stores $PM_{2.5}$ exhaust emission rates by pollutant process (start, running, extended idle), operating mode, sourcebin (fuelType, engine technology, regulatory class, model year), and vehicle age. MOVES2014 stores base exhaust rates for $PM_{2.5}$ divided into two primary components (EC and nonECPM). The base rates are stored by EC and nonECPM so that the $EC/PM_{2.5}$ ratio can vary across operating modes, which is the case for the conventional heavy-duty diesel vehicles emission rates in MOVES2014 (MOVES2014 Heavy-duty Vehicle Emissions Report). The $EC/PM_{2.5}$ ratios vary across processes (start vs. running) for gasoline vehicles, but not by operating mode like conventional heavy-duty diesel vehicles (EPA, 2014). The capability for separate $EC/PM_{2.5}$ ratios by operating mode is maintained (but not implemented) for all sources in MOVES2014.

Step 2. MOVES2014 calculates sulfate and particulate water emissions from the nonECPM using values obtained from the $PM_{2.5}$ speciation profiles. The remaining nonECPM is renamed nonECnonSO4PM. This intermediate species contains organic matter, elements, ions, and unspeciated portion of $PM_{2.5}$. Because there are no data to support individual fuel or temperature

effects among these species, the nonECnonSO4PM is adjusted for temperature and fuel effects to reduce computation time.

Step 3. MOVES2014 adjusts the intermediate species (EC, SO4, H2O, and NonECnonSO4PM) according to fuel effects. $SO_4$ and $H_2O$ are adjusted according to the fuel sulfur level. EC and nonECnonSO4 are adjusted according to additional fuel properties depending on the applicable model (e.g. EPAct model for 2001 and later light-duty gasoline). The fuel adjustments and calculators are described in the MOVES2014 Fuel Adjustment Report[21].

Step 4. The intermediate species are adjusted for temperature effects. The temperature effects differ for process (e.g. start exhaust, running exhaust, extended idle.), model year groups, and fuel type. Currently, temperature effects only apply to gasoline vehicles. The temperature adjustments currently apply equally to each intermediate species, and are documented in the MOVES2014 Highway Vehicle Temperature, Humidity, Air Conditioning, and Inspection and Maintenance Adjustments Report[22].

Steps 5 – 8 are outlined in Figure 3.

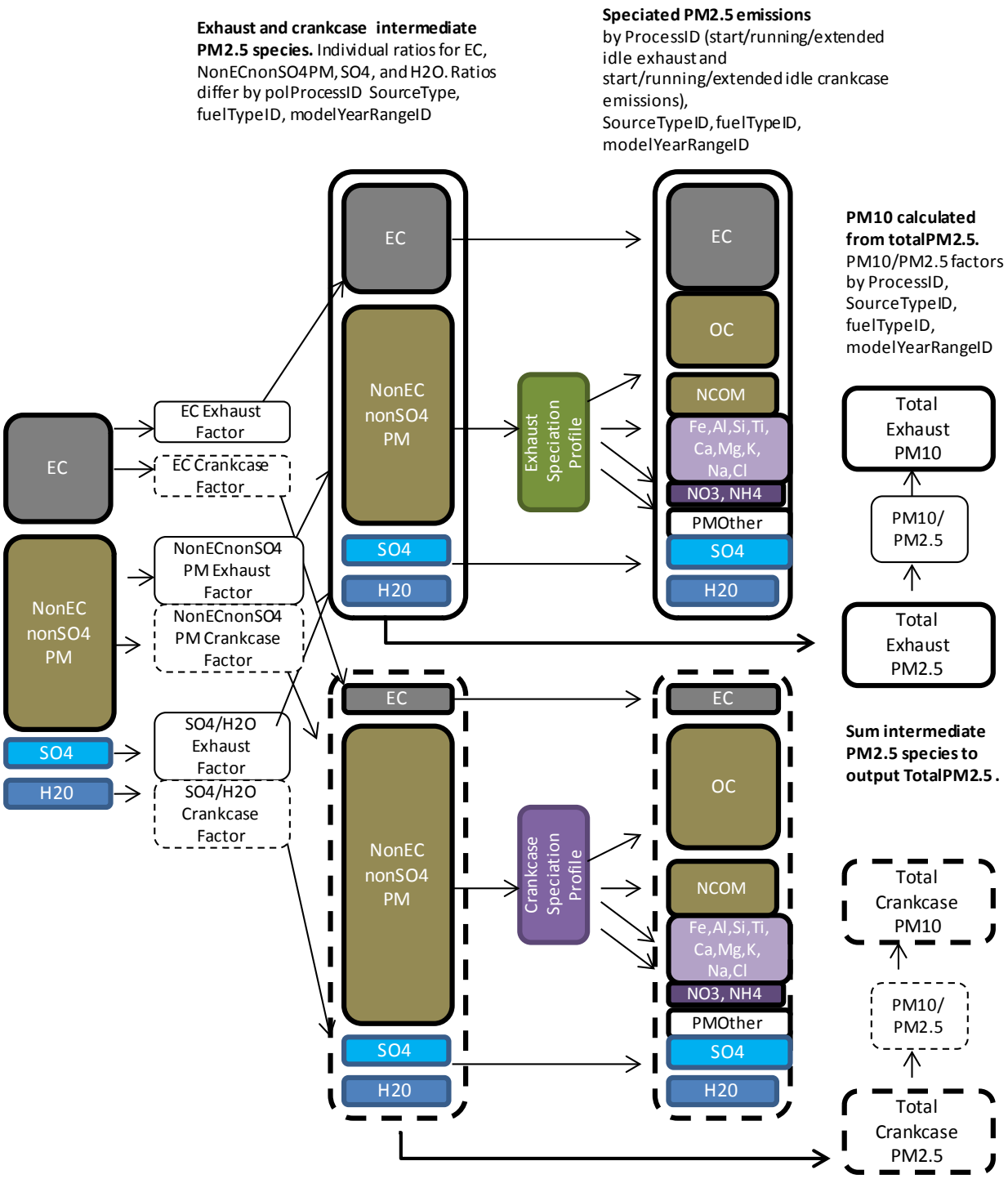


**Figure 3. Flow Chart of Calculation of exhaust and crankcase $PM_{2.5}$ and $PM_{10}$ emission rates, and $PM_{2.5}$ exhaust and crankcase speciation.**

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

according to pollutant, process, source type, fuel type, and model year range as shown in Table 7.

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

For other vehicles types (pre-2007 diesel, gasoline, CNGvehicles), the exhaust emissions are unadjusted and 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 sources of the diesel crankcase emission factors are documented in the MOVES2014 Heavy-duty Emissions Rate Report and the gasoline crankcase emission factors are documented in the MOVES2014 Light-duty Emissions Rates Report (EPA, 2014). The factors are applied by intermediate subspecies, to account for differences in PM2.5 speciation between crankcase and tailpipe particulate matter emissions. For MOVES2014, the pre-2007 conventional diesel has different PM composition between exhaust and crankcase emissions, as shown in Table 11.

**Table 14. Exhaust and Crankcase Ratios by Pollutant, Process, Model Year Group, and Fuel Type, and Source Type**

| | | Pre-2007 Diesel | | | 2007+ Diesel | 1969-2050 Gasoline/ CNG | 1960-1968 Gasoline Vehicles | Gasoline Motor-cycles |
|---|---|---|---|---|---|---|---|---|
| Pollutant | Process | Start | Running | Extended Idle | All processes | All processes | All processes | All processes |
| EC | Exhaust | 1 | 1 | 1 | 0.62 | 1 | 1 | 1 |
| nonECnonSO4PM | | 1 | 1 | 1 | 0.62 | 1 | 1 | 1 |
| SO4 | | 1 | 1 | 1 | 0.62 | 1 | 1 | 1 |
| H2O | | 1 | 1 | 1 | 0.62 | 1 | 1 | 1 |
| EC | Crank-case | 0.009 | 0.004 | 0.012 | 0.38 | 0.008 | 0.2 | 0 |
| nonECnonSO4PM | | 0.295 | 0.954 | 0.268 | 0.38 | 0.008 | 0.2 | 0 |
| SO4 | | 0.295 | 0.954 | 0.268 | 0.38 | 0.008 | 0.2 | 0 |
| H2O | | 0.295 | 0.954 | 0.268 | 0.38 | 0.008 | 0.2 | 0 |

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

Step 7. MOVES2014 calculates primary exhaust and crankcase $PM_{10}$ emissions from the primary $PM_{2.5}$ emissions using $PM_{10}/PM_{2.5}$ ratios. The MOVES2014 $PM_{10}/PM_{2.5}$ ratio used for primary exhaust and crankcase emissions are listed in Table 12. MOVES2014 has the capabilityi 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. A single value of the $PM_{10}/PM_{2.5}$ ratios is also applied

to the total $PM_{2.5}$ emission rates. No speciation is conducted within MOVES2014 for $PM_{10}$ emissions, because it is not needed for air quality modeling purposes[ii,23]. The derivation of the $PM_{10}/PM_{2.5}$ ratio is presented in Appendix B.

**Table 15. $PM_{10}/PM_{2.5}$ Ratios for primary exhaust and crankcase emissions**

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

Step 8. MOVES2014 calculates speciated $PM_{2.5}$ emissions, by applying speciation profiles to the adjusted nonECnonSO4 fraction to calculate the individual $PM_{2.5}$ species. The data sources and documentation for the PM2.5 profiles are included in Table 13. Each of the $PM_{2.5}$ profiles has been developed or updated for use in MOVES2014. The development of the $PM_{2.5}$ Speciation profiles is documented in Appendix A.

**Table 16. MOVES2014 $PM_{2.5}$ Speciation Profiles**

| Profile ID | Profile Name | Profile Source | Source Data | Additional Documentation |
|---|---|---|---|---|
| 8992 | Light-duty Gasoline Exhaust - Start | Next release of SPECIATE | 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. | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |
| 8993 | Light-duty Gasoline Exhaust- Hot Stabilized Running | Next release of SPECIATE | 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. | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |
| 8994 | Conventional HDD - Idle | Next release of SPECIATE | 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 | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |
| 8995 | Conventional HDD – Hot Stabilized Running | Next release of SPECIATE | 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 | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |
| 8996 | 2007 and Newer Diesel Exhaust Composite | Next release of SPECIATE | Khalek, I. A.; Bougher, T. L; Merrit, P. M.; Phase 1 of the Advanced Collaborative Emissions Study. CRC Report: ACES Phase 1, June 2009. | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |

[ii] Within CMAQv5.0, the US EPA assumes a single speciation profile for all anthropogenic coarse PM (Bhave et al. 2011).

| | | | | |
|---|---|---|---|---|
| not assigned | CNG Compression Ignition Transit Bus Exhaust with no control | Next release of SPECIATE | Okamoto, R. A.; Kado, N. Y.; Ayala, A.; Gebel, M.; Rieger, P.; Kuzmicky, P. A.; Kobayashi, R.; Chemical and Bioassay Analyses of Emissions from Two CNG Buses with Oxidation Catalyst. http://www.arb.ca.gov/research/veh-emissions/cng-diesel/cng-diesel.htm. | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |
| not assigned | CNG Compression Ignition Transit Bus Exhaust with oxidation catalyst | Next release of SPECIATE | Okamoto, R. A.; Kado, N. Y.; Ayala, A.; Gebel, M.; Rieger, P.; Kuzmicky, P. A.; Kobayashi, R.; Chemical and Bioassay Analyses of Emissions from Two CNG Buses with Oxidation Catalyst. http://www.arb.ca.gov/research/veh-emissions/cng-diesel/cng-diesel.htm. | MOVES2014 Technical Report: TOG and PM Speciation in MOVES for Air Quality Modeling: Appendix: PM2.5 Speciation in MOVES. Available at: http://www.epa.gov/otaq/models/moves/moves-reports.htm |

The $PM_{2.5}$ profiles used for the applicable source type, fuel, pollutant process, and model year ranges are shown in Table 14.

**Table 17. Application of MOVES2014 $PM_{2.5}$ Speciation Profiles**

| Profile ID | Description | Fuel | Affected Vehicles | MOVES ProcessID |
|---|---|---|---|---|
| 8992 | Light-duty Gasoline Start | All gasoline vehicles (E0 to E85) | All model years | 2,16, |
| 8993 | Light-duty Gasoline Running | All gasoline vehicles (E0 to E85) | All model years | 1,15 |
| 8994 | Conventional HDD Idle | Diesel | Pre-2007 and all MY auxiliary power units | 2,16,17,90,91 |
| 8995 | Conventional HDD Running | Diesel | Pre-2007 | 1,15 |
| 8996 | Composite 2007+ HDD | Diesel | 2007+ | 1,2,15,16,17,90 |
| to be assigned | CNG Compression Ignition Transit Bus Exhaust with no control | CNG | pre-2002 transit buses | 1,2,15,16,17,90 |
| to be assigned | CNG Compression Ignition Transit Bus Exhaust with oxidation catalyst | CNG | 2002+ transit buses | 1,2,15,16,17,90 |

MOVES2014 uses the two light-duty 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 profile is used to represent all pre-2007 on-highway diesel vehicles in MOVES, including light-duty duty passenger cars and trucks, medium, and heavy-duty trucks, and diesel buses. Crankcase nonECnonSO4 emissions emitted during extended idle and start are

speciated using the Start/Extended Idle Profile. Crankcase nonECnonSO4emissions emitted during running are speciated using the running profile. In addition, the idle profile is used to characterize nonECnonSO4emissions from diesel-powered auxiliary power units used on heavy-duty diesel trucks.

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

The CNG compression ignition profile is applied to the pre-2002 model CNG transit buses, and the CNG profile with oxidation catalyst profile is applied to the 2002+ model year CNG transit buses. This technology is determined to be most representative of the available PM2.5 speciation data according to the analysis conducted in the MOVES2014 Heavy-duty vehicle emissions report.

Step 9. (Not shown in Figure 2 or 3). MOVES2014 calculates additional particulate-phase species, required for the National Emission Inventory (NEI) and National Air Toxics Assessment. Listed in Table 15, these include: manganese, nickel, chromium, arsenic, and particulate mercury. The metals are emitted in exhaust as $PM_{2.5}$, but are calculated through a separate calculator than the other $PM_{2.5}$ species. The emission rates for these metals are not chained from NonECSO4PM, but are provided with their own mass/distance rates as documented in the MOVES2014 Additional Air Toxics Emission Report (EPA, 2014). The mass of these compounds is not used in the summation to calculate $PM_{2.5}$ due to the very small mass, but are important $PM_{2.5}$ exhaust species from a health effects perspective. Of the toxic metals, CMAQv5.0 only requires manganese as a required $PM_{2.5}$ species. By default, MOVES2014 calculates manganese emission rates when the user requests $PM_{2.5}$ speciation. Chromium, nickel, arsenic, and particulate mercury emission rates are produced when requested by the user.

**Table 18. Metal Air Toxics produced by MOVES2014**

| Pollutant |
|---|
| Chromium 6+ |
| Chromium 3+ |
| Manganese |
| Nickel |
| Particulate Hg |
| Arsenic |

# 6 References


[1] US EPA. *Conversion Factors for Hydrocarbon Emission Components*. EPA420-P-03-002. May 2003

[2] 40 CFR 1065 "Engine-Testing Procedures." Code of Federal Regulations.

[3] 40 CFR 1066 "Vehicle-Testing Procedures." Code of Federal Regulations.

[4] " Estimation of Air-Toxic Emissions from Highway Vehicles in the Motor Vehicle Emissions Simulator (MOVES 2014)."

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

[6] Eastwood, P. *Particulate Emissions from Vehicles*; SAE International: Warrendale, PA. 2008. ISBN: 978-0-7680-2060-1.

[7] Greg Yarwood, Sunja Rao, Mark Yocke, and Gary 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.

[8] Heather Simon and Prakash V. Bhave. *Simulating the Degree of Oxidation in Atmospheric Organic Particles*. Environmental Science & Technology 2012 46 (1), 331-339

[9] U.S. EPA 2014. MOVES2014 Greenhouse Gas and Energy Consumption Rates. [to be released]

[10] U. S. EPA. 2013. *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 Report No. EPA-420-R-13-004, March, 2013.

[11] Hsu ,Y., and Mullen, M. 2007. *Compilation of Diesel Emissions Speciation Data*. Prepared by E. H. Pechan and Associates for the Coordinating Research Council. CRC Contract No. E-75, October, 2007. Available at www.crcao.org.

[12] Khalek, I., Bougher, T., and Merritt, P. M. 2009. *Phase 1 of the Advanced Collaborative Emissions Study*. Prepared by Southwest Research Institute for the Coordinating Research Council and the Health Effects Institute, June 2009. Available at www.crcao.org.

[13] Haskew, H.M., and Liberty, T.F. *Exhaust and Evaporative Emissions Testing of Flexible-Fuel Vehicles. Final Report*. Coordinating Research Council. CRC Report No. E-80, August, 2011. Available at www.crcao.org.

[14] Haskew, H. M. and Liberty, T. F. *Evaporative Emissions from In-Use Vehicles: Test Fleet Expansion*. June 2010. CRC Project E-77-2b, http://www.crcao.org.

[15] Haskew, H. M., Liberty, T. F. 2010. *Study to Determine Evaporative Emission Breakdown, Including Permeation Effects and Diurnal Emissions, Using E20 Fuels on Aging Enhanced Evaporative Emissions Certified Vehicles*. December 2010. CRC Project E-77-2c. http://www.crcao.org.

[16] For data and documentation, see http://www.epa.gov/ttnchie1/software/speciate.

[17] Heather Simon, Lee Beck, Prakash V. Bhave, Frank Divita, Ying Hsu, Deborah Luecken, J. David Mobley, George A. Pouliot, Adam Reff, Golam Sarwar, Madeleine Strum. The development and uses of EPA's SPECIATE database. *Atmospheric Pollution Research*, 1 (2010) 196-206.

[18] Madeleine Strum, Laurel Driver, Gerald Gipson, William G. Benjey, Rich Cook, Marc Houyoux, Catherine Seppanen, and Greg Stella, *The Use of SMOKE to Process Multi-pollutant Inventories - Integration of Hazardous Air Pollutant And Volatile Organic Compound Emissions*. Presented at the 12th International Emission Inventory Conference, San Diego, CA, April 28 - May 1, 2003. Available at http://www.epa.gov/ttn/chief/conference/ei12/modeling/strum.pdf. Presentation slides are available at http://www.epa.gov/ttn/chief/conference/ei12/modeling/present/strum.pdf.

[19] Simon, H.; *CMAQv5.0 PM other speciation*. http://www.airqualitymodeling.org/cmaqwiki/index.php?title=CMAQv5.0_PMother_speciation

[20] *CAMx v5.40 User's Guide*, September 2011. Chemistry Mechanisms. http://www.camx.com/camx/files/b6/b65abed0-a7d4-498b-8698-b2cf5c23cbfd.pdf

[21] U.S. EPA 2014. MOVES2014 Fuel Adjustment Report.. EPA-420-R-11-009 , [to be released]

[22] U.S. EPA 2014. MOVES2014 Highway Vehicle Temperature, Humidity, Air Conditioning, and Inspection and Maintenance Adjustments. [to be released]

[23] Bhave, P.; Sarwar, G.; Pye, H.; Pouliot, G.; Simon, H.; Young, J.; Nolte, C.; Schere, K.; Mathur, R.; *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.