Appendix: PM2.5 Speciation in MOVES

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

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

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

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

The Kansas City Light-duty Vehicle Emissions Study (KCVES) is the primary source of $PM_{2.5}$ emission rates for light-duty vehicles in MOVES2014 (EPA, 2014). 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. The overview of the sample size of the vehicles included in the chemical subset is included in Table A-1.

Table A-1. Vehicle sample size in the Kansas City Light Duty Vehicle Emissions Study.

Vehicle Type[1]	Strata	Model Year Group	% of KC LDGV Vehicle Population[2]	% of KC LDGV Vehicle Miles Traveled (VMT) [3]	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

[1]The definition for Car and Truck, and the population percentages[2], are estimated from the 2004 Kansas City Travel Behavior Survey (*cite*): Passenger cars are defined as coups, sedans, and wagons, trucks are defined as minivans, sport-utility vehicles, and pickups. [3]The VMT contribution by strata is calculated based on the population percentages combined with annual VMT by vehicle age estimated from the 2001 National Household Travel Survey (NHTSA, 2006).

The derivation of the $PM_{2.5}$ gasoline profile for MOVES2014 is documented in Sonntag et al. (2013 submitted article). An overview of the major updates is included in this report. 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 was confounded by the different vehicles tested in each season. The data used equally weighted data from the summer and winter tests to calculate a profile that incorporates data from both seasons.

We discovered high concentrations of silicon in some of the $PM_{2.5}$ measurements, likely due to contamination from silicone rubber couplers used in KCVES. The silicone contamination occurred primarily on bag 2 of the LA-92 drive cycle which was used for developing the running $PM_{2.5}$ speciation profile and emission rates. The silicone contamination was larger for trucks than cars due to their higher exhaust temperatures. The silicone contamination was removed from the developed profile using the silicone emissions data as documented in Sonntag et al. (2013). The primary exhaust $PM_{2.5}$ emission rates were corrected in MOVES2014 to account for the silicone contamination (EPA, 2014 - documented in the light-duty gasoline emissions report). 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 were pooled together to develop single start and running $PM_{2.5}$ speciation profiles for all light-duty gasoline vehicles.

Important differences in the $PM_{2.5}$ composition were detected in the $PM_{2.5}$ composition by model year groups. Rather than calculating a model year group specific profiles, fleet-average profiles were calculated. A fleet-average PM profile was proposed to better capture the impact of deterioration within all model year groups, and 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 (Robert et al. 2007, Carroll et al. 2011, Lough et al. 2007b, Cadle et al. 1999). 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 (Sonntag et al. 2012). Other test programs have confirmed that high emitting gasoline vehicles also occur in modern vehicles, such as 1990's era vehicles with electronic fuel injection (Robert et al. 2007, Carroll et al. 2011, Lough et al. 2007b). The speciation sample size was deemed too limited to accurately capture the impact of deterioration and high-emitting vehicles within each model-year group. By using all the data in a fleet-average approach, we incorporated the impact of deteriorated vehicles on the fleet-average $PM_{2.5}$ emissions.

The fleet-average PM speciation profiles are calculated using seasonal, vehicle-miles-traveled (VMT), and PM mass-weighting. The PM profile is calculated using the ratio of the means, also referred to as a mass-normalized emission profile (Shauer et al. HEI 2006). The vehicle tests from each season are equally weighted, and the vehicle tests are averaged according to the calculated contribution to annual VMT in the Kansas City MSA (Table A-1). 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 contribution down based on their relatively small contribution of vehicle miles traveled. For application in MOVES2014, the fleet-average profile is used to characterize $PM_{2.5}$ emissions across all model year groups, and all ages of vehicles used to represent deterioration.

The developed $PM_{2.5}$ profiles used in MOVES2014 for gasoline exhaust are included in Table A-2. The number of samples for each $PM_{2.5}$ species are also shown in Table 4. EC was measured on each vehicle test and has a much greater sample size than the other species. The EC and nonECPM emission rates in MOVES2014 are updated to be consistent with the EC fractions developed in Table A-2.

For application in MOVES2014, only the $PM_{2.5}$ species required by CMAQv5.0 are reported. A revision of the metal emission rates for Mn, Cr, and Ni for gasoline vehicles based on the KCVES is provided in the Fuels and Toxics Report. The $PM_{2.5}$ ratios that were not significantly greater than 0 at the 95% confidence intervals were reported as 0, which removed 5 $PM_{2.5}$ species pollutants from the start profile. Fuel samples analyzed for 171 of the vehicles tested in KCVES yielded an average fuel sulfur content of 161.2 ppm Fuel sulfur content in the US is now lower after implementation of the Tier 2 Vehicle & Gasoline Sulfur Program Final Rule (effective beginning 2006-2008) which set a gasoline sulfur fuel limit of 30 ppm. In MOVES2014, the baseline sulfate emissions estimated from the $PM_{2.5}$ profile are adjusted according to the user-supplied fuel sulfur content as discussed in the Fuel Adjustments & Toxics Report (US EPA, 2014).

Details on the data, quality control measures, and statistical methods used to develop the profile are documented in the Sonntag et al. (2013). 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. Factors for additional $PM_{2.5}$ species (P, Cu, Zn, Br, Mo, and Pb) that are not included in MOVES2014 are also presented.

Table A-2. Gasoline $PM_{2.5}$ Profile for Start and Running Emissions weighted average using Vehicle Miles Traveled (VMT)

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

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

An updated $PM_{2.5}$ profile for pre-2007 conventional diesel trucks was developed from the CRC E55/59 Study: Heavy-Duty Vehicle Chassis Dyno Testing for Emissions Inventory Clark and Guatam al. 2007). The E55/59 program is the current source for $PM_{2.5}$ emission rates for medium and heavy-duty conventional diesel trucks in MOVES2014, and is the source of the conventional diesel TOG speciation profiles (Table 5). By using the E55/59 study for $PM_{2.5}$ speciation profiles we are using a consistent study for the $PM_{2.5}$ emission rates and the speciation profiles in MOVES2014.

The E55/59 profile replaces the previous profile used to conduct $PM_{2.5}$ speciation based on the Northern Front Range Study Air Quality Study (NFRAQS) conducted in the late 1990's (Zielinska et al. 1998). The MOVES2014 E55/59 $PM_{2.5}$ profile includes measurements from eight heavy-duty trucks, ranging from a 1985 to 2004 model year as shown in Table A-3. The E55/59 fuel properties are more aligned with those in-use today, with sulfur content ~ 172 ppm, as opposed to ~ 340 ppm sulfur used in NFRAQS (Cadle et al. 1999, Zielinska et al. 1998).

The CRC -55/59 study was conducted from 2001-2005 in several phases. In phase 1 and phase 2 of the study, chemical characterization of $PM_{2.5}$ emissions was conducted for total of 9 trucks, as shown in Table A-3. In total, 9 of the 75 trucks tested in the E-55/59 study were analyzed for chemical species, ranging from a 1985 to a 2004 model year truck.

Table A-3. Vehicle Information from the Speciated E-55/59 Trucks

Phase E55	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

The speciated data from the E55/59 study was compiled from the speciation database compiled in CRC Report No. E-75-2: Diesel Unregulated Emission Characterization Report (Maureen, 2010). [1] 65 tests were conducted on the 9 trucks selected for PM speciation. Phase 1 tested 3 heavy heavy-duty diesel trucks (HHDTs) for PM speciation on four modes of the Urban Dynamometer Driving Schedule (UDDS), including: Idle, Creep, Transient, and Cruise. Phase 2 tested 6 additional heavy-duty diesel trucks, and 1 medium heavy-duty truck (MHDT). In Phase 2, the HHDTs were also tested on the UDDS, as well as a high speed cruise mode added after Phase 1. The MHDT was tested on MHDT schedule developed by the California Air Resources Board that included two transient modes and a cruise mode. For chemical speciation, some tests were repeated in sequence to collect additional mass on the filter, including extended idle and extended creep. In phase 2, the speciation data was not collected for the creep mode (Clark et al. 2007).

The data reduction steps used to develop a $PM_{2.5}$ speciation profile from the E55/57 speciated data are outlined in the following paragraphs.

Step 1. We first calculated the average $PM_{2.5}$ profile by each individual truck and 4 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 E-75-2 (Maureen, 2010). 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 for tests that include only one idle test. The average profile for each vehicle/test cycle classification are shown in Figure 1-1. 30 average speciation profiles were calculated from the 65 tests as shown in Figure 1-1. Typically, each truck/cycle average contains two tests.

[1] The $PM_{2.5}$ emission rates for the Phase 1 speciated tests were missing in the E-75-2 database, and were obtained from Table 17 of the E-55-59 Phase 1 report (Clark and Guatam al. 2003).

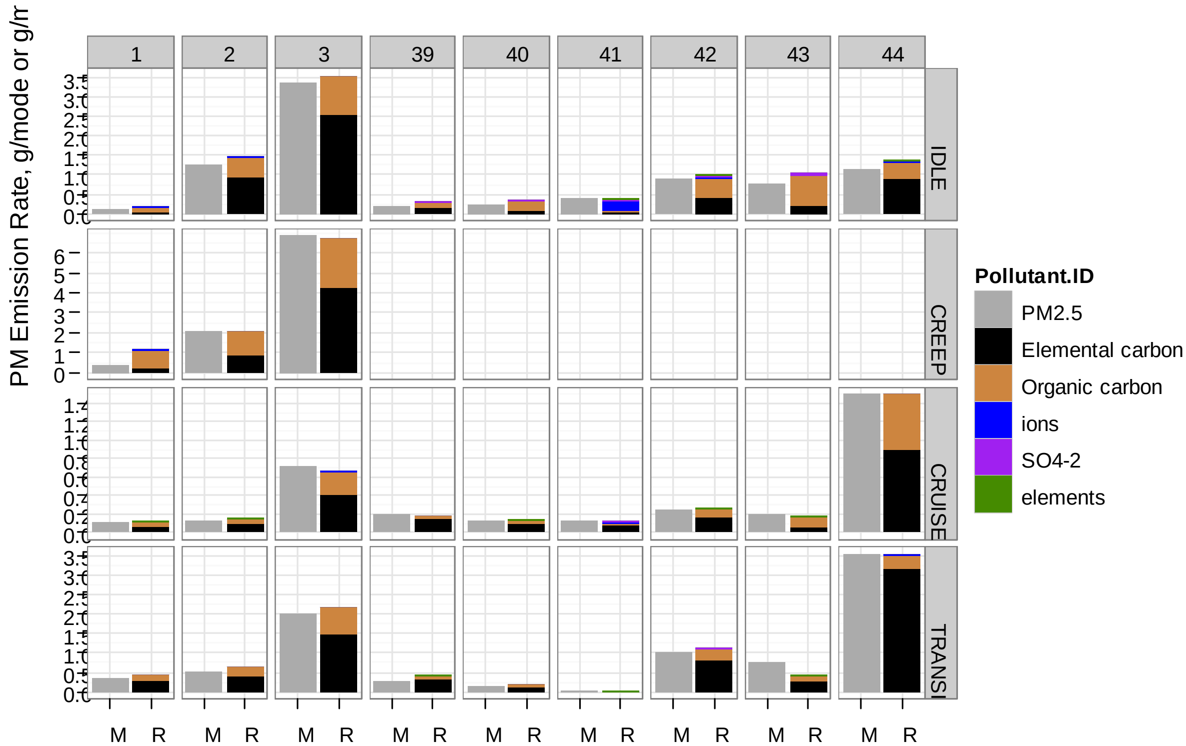

Figure 1-1. Average $PM_{2.5}$ Speciation Profiles by Truck and Test Cycle from the E55/59 Program.

Step 2. We removed the average $PM_{2.5}$ profiles with suspect data. As shown in Figure 1-1, 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. The composition of the medium duty PM does not compare well with previous data in the literature (Schauer et al. 1999), and the medium-duty truck is removed from further analysis.

Step 3. We calculated a median PM profile using the average truck/test cycle PM profiles calculated in steps 1 and 2. The median is used rather than the mean due to the small sample (8 trucks), in contrast to the variety of truck technologies, exhaust control systems, and ages of the trucks. A mass-weighted mean would have dominated the results by Truck 3 and Truck 44, which had the highest PM emission rates. Instead we used 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) reproduced in Table A-4.

Table A-4. 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% 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% 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, the organic carbon emission rates are scaled down to achieve mass balance, and correct for positive OC artifact measurements, as was done in previous work including for the light-duty gasoline profile (Sonntag et al. 2013), and other combustion sources (Reff et al. 2009). The scaled-down OC rates are treated as the organic mass (OM) emission rate, and are split into organic carbon and non-carbon organic matter using the following relationship: OM = 1.2 * OC used by Kleeman et al. (2000) and developed from work conducted on medium-duty diesel emissions (Schauer et al. 1999). The initial and corrected OC/PM factors are shown in Table A-5. The adjusted OC speciation factor 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 (Noll and Bircher, 2008).

Table A-5. 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 A-6. 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 is currently modeled in MOVES for conventional diesel.

Table A-6. $PM_{2.5}$ Profiles for Conventional Diesel Exhaust developed for MOVES2014

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

As discussed in $PM_{2.5}$ overview, the exhaust $PM_{2.5}$ speciation profiles are used to speciate the non-EC emission rates in MOVES2014. In the case of conventional diesel, the EC emission rates were developed separately by weight class, and operating mode bin as discussed in the MOVES2014 Heavy-duty report (US EPA, 2014). The EC fraction from a MOVES calendar 2014 model run are compared to the EC fraction in the developed profile in Table A-7. The MOVES2014 EC/PM factor varies by operating mode and regulatory class, and changes for different MOVES scenarios depending on the age distribution, fleet characteristics, and driving mix of driving on different road types. MOVES2014 reflects the lower EC/PM fraction for extended idle and start emissions, which was also shown in the E55/59 profile. Running emissions represent over 80% of the $PM_{2.5}$ emissions from conventional diesel trucks. The EC/PM ratio for running compares very well (<1%) between the MOVES estimates and the E55/59 running $PM_{2.5}$ speciation profile. The comparison validates the consistency in using the operating mode specific values in MOVES for the EC emission rates, and using the E55/59 profile to calculate the remaining $PM_{2.5}$ species.

Table A-7. MOVES EC/$PM_{2.5}$ fraction from conventional Diesel (pre-2007) calendar year 2014, compared to the EC/$PM_{2.5}$ fraction from the developed profile from E55/59

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

The MOVES2014 conventional diesel profiles developed from the E-55/59 Study are compared to composite profile developed by Schauer et al. (2006) from measurements taken from the DOE Gasoline/Diesel PM Split Study, as well as the NFRAQS heavy-duty diesel profile in Table A-8. The EC/PM fraction from the transient cycle compares well to both the composite profiles. The MOVES2014 idle profile has a substantially lower EC/PM fraction than the composite profiles, with a corresponding higher fraction of organic matter. The MOVES2014 sulfate fractions appear are more aligned with the DOE Split study, which could be due to newer technology diesel and lower altitude testing. Elements and ion emission rates compare well to the DOE gasoline/diesel PM split study. Even though the E55/59 speciation sample is limited, it appears to be validated by comparison to other available studies.

Table A-8. Comparison of MOVES2014 Conventional Diesel Profiles with other $PM_{2.5}$ Conventional Diesel Profiles

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

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

The $PM_{2.5}$ speciation profile for 2007 and later technology is based on Phase 1 of the Advanced Collaborative Emissions Study (ACES) Report. The purpose of the ACES report is 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, which was 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% 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 to develop a profile to be as consistent with the summarized results in the ACES Phase 1 report, while assuring the $PM_{2.5}$ species achieved 100% mass-balance. 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 3 of the 4 engines. The ACES researchers did not report OC corrected by a backup-quartz filter out because of concern of under-representing OC emissions (Khalek et al. 2001). Similarly, species for elements and ions were not corrected for tunnel blanks.

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 (Khalek et al. 2009). In the absence of these species, the sulfate is expected to exist as hydrated sulfuric acid. Khalek et al. 2011 reported that accounting for the water-bound sulfate would increase the summed mass of the individual species 37% 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), but was not conducted due to the uncertainty of reconciling the filter mass and the sum of the measured species. Khalek et al. 2011 discusses the possible approaches for correcting the measured OC to organic matter, and mentions this as an area for future work for 2007 diesel engines.

In keeping with these assumptions, Abt Associates developed a profile that summed the measured species to 100%, and included it in the SPECIATE4.3 database as profile #5680. This profile is incorporated into MOVES with one adjustment. CMAQ5.0 needs organic matter reported as OC and noncarbon organic matter (NCOM). We treated the reported organic carbon in the speciate profile 5680 as organic matter, and calculate OC and NCOM using the same split (5:1) as used for conventional diesel and light-duty gasoline. The species not needed by CMAQ5.0 from the ACES Phase 1 profile are summed into the CMAQ5.0 unspeciated fraction. Metal emission rates for manganese, chromium, and nickel MOVES2014 are derived from the ACES Phase 1 data (Fuels Report). They are estimated using the metals calculator with mass/mile emission rates, and so are not reported again in the $PM_{2.5}$ speciation profile.

Table A-9. $PM_{2.5}$ Speciation Profile Developed from the 16-hour cycle from four heavy-duty diesel engines in the ACES Phase 1 Program.

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

The 2007+ diesel EC/PM fraction in MOVES2014 is a constant 8.61% based on previous analysis documented in the heavy-duty diesel report. This value is quite similar to the 9.98% EC/PM fraction estimated from Phase 1 of the ACES program. Due to the similarity in the EC/PM fraction, the previous value of 8.61% is also used in MOVES2014. However, the ACES Phase 1 data is used to speciate the remaining species listed in Table A-9.

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

The California Air Resource Board (CARB) conducted several emission characterization studies on compressed natural gas vehicles. We used test data collected on CNG New Flyer bus with a 2000 MY Detroit Diesel Series 50G engine, equipped with and without an oxidation catalyst to develop PM2.5 speciation profiles. CARB also conducted tests on a CNG bus with a 2001 Cummins Westport engine. We developed the profile on the Detroit Diesel bus, with and without catalyst to estimate the impact of oxidation catalyst control, without introducing differences in engine technology. CARB characterized the PM emissions on a steady-state cycle, and a central business district cycle (CBD). We used data collected on the central business district (CBD) cycle, which was consistent with the criteria pollutant analysis in the MOVES2014 Heavy-duty Emissions Report, and is also deemed to be more representative of typical transit bus behavior.

We elected to use only the data reported by CARB on the DDC 50G engine to develop the profile. Using a single profile was used to provide consistency in the PM characterization estimates. The PAH/OC ratios were also developed from the CARB measurements on the DDC 50 G as documented in the MOVES2014 toxics report. Using a single profile, also assures that the organic carbon emissions are reduced with implementation of oxidation catalyst controls. Other studies that reported EC/OC did not measure emission rates for elements (Lanni et al. 2003). We used measurements made on the same tests to construct the profile in Table A-10.

Table A-10. PM2.5 Speciation Profiles for CNG Compressed Ignition Transit Bus Exhaust.

Pollutant	Uncontrolled	Oxidation Catalyst
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 PM2.5	43.04%	39.74%

We used PM, EC, OC, and element emission rates for two repeat tests under each of the exhaust control condition. The emission rates are also reported in published journal articles (Okamoto et al. 2006, Ayala et al. 2003). CARB measured 13 elements by XRF , but no ions (sulfate, ammonium, or nitrate) measurements were made. 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 ID 91112). We assume that the missing ammonium and nitrate emissions are 0, based on the negligible ammonium and nitrate measurements from modern spark-ignition CNG buses equipped with three-way catalysts (Gautam et al. 2011). Sodium and magnesium were the largest elements measured (sodium was over 7% of the PM2.5 measured in the uncontrolled test), which is likely do to known measurement artifact for XRF measurements of sodium and magnesium. As such the sodium and magnesium emission rates are reported as 0.

The use of the oxidation catalyst reduced the PM2.5 emission rates from 28 mg/mile to 20.3 mg/mile on the CBD cycle (27.5% decrease). As shown in Table A-10, the composition of the PM2.5 stayed fairly constant. The fraction of EC and OC fractions between the two control conditions are not statistically different. The estimated sulfate emissions are significantly higher with the oxidation catalyst, which is to be expected. Both profiles contain a large amount of unspeciated PM2.5 emissions. The source of the discrepancy is unknown, but is likely attributed to the different sampling media for the total PM2.5 emission rates, EC/OC, and element emission rates. The absence of ion measurements may also be a contributing factor.

The real-world variability in the PM composition is larger than the developed profiles suggest. The OC/PM fraction for the 2001 Cummins Westport with oxidation catalyst was 61.9%, which is much larger than that measured on the 2000 Detroit diesel engine. Lanni et al. (2003) reported that the OC/PM fraction on three CNG transit buses with DDC Series 50 G engines ranged from 29% to 74% of the PM2.5. The EC emissions measured by Lanni et al. (2003) were below the detection limit, but the presented results compare well with the 2001 Cummins Westport measured by CARB (12.7% EC/PM). The sulfate fraction for the oxidation catalyst presented in Table A-10 compares well with the sulfate fraction reported for the 2001 Cummins Westport by CARB (2.8%), and by Lanni et al. (1.5% to 2.4%).

Appendix B. Development of $PM_{2.5}/PM_{10}$ in MOVES2014

The gasoline $PM_{10}/PM_{2.5}$ factor is based on measurements of 1991-1997 model year vehicles tested by Norbeck et al. (1998) (CRC E-24-2). This ratio estimates that roughly 10% 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).

The diesel $PM_{10}/PM_{2.5}$ factor is based on a 1985 EPA report, which reports that 92% of particulate mass is measured below a 2.5 um cut-off (EPA, 1985). Although from 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), who states that the coarse mode contains 5-20% of the total aerosol mass. Unfiltered crankcase emissions reported by Donaldson, 2011 have similar reported mass distributions with ~ 93 to 97% of the cumulative mass particles smaller than 2.5 um. In contrast, Tatli and Clark (2008) report that the particle mass size distribution is significantly different from crankcase and tailpipe diesel emissions for particles below 1 um. Due to the limited information on coarse mode, 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 (Dollmeyer, SAE 2007-01-4170, Kalayci, 2011). 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 were available on the $PM_{10}/PM_{2.5}$ ratio for CNG emissions, and the gasoline ratio is used for CNG emissions. Table B-1 contains the selected exhaust $PM_{10}/PM_{2.5}$ ratios used in MOVES.

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

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

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