Report: Modeling Effects of Fuel Properties in the Motor Vehicle Emissions Simulator (MOVES2014): DRAFT Report.

Chapter: MOVES2014 Sulfate and Sulfur Dioxide Emissions Calculator

Introduction

Sulfate (SO_4) is an important contributor to primary exhaust particulate matter emissions from motor vehicles. The formation of sulfate from motor vehicles is a function of the engine combustion emission control technology conditions, and the sulfur content in the fuel and the lubricating oil. MOVES2010b assumed that all sulfate emissions originated from the fuel sulfur, and based the sulfate calculations entirely from fuel consumption. With the lower sulfur concentrations in-use in the modern fuels, a significant fraction of the sulfate emissions from the modern fleet originate from the sulfur in the lubricating oil. Research on current technology diesel engines has shown that at current diesel fuel sulfur levels, the sulfur contribution of lubricating oil can be more important than the fuel contribution in forming sulfate emissions (Kittelson et al. 2008). For diesel engines equipped with catalyzed diesel particulate filters, the sulfate contribution from lubricating oil can also consist of a substantial fraction of the $PM_{2.5}$ exhaust emissions.

MOVES2014 includes two major changes to improve the modeling of sulfate emissions. First, sulfate emissions are estimated from the $PM_{2.5}$ emissions rather than from the fuel consumption. This assures that the reference fraction of sulfate is consistent with the $PM_{2.5}$ emissions profile. Second, MOVES2014 accounts for the sulfate contribution from both the lubricating oil and the fuel. Using particulate matter test programs conducted by the US EPA and reported in the literature, the relative contribution of sulfate emissions from lubricating oil and fuel is estimated.

This chapter includes an overview of the MOVES2014 sulfate calculator, and analysis conducted to determine the necessary inputs for 1) gasoline engines, 2) conventional diesel engines, 3) 2007 technology diesel engines, and 4) compressed natural gas engines. Additionally, the MOVES2014 algorithm for estimating sulfur dioxides is included in this chapter for consistency. The algorithm for gaseous sulfur dioxide (SO_2) emissions remains the same as in MOVES2010b and is based on fuel consumption, but the parameters have been updated in MOVES2014 to be consistent with the changes to the sulfate emission factors.

Sulfate Calculator Summary

The MOVES2014 sulfate calculator adjusts the reference sulfate emissions using the following assumptions:

1. Sulfate emissions from the lubricating oil are constant regardless of the fuel sulfur level.
2. Sulfate emissions originating from the fuel scale linearly with changes in fuel sulfur level.

These assumptions are shown in schematic Figure 1. Research on sulfur levels in lubricating oil and diesel fuel has supported these assumptions. Warren, J. P. et al. (2000) and Kittelson et al. (2008) treated that the sulfate contribution from the lubricating oil as independent of the fuel sulfur level from diesel engines. Wall et al. (1987) demonstrated that sulfate emissions from diesel engines decreases linearly with decreases in the diesel fuel sulfur level down to 100 ppm and 0 ppm. Baranescu (1988) and Hochhauser (2006) affirmed that changes in sulfur did not affect the sulfur to sulfate conversion factor from conventional diesel engines operating on broad ranges of sulfur content in the fuel and different driving cycles. Kittelson et al. (2008) also assumed a constant relationship between fuel sulfur level and particle number emissions from modern trap-equipped diesel engines.

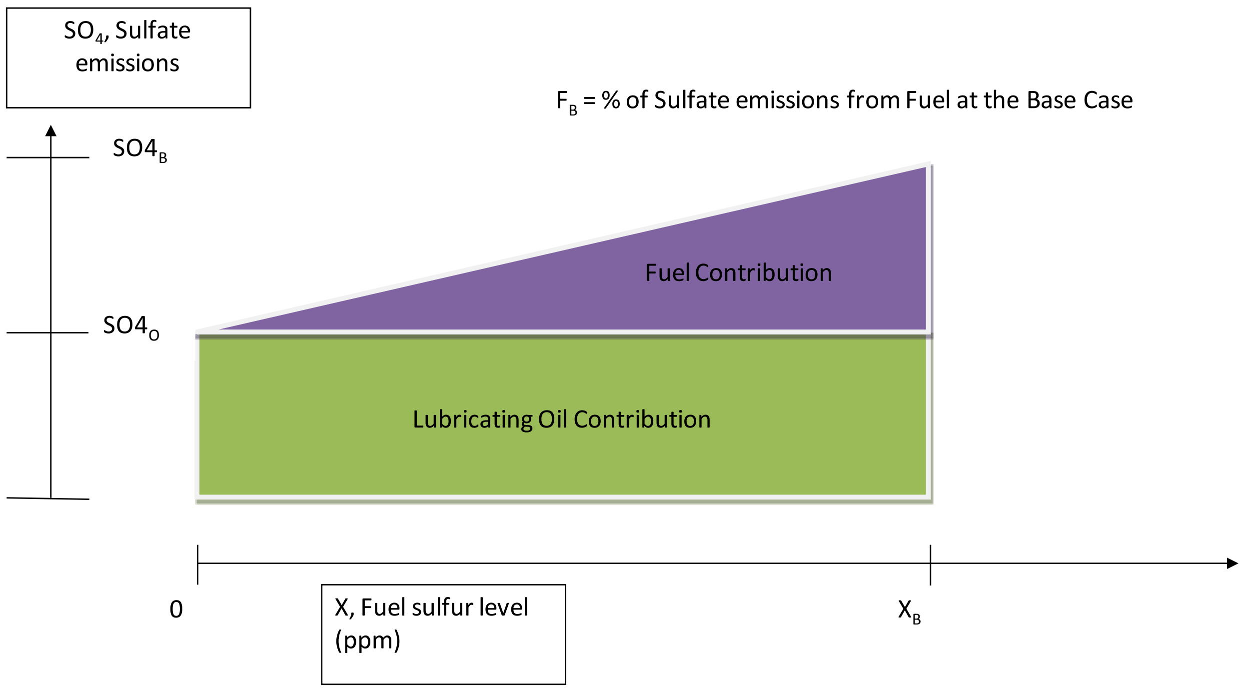

Figure 1. Schematic of Fuel and Lube Oil Contribution in MOVES2014.

The sulfate calculator uses the concept of reference emission rates and sulfate fractions. MOVES2014 adjusts the sulfate emissions based on differences between the sulfur content of the reference test program, and the user-supplied sulfur content in a MOVES run. In MOVES2014, the base $PM_{2.5}$ rates are divided between elemental carbon (EC) and the remaining PM that is not elemental carbon (NonECPM). The reference sulfate emissions are calculated from the NonECPM rates using the presented SO4/NonECPM fraction fractions in Table 1.

MOVES2014 incorporates these modeling assumptions into the following equation:

$$SO4_x = NonECPM \times S_B \times \left[1 + F_B \times \left(\frac{x}{x_B} - 1\right)\right] \quad (1)$$

Where: $NonECPM$ is the reference non-elemental carbon $PM_{2.5}$ emission rates, S_B = reference sulfate fraction, x = the user- supplied or default fuel sulfur level for the MOVES run, x_B = reference fuel sulfur level, and F_B =the percentage of sulfate originating from the fuel sulfur in the reference case, and $SO4_x$ = sulfate emissions at the fuel sulfur content for the MOVES run. The derivation of Equation (1) is included in the appendix. Each of the needed parameters for the sulfate calculator (S_B, F_B, x_B) are provided in Table 1. Sulfate-bound water (H_2O aerosol) is a new pollutant in MOVES2014. If included in the $PM_{2.5}$ speciation profile, the H_2O aerosol is assumed to be associated with sulfate, and is scaled using the same relationship with fuel sulfur level:

$$(H_2O)_x = NonECPM \times (H_2O)_B \times \left[1 + F_B \times \left(\frac{x}{x_B} - 1\right)\right] \quad (2)$$

Where $(H_2O)_B$ is the fraction of water-bound sulfate in the $NonECPM$.

Table 1. Coefficients for the Sulfate Calculator in MOVES2014

Source	Process	SO4/PM2.5 fraction	SO4/NonECPM fraction (S_B)	Fuel sulfur Level, ppm (x_B)	Estimated fraction from fuel sulfur (F_B)
Light-duty gasoline	running exhaust	7.2%	8.4%	161.2	68.7%
	start exhaust	0.9%	1.7%		
Pre-2007 diesel	running exhaust	1.0%	4.9%	172.0	72.6%
	extended idle and start	5.3%	9.8%		
2007+ diesel	running, extended idle, start	67.6%	73.6%	11.0	48.3%
Pre-2002, compressed natural gas	running, extended idle, start	0.6%	0.7%	5.0	0.0%
2002+ Compressed natural gas	running, extended idle, start	1.0%	1.2%	5.0	0.0%

The following section discusses the derivation of the parameters in Table 1 for 1) gasoline vehicles, 2) conventional diesel vehicles, 3) 2007 technology diesel vehicles, and 4) compressed natural gas vehicles.

Gasoline Vehicles

The reference sulfate fractions and the reference fuel sulfur level for gasoline vehicles are estimated from the Kansas City Light-Duty Vehicle Emissions Study (KCVES). The use of the

KCVES for estimating $PM_{2.5}$ emission rates is documented in the MOVES2014 Light-duty Vehicle Emission Rate report, and the derivation of the sulfate emission factor is documented in the MOVES 2014 TOG and PM Speciation Report. The reference fuel sulfur content (161.2 ppm) was calculated using 171 fuel analysis samples from the KCVES.

The reference contribution of fuel sulfur to the sulfate emissions (68.7%) is estimated from an analysis that combined data from the KCVES, which tested vehicles using high fuel sulfur content, with light-duty gasoline vehicles tested at a low fuel sulfur content (6 ppm) as part of the Full Useful Life (FUL) Test Program (Sobotowki, 2013). The FUL program was the most relevant study available to the US EPA that measured sulfate emissions from low sulfur gasoline available that could be used to evaluate the impact of low sulfur gasoline fuel on light-duty engines. An overview of the data and the analysis to calculate the reference contribution of fuel sulfur to sulfate emissions is provided in Appendix 1.

The sulfate values derived in Table 1 are used for all gasoline sources in MOVES, including motorcycles, light-duty, medium-duty and heavy-duty gasoline trucks, and gasoline-powered buses.

Pre-2007 Diesel Vehicles

The reference sulfate fraction of $PM_{2.5}$ is derived from the Heavy-Duty Vehicle Chassis Dynamometer Testing for Emissions Inventory, Air Quality Modeling, Source Apportionment and Air Toxics Emissions Inventory (E55/59) (Clark, 2007).The E55/59 study is also used to derive the $PM_{2.5}$ emission rates for medium and heavy-duty diesel in MOVES2014 (MOVES2014 heavy-duty report). The estimated fuel sulfur content of diesel trucks tested in E55/59 is 172 ppm.

To estimate the relative contribution of lubricating oil and fuel from conventional diesel engines, data collected from the Diesel Emissions Control- Sulfur Effects Project (DECSE) was used (DECSE, 2001). The DECSE project was conducted to investigate the impact of low-sulfur diesel fuel standards on diesel emissions. Specifically, the DESCE conducted testing of two engines at four sulfur levels: 3, 30, 150, and 350 ppm. Sulfate emissions were measured at each of the levels. These data were used to calculate the 72.6% contribution of the fuel to sulfate emissions at the reference fuel sulfur level (172 ppm) of the base pre-2007 diesel rates in MOVES2014. The sulfate emissions estimated from the fuel sulfur (72.6%) are then scaled linearly with changes in fuel sulfur from the references fuel sulfur level (172) ppm. Details on the analysis used to derive the relative fuel contribution to pre-2007 diesel sulfate emissions from the DESCE data are provided in the appendix.

2007 and Later Technology Diesel Vehicles

The sulfate contribution of the fuel and lubricating oil for 2007 and later diesel vehicles is based on a study designed and conducted by Kittelson et al. (2008). The Kittelson et al. (2008) study evaluated the contribution of lubricating oil and diesel fuel to ultrafine particle emissions from a modern diesel engine equipped with a catalyzed diesel particle-filter equipped (C-DPF). Kittelson et al. (2008) estimated a linear model that predicts the ultrafine particle number emissions from the sulfur content in the lubricating oil and the fuel. We used the Kittelson et al. (2008) analysis by assuming that the relative contribution of lubricating oil and fuel to sulfate emissions is the same as their relative contribution to the ultrafine particle emissions. We applied the coefficients developed by Kittelson et al. (2008) to estimate the relative contribution of lubricating oil and fuel to sulfate emissions at 11 ppm fuel sulfur level and 3,000 ppm lubricating oil sulfur level. 11 ppm is selected as the reference fuel sulfur content used in MOVES2014. 3,000 ppm is the sulfur content assumed by Kittelson et al. (2008) for lubricating oil in trap-equipped diesel engines, which is lower than 4,000 ppm limit specified by API category CJ-4 lubricating oil used for 2006 and later diesel engines (Jääskeläinen, H.; Majewski 2012). Using these assumptions, the lubricating oil is estimated to contribute the majority of the sulfate emissions (51.7%) when the fuel sulfur is 11 ppm.

The reference sulfate fraction is based on the $PM_{2.5}$ speciation profile for 2007 and newer on-highway diesel technology is based on Phase 1 of the Advanced Collaborative Emissions Study (ACES). Phase 1 of ACES tested four heavy-duty diesel engines, each equipped with a catalyzed diesel particulate filter (C-DPF). The $PM_{2.5}$ speciation profile for 2007 and later diesel engines used in MOVES2014 (TOG and PM Speciation in MOVES2014) is based on the four engines tested on a 16-hour cycle developed specifically for the ACES program. The fuel sulfur level tested in the ACES program is 4.5 ppm (Khalek et al. 2009). The sulfate fraction from the ACES Phase 1 project is adjusted to account for 11 ppm fuel assumed for the base 2007 and later diesel $PM_{2.5}$ rates. Using equation (1) and the derived parameters in Table 1, a $SO_4/PM_{2.5}$ fraction for 11 ppm fuel is estimated to be 67.6% (as compared to 59.1% at 4.5 ppm). This fraction is used as the reference sulfate fraction for 2007 and later diesels in MOVES2014 as shown in Table 1. Additional details on the analysis are included in the appendix.

Compressed Natural Gas

We had more limited data on sulfate emissions from compressed natural gas, especially regarding the relative contribution of the lubricating oil and CNG fuel to sulfate emissions. As such, we do not adjust the sulfate emissions according to fuel sulfur level. We derived the fraction of sulfate emissions from elemental sulfur emissions measured by CARB on a CNG transit bus with a 2000 MY Detroit Diesel Series 50 engine with and without an oxidation catalyst as documented in the TOG and PM Speciation Report. We set F_B coefficient to 0, so that MOVES estimates the same sulfate emissions regardless of the sulfur level in the CNG fuel.

Sulfur Dioxide Emissions Calculator

The sulfur dioxide (SO_2) emissions algorithm is unchanged from MOVES2010b, but the parameters are updated to be consistent with the updated analysis on sulfate emissions. The

MOVES sulfur dioxide algorithm calculates sulfur dioxide emissions using three parameters (1) total fuel consumption, (2) fuel sulfur level, and (3) the % of fuel sulfur emitted as sulfate emissions.

Unlike the sulfate calculator, the sulfur dioxide calculator assumes that all of the sulfur dioxide emissions originate from the fuel. This assumption is reasonable because on a mass-balance most of the sulfur originates from the fuel, even at low fuel sulfur levels. The reason the sulfur in the lubricating oil has a large impact on sulfate emissions, is that the sulfur in the lubricating oil has a much high propensity to form sulfate then sulfur burned in the fuel (Kittelson et al. 2008).

SO_2 emissions are calculated using equation (3):

$$SO_2(g) = FC(g) \times Fuel\ S\ conc\ (ppm) \times \frac{molar\ mass\ SO_2}{molar\ mass\ S} \times SO_2\ conversion \times \left(\frac{10^{-6}}{ppm}\right) \quad (3)$$

Where

$FC(g)$= fuel consumption in grams

$Fuel\ S\ conc\ (ppm)$= fuel sulfur concentration in ppm

$$\frac{molar\ mass\ SO_2}{molar\ mass\ S} = \frac{32 + 2 \times 16}{32} = 2$$

$SO_2\ conversion$ = Fraction of fuel sulfur that is converted to gaseous SO_2 emissions. The SO_2 conversion fraction is calculated as the fraction of fuel sulfur not converted to sulfate.

In MOVES2014, the sulfur dioxide calculator first calculates the product of $FC(g) \times Fuel\ S\ conc\ (ppm)$. Then it multiplies the product by the sulfur dioxide emission factor which combines the last three terms of equation (2).

$$SO_2\ EF\left(\frac{1}{ppm}\right) = \frac{molar\ mass\ SO_2}{molar\ mass\ S} \times SO_2\ conversion \times \left(\frac{10^{-6}}{ppm}\right) \quad (4)$$

The SO_2 conversion values and resulting SO_2 emission factors for use in MOVES2014 are displayed in Table 2.

Table 2. SO_2 conversion values and MOVES SO_2 emission factors

Source	SO2 conversion values (%)	SO2 EF (1/ppm)
Gasoline	99.69%	1.994E-06
Pre-2007 Diesel	97.48%	1.950E-06
2007 Diesel	88.15%	1.763E-06

CNG	100%	2.000E-06

The gasoline sulfur dioxide conversion factors are based on the VMT-weighted values from the Kansas City study. The updated sulfur dioxide conversion values (99.69%) for gasoline engines are slightly higher than the previous values used in MOVES2010b (99.84%), which is required to provide consistent rates with the updated sulfate emission rates. These values are used for all highway gasoline sources.

Fuel consumption data were not available from the E55/59 study which was used as the source of the sulfate emission rates. The updated sulfur dioxide conversion values for the pre-2007 diesel were calculated by achieving sulfur balance with the estimated fuel sulfur consumed and sulfate emissions from pre-2007 diesel trucks using MOVES. A 2014 national MOVES inventory was calculated for pre-2007 single and combination diesel trucks, with the fuel sulfur at the estimated level of the E55/59 study (172 ppm). The sulfate speciation factor and percentage of sulfate coming from the fuel were taken from Table 1. The analysis estimated that 2.52% of the fuel sulfur forms sulfate emissions, leaving an estimated sulfur dioxide conversion value of 97.48%. This compares well with the 2% fuel sulfur to sulfate conversion factor from the US EPA PART5 model used in previous versions of MOVES and MOBILE (EPA, 2003).

The 2007 diesel sulfur dioxide emissions factor is based on calculations using the reported fuel consumption and sulfate emissions from the ACES Phase 1 report, along with the data from the sulfate calculator for sulfate emissions. The sulfur dioxide conversion factor for 2007 and later diesel (88.15%) is considerably larger than the sulfur dioxide assumed in MOVES2010b (54.16%). The reason for the large shift is the large contribution of lubricating oil to sulfate emissions accounted for in MOVES2014. The diesel values are used for all on-highway diesel sources.

In the absence of other data, we assume 100% of the fuel in the CNG fuel forms SO_2 emissions. This is a reasonable simplification because the sulfur content of fuel sulfur is low in comparison to diesel and gasoline, and because lubricating oil also contributes to SO_2 emissions. This assumption is also consistent with our assumption made for the formation of sulfate emissions from CNG engines. Lanni et al. (2003) measured SO_2 and SO_4 emissions from three CNG transit buses. The sulfur content of the CNG fuel was not reported, but assuming that all of the fuel sulfur is converted to SO_2 emission, yielded an estimated CNG sulfur content of 7.6 ppm. Ayala et al. (2002) reported that the maximum allowable fuel sulfur content for use in CNG motor vehicles is 16 ppmv. The Energy Information Administration reports that the fuel sulfur content of natural gas at the burner tip is less than 5 ppm (EIA, 1998). For use in MOVES, we selected the default sulfur level of CNG to be 7.6 ppm, to be consistent with the sulfur dioxide measurements conducted by Lanni et al. (2003).

Appendix 1: Derivation of Equation (1) in the MOVES2014 Sulfate Calculator

The following equation is used to model the Sulfate emissions:

$$SO4_x = (Sulfate\ from\ oil) + (Sulfate\ from\ Fuel)$$

$$SO4_x = NonECPM \times \left(S_B \left(\frac{S_O}{S_B}\right) + (S_B - S_O)\left(\frac{x}{x_B}\right)\right) \qquad \text{(a)}$$

Where: $SO4_x$ = Sulfate level at fuel sulfur x, S_O =Fraction of sulfate emissions from lubricating oil, S_B = Sulfate fraction in the reference case . x_B = fuel sulfur level in the reference case.

$$Let\ F_B = \%\ of\ Sulfate\ from\ the\ fuel\ sulfur\ at\ the\ baseline\ case$$

$$F_B = \frac{(S_B - S_O)}{S_B}$$

Substitute F_B into equation a:

$$SO4_x = NonECPM \times \left(S_B \times (1 - F_B) + S_B \times F_B \times \left(\frac{x}{x_B}\right)\right)$$

$$= NonECPM \times \left(S_B \times \left[1 - F_B + F_B \times \left(\frac{x}{x_B}\right)\right]\right)$$

$$= NonECPM \times \left(S_B \times \left[1 + F_B \times \left(\frac{x}{x_B} - 1\right)\right]\right) \qquad (1)$$

Using equation (1), the sulfate emissions can be modeled, with the user supplied values of x (fuel sulfur level), and model parameters, S_B, F_B and x_B.

Similarly, the particulate water (H_2O) depends on the amount of sulfate in the exhaust, and thus the amount of fuel sulfur. The same adjustment to the sulfate-bound water will be applied to the reference water emission rate as shown in Equation (2).

$$(H_2O)_x = NonECPM \times \left((H_2O)_B \times \left[1 + F_B \times \left(\frac{x}{x_B} - 1\right)\right]\right) \qquad (2)$$

Appendix 2: Derivation of the Sulfate Calculator Parameters used in MOVES2014

Light-duty Gasoline Vehicles

The KCVES collected $PM_{2.5}$ measurements from a statistically representative sample of vehicles in the Kansas City Metropolitan Area. The study was conducted in the summer of 2004 (Phase 1) and winter of 2004/2005 (Phase 2). In total, 496 vehicles were measured over both phases of the program. Chemical speciation was estimated from a subset of 99 vehicles from the initial 496 vehicles. The vehicles were tested on the LA-92 cycle. The details of the KCVES are located in US EPA (2008) and Fulper et al. (2010).

Fuel Sulfur Content

The first step is to determine the sulfur content for the Kansas City vehicles from which the reference sulfate emission rates are derived. Analysis of the fuel properties was conducted on a subset of vehicles in KCVES. 171 vehicle tests in the KCVES were matched with a fuel analysis reported in the Kansas City PM Characterization Report[1]. The average fuel sulfur content is shown in Table 2-1, with associated 95% confidence intervals. The mean sulfur content is significantly smaller in the summer, as shown by the 95% confidence intervals. Interestingly, the winter measurements had higher sulfur content, although they were closer to the phase-in of the Tier 2 low-sulfur standards.

Table 2-1. Mean Fuel Sulfur content by Season

Season	n	Mean sulfur content	sd	95% Lower Confidence level	95% Upper Confidence level
summer	98	138.8	83.0	122.1	155.4
winter	73	183.6	87.4	163.2	204.0

Because most of the vehicles that had a chemical analysis of the emissions did not have the fuel analysis conducted, the average fuel sulfur content from all the tests is used to represent the reference case fuel sulfur level. An equally weighted average of the summer and winter is used of 161.2 ppm.

[1] The fuel sulfur content from 87 vehicles is reported in Tables 4-11 and 4-15 from the KC PM Characterization Report. An additional 84 fuel samples were transcribed from the fuel analysis reports in Appendix ff, because the tests were not complete by the release of the initial report.

Fuel Sulfur Contribution Analysis

The sulfate-adjustments in MOVES 2014 consider the sulfate contribution from both the fuel and the lubricating oil. The following equation is used to estimate the fuel and lubricating oil contribution for the gasoline engines:

$$\beta_1 \cdot OSE + \beta_2 \cdot FSC = SES \qquad (2\text{-}1)$$

Where: β_1 = Fraction of oil sulfur converted to sulfate, OSC = Oil-sulfur emissions in mg/mi, $\beta_2 =$ Fraction of fuel sulfur converted to sulfate, FSC = fuel-sulfur consumption in mg/mi, SES = Sulfur- emitted as sulfate (mg/mi). To estimate parameters in equation (2-1) requires at least two data points, ideally one data point at a high fuel sulfur level, and another at a low fuel sulfur level.

We used the KCVES as our data source from gasoline testing at a high fuel sulfur level. And we used a recent gasoline test program, the Full Useful Life (FUL) Test Program conducted at the National Vehicle Fuels & Emissions Laboratory in 2011 as our test program on low fuel sulfur. The Full Useful Life (FUL) Test Program conducted at the National Vehicle Fuels & Emissions Laboratory in 2011 evaluated light-duty gasoline Tier-2 vehicles (model year 2005 – 2009 vehicles) at ~ 120,000 miles. The FUL vehicles were tested at low fuel sulfur content (6 ppm), and sulfate measurements are made from the samples, on cold UDDS (bag 1 + bag 2 of the FTP), hot UDDS cycles, and hot US06 cycles. Documentation of the FUL test program is located in Sobotowski (2013).

Unfortunately, different vehicles were tested between the two studies. To best match the vehicle technologies and testing conditions, we only used the emissions data collected from the 1996-2004 vehicles in the KCVES, and only used the summer round data. Because the fuel sulfur content was not measured for each of the KCVES vehicles, we assumed that the fuel sulfur content is the mean fuel sulfur level measured in the summer (138.8 ppm).Comparisons of the particulate measurements of the elements are compared for the newest vehicles from Kansas City LA-92 cycle, with the three cycles measured in the FUL program in Figure 2-1.

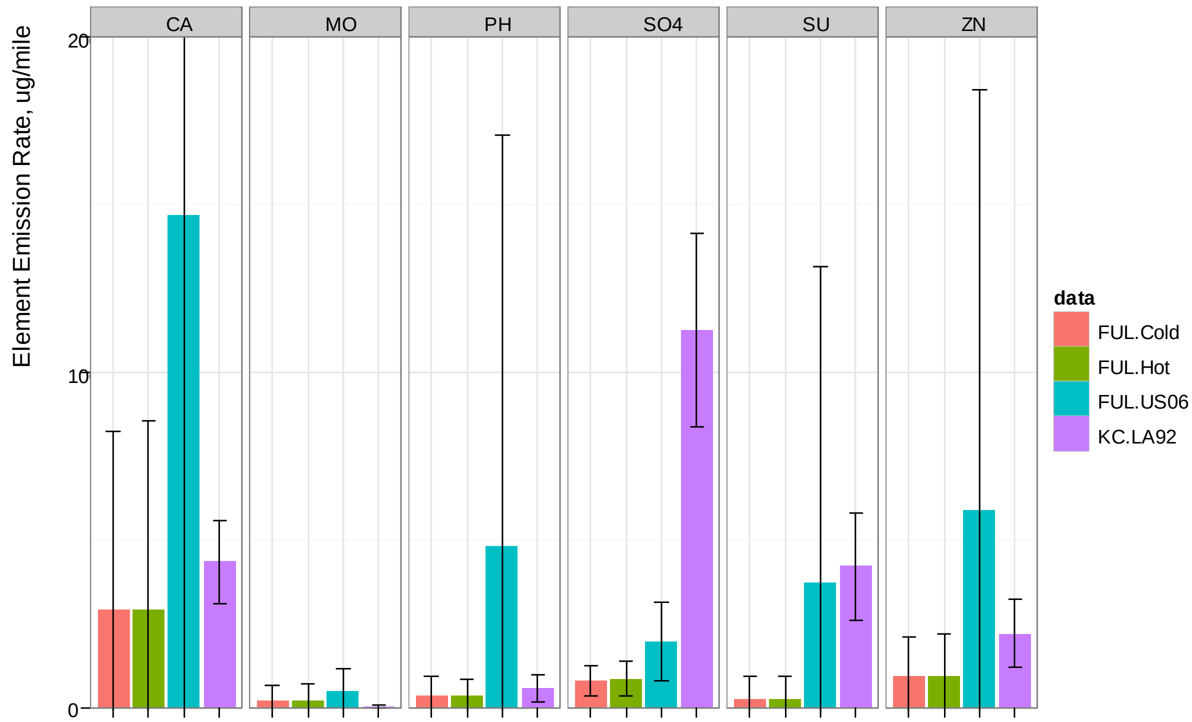

Figure 2-1. Oil-derived metals (calcium, molybdenum, phosphorous, zinc), and sulfate and sulfur emission rates from the Full Useful Life Program, and the newest vehicles from the Kansas City study (1996-2004).

Figure 2 contains the oil-derived metals (calcium, molybdenum, phosphorous, zinc), and sulfate and sulfur emission rates from the Full Useful Life Program, and the newest vehicles from the Kansas City study (1996-2004) that are tested in the summer round. Calcium is the dominant element emitted in the exhaust, as well as the dominant metal component of lubricating oil. As shown, the calcium emissions on the FUL UDDS tests are comparable to the calcium emissions on the Kansas City LA-92 tests. The calcium emission rates from KCVES are slightly higher, which would be expected due to the slightly more aggressive LA-92 cycle compared to the FTP. In contrast, the US06 has very high oil element emissions in the FUL which is a very aggressive cycle, which could lead to high oil consumption/and or burn-off of particles on the catalyst and exhaust system. Overall, the oil consumption based on the element emission rates, appears to be comparable between the FUL and newest KCVES vehicles. The KCVES vehicles has much higher sulfate emission rates, which is expected due to the higher sulfur content in the fuel.

The two data sets (FUL vehicles, and the newest vehicles from KCVES) were combined to estimate the relative contribution of sulfate from the lubricating oil and the fuel. In combining the data sets, the 4 gasoline-direct injected vehicles are excluded from the FUL program to provide a comparison of port-fuel injection technology. Only the KCVES vehicles tested in the summer are included to minimize any confounding effects of temperature on sulfate and oil emissions. The following assumptions regarding the two sets of vehicles are made to estimate the sulfate contributions:

1. Sulfur that is consumed with the lubricating oil in the engine forms sulfate emissions with the same propensity between the FUL and KCVES vehicles. Oil consumption is not measured on the vehicles over each cycle. The sulfur emitted in the oil is estimated using the measured calcium emission rates, and the average sulfur to calcium concentration measured in the lubricating oil from the FUL test program. The ratio between calcium to sulfur concentration in the lubricating oil is assumed to be equal between the 1996-2004 KCVES vehicles and the FUL program vehicles.
2. The fraction of fuel sulfur converted to sulfate is the same between the FUL and 1996-2004 Kansas City vehicles. Both set of vehicles have port-fuel injected, closed looped engines with three-way catalysts emission control technologies.

The mean values from the KCVES (1996-2004) and the FUL vehicles are used to estimate the parameters in equation (1). Weighted means were calculating, using the distribution of the cars and trucks from the KCVES for the 1996-2004 model years (57% cars, 43% light-duty trucks). The following data were used with equation (2-1):

For Kansas City: $\beta_1 \cdot \overline{OSE}_{KC} + \beta_2 \cdot \overline{FSC}_{KC} = \overline{SES}_{KC}$

For the Full Useful Life Program: $\beta_1 \cdot \overline{OSE}_{FUL} + \beta_2 \cdot \overline{FSC}_{FUL} = \overline{SES}_{FUL}$

Assumption 1 implies $\beta_1 = \beta_1$, and assumption 2 implies $\beta_2 = \beta_2$. With two unknowns, and two equations, β_1 and β_2 are estimated, and the model parameters are displayed in Table 2-2. The fuel is estimated to contribute ~20% of the sulfate emissions for the FUL program vehicles, and over 70% of the sulfate emissions for the Kansas City vehicles.

Table 2-2. Data, estimated coefficients, and estimated contributions of sulfate from the lubricating oil and fuel from the FUL and Kansas City studies.

	FUL (FTP)	Kansas City (LA-92)	Kansas City (LA-92)
Vehicle Model Year Range	2005-2009	1996-2004 (Summer only)	1968-2004 (VMT weighted)
Sulfur, ppm (x_B)	6	138.8	161.2
Calcium emissions, mg/mi	0.028	0.067	0.089
Sulfur/Calcium lubricant concentration ratio	0.697	-	-
Estimated oil sulfur emission, mg/mi (OSE)	0.020	0.047	0.062
Estimated fuel sulfur consumption, mg/mi FSC	0.849	21.648	25.033
Sulfate emissions, mg/mi	0.024	0.163	0.340
Fraction of Oil Sulfur Converted to Sulfate Emissions (β_1)	0.333	0.333	0.575
Fraction of Fuel Sulfur Converted to Sulfate Emissions (β_2)	0.0018	0.0018	0.003
Sulfate conversion adjustment (α)	1	1	1.726
Oil Sulfate Contribution, mg/mi	0.020	0.047	0.106
Fuel Sulfate Contribution, mg/mi	0.005	0.117	0.233
Oil Sulfate Contribution %	81.1%	28.5%	31.3%
Fuel Sulfate Contribution % (F_B)	18.9%	71.5%	68.7%

The sulfate PM speciation factors needed for MOVES 2014 gasoline vehicles were based on a fleet-average of the both the summer and winter tests. The model parameters were adjusted to be applicable for the fleet of vehicles measured in Kansas City. As stated earlier, the winter tests had significantly higher sulfur contents in than the summer tests. For modeling the fleet sulfate contributions in MOVES2014, the fuel contribution to sulfate emissions was estimated from the mean fuel sulfur level of both the summer and winter sulfur levels: 161.2 ppm. The average calcium emissions and fuel consumption were calculated using all 99 vehicles selected for chemical analysis in the Kansas City study. The means were calculated using a VMT-weighting, and an equal weight to both the summer and winter data. The VMT weighting places most of the weight on the 1996-2004 vehicles.

To estimate the relative oil and fuel contribution from fleet-average emissions, the model coefficients were adjusted to account for different sulfate formation rates. Both the parameters (β_1, β_2) were adjusted equally with a sulfate conversion adjustment, (α). such that equation (2-2) estimated the fleet-weighted sulfate emissions data.

$$\alpha \cdot \beta_1 \cdot \overline{OSE}_{KC} + \alpha \cdot \beta_2 \cdot \overline{FSC}_{KC} = \overline{SES}_{KC} \quad (2\text{-}2)$$

An adjustment value of 1.726 was estimated to fit the VMT-weighted average, meaning that the sulfur in the fuel and oil is 1.7 times as likely to form sulfate emissions using the fleet-average KCVES data set compared to only the summer 1996-2004 vehicles. The increase could be due to increase in oil emissions with older vehicles and the use of oxidation catalysts in older vehicles which increase the formation of sulfate emissions. Table 2-2 displays the estimated fuel sulfate contribution and oil contribution for the VMT-weighted KCVES data. 68.7% of the sulfate emissions in the KCVES study are estimated to be originating from the gasoline fuel at the sulfur. In MOVES2014, the fuel sulfate contribution (68.7%) scales linearly with changes in fuel sulfur level, but the MOVES2014 retains the lubricating oil sulfate contribution regardless of the fuel sulfur level. The sulfur levels (x_B), and the fuel sulfate contribution values (F_B) in Table 2-2 for the fleet results are the parameters that are used in MOVES2014 to adjust the gasoline sulfate emissions (Table 1).

Appendix 3: Sulfate Calculator- Conventional Diesel

In Phase 1 of the DECSE, two engines were tested with diesel oxidation catalysts: a 1999 Cummins ISM370 and a 1999 Navistar T443 engine. The Cummins is a heavy-duty diesel engine, and the Navistar is a medium-duty engine used in light duty trucks. The engines were tested on steady-state 4-mode test cycles, as well as a transient FTP hot-cycle test. The engines were tested at 4 sulfur fuel levels: 3, 30, 150, and 350 ppm. The lubricating oil used in the study was Shell Rotella T15W40, which is a commercially available CH-4 diesel lubricating oil specified for use in diesel trucks running on sulfur fuel <500 ppm, and engines that comply with the 1998 US EPA engine standards. The sulfur content of the engine oil was measured at 3520 ppm (DECSE phase 1). The PM and sulfate emissions were measured engine-out, and post-catalyst to examine the impact of the diesel oxidation catalyst on emissions. The engine-out and post-catalyst SO4 emissions are plotted at the four sulfur levels in Figure 3-1 and 3-2.

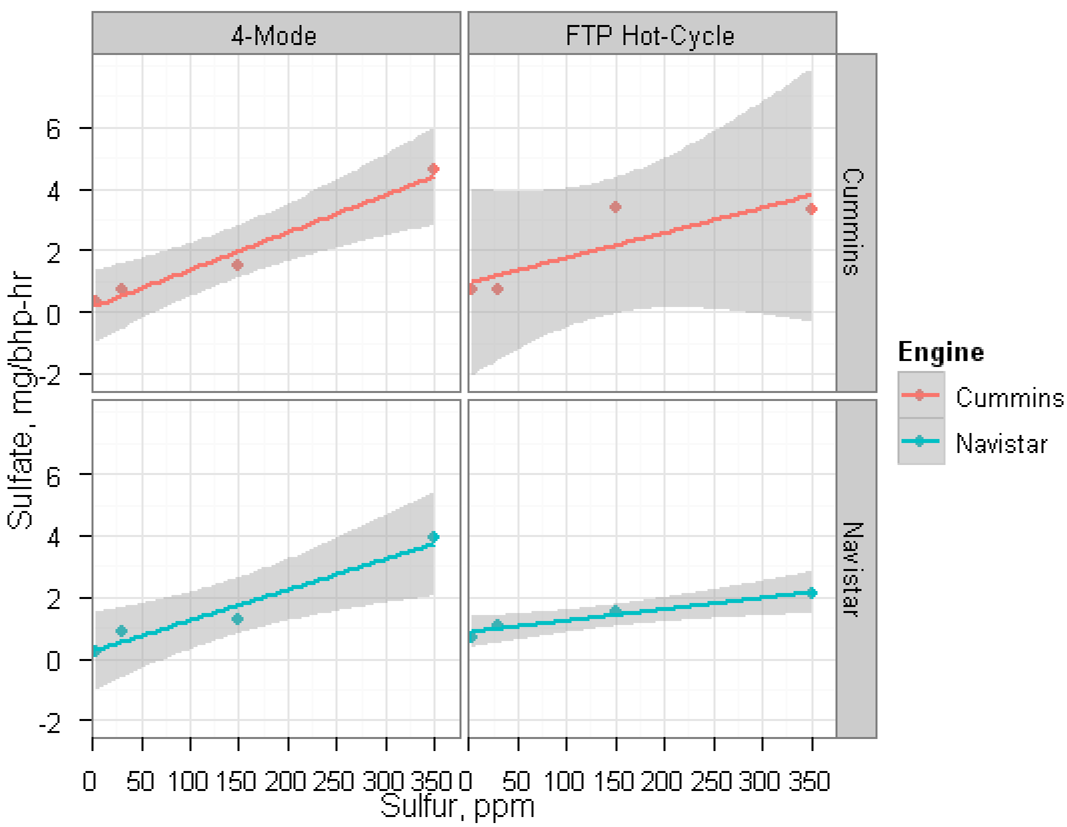

Figure 3-1. Engine-out sulfate emissions at four fuel sulfur levels (3, 30, 150, 350) measured on a 4-mode and FTP engine test cycle, from a heavy-duty engine (Cummins) and a medium-duty engine (Navistar).

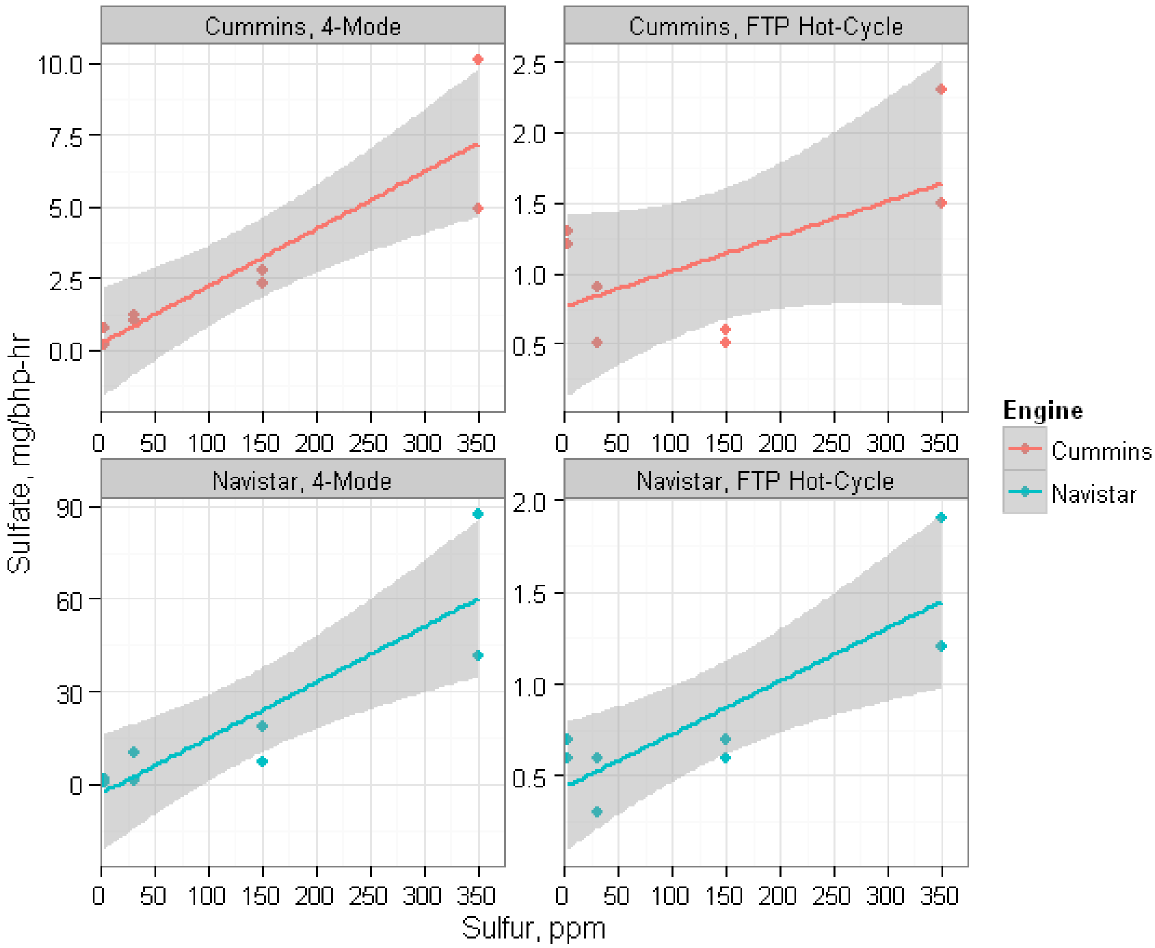

Figure 3-2. Post-catalyst sulfate emissions at four fuel sulfur levels (3, 30, 150, 350) measured on a 4-mode and FTP engine test cycle, from a heavy-duty engine (Cummins) and a medium-duty engine (Navistar).

The post-catalyst results produced much more variable results with respect to fuel sulfur. On the steady-state cycle, the medium-duty engine was very sensitive to fuels sulfur level, and produced over 90 mg/mile of Sulfur at the elevated fuel sulfur level. The engine-out results (Figure 3-1) produced more consistent results between driving cycles and between the heavy-duty and medium-duty engines. Because this data produced more consistent results, the engine-out sulfate data is used to estimate the relative contribution of lubricating oil and fuel to the sulfate emissions for diesel engines in MOVES. Figure 3-3 plots the engine-out sulfate results with respect to fuel sulfur level for the two engines and two driving cycles.

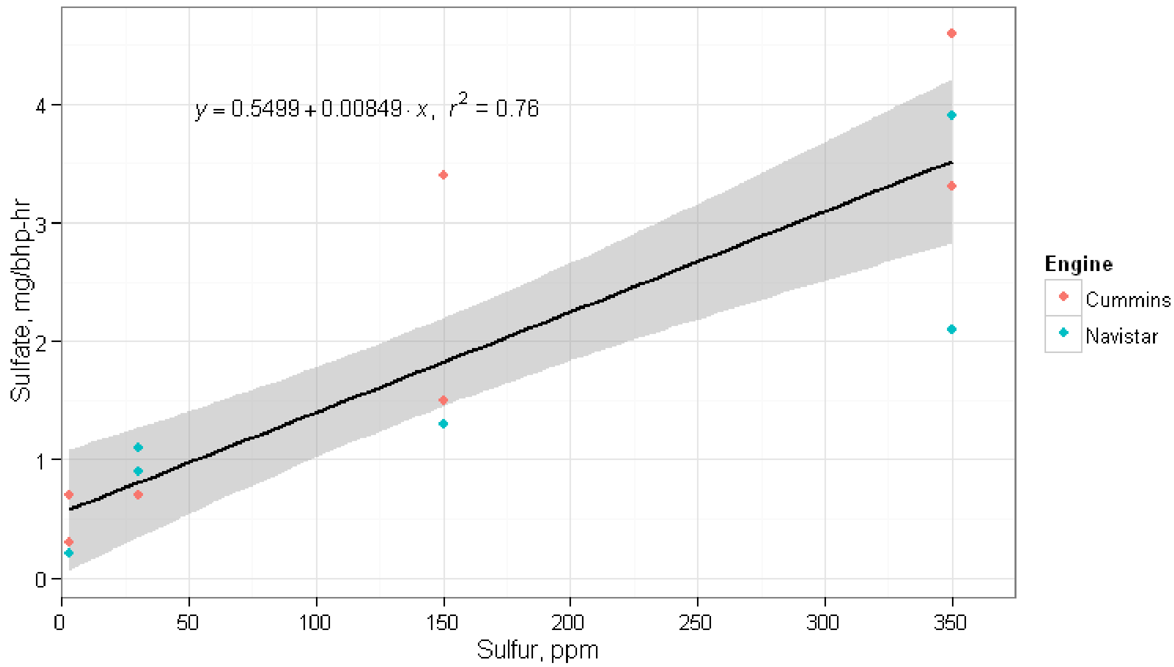

Figure 3-3. Simple linear regression fit of the engine-out sulfate emissions and fuel sulfur level data. This includes the medium and heavy-duty engine, and both the steady-state 4-mode cycles and the FTP cycles. The shaded areas are the 95% confidence intervals of the mean-value of the regression.

Using the simple linear regression fit, the relationship between sulfur content and fuel is estimated. The intercept can be interpreted as the sulfate contribution from the lubricating oil (Warren et al. 2000). Using the model coefficients in Figure 3-3, the fuel sulfate and oil sulfate contributions are calculated for four sulfur levels in Table 3-1 (0, 11, 172, and 350). At 0 ppm sulfur, the fuel sulfate contribution is 0, and all the estimated sulfur is from the lubricating oil. At 350 ppm fuel sulfur, most of the estimated sulfate is from the fuel sulfur. 11 ppm is the national default fuel sulfur level in MOVES for heavy-duty trucks. 172 ppm is the estimated sulfur content associated with the estimated fuel sulfate contribution from the E55/59 study used to populate the base PM rates in MOVES. In MOVES runs, the estimated fuel sulfate contribution from the E55/59 (72.6%) will be scaled linearly with changes in fuel sulfur from 172 ppm.

Table 3-1. Estimated oil and fuel sulfate contributions to the model.

	Sulfur level, ppm (x)			
	0	11	172	350
Oil Sulfate Contribution (mg/bhp-hr)	0.55	0.55	0.55	0.55
Fuel Sulfate Contribution (mg/bhp-hr)	0.00	0.09	1.46	2.97
Oil Sulfate Contribution (%)	100.0%	85.5%	27.4%	15.6%
Fuel Sulfate Contribution (%)	0.0%	14.5%	72.6%	84.4%

Appendix 4: Sulfate Calculator- 2007 and later Diesel

Table 4-1. Model Parameters for predicting particle number contribution from sulfur in the fuel and the lubricating oil from Kittelson et al. (2008)

Parameter	Estimate	90% Confidence Intervals
Fuel sulfur concentration	36.2	(24.3 to 48.1)
Lubricating Oil concentration	0.142	(0.054 to 0.23)

The relative contributions of sulfate emissions are computed using the contributions from fuel and oil parameters from Table 4-1. Table 4-2 displays the contributions from lubricating oil, assuming 3,000 ppm sulfur content, and varying levels of sulfur content in the diesel fuel. 4.5 ppm is selected because it is the fuel sulfur level used in the ACES phase 1 program, from which the sulfate emissions for post-2007 emissions are derived. 15 ppm is the sulfur limit mandated by the 2007 ultra-low fuel sulfur. 11 ppm is the current default sulfur content used in MOVES2014. As shown in Table 5, the lubricating oil is estimated to contribute the majority of sulfate emissions when the fuel sulfur level is below 12 ppm.

Table 4-2. Estimation of the relative contribution of fuel sulfur and lubricating oil sulfur on sulfate emissions

	Sulfur level (x) ppm		
	4.5	11	15
Oil Particle Number Contribution $(CPC/cm^3)/10^6$	426.00	426.00	426.00
Fuel Particle Number Contribution $(CPC/cm^3)/10^6$	162.90	398.20	543.00
Oil Sulfate Contribution (%)	72.3%	51.7%	44.0%
Fuel Sulfate Contribution (%)	27.7%	48.3%	56.0%

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