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

Calculating the Effects of Gasoline Sulfur on Exhaust Emissions

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1. Introduction

This chapter describes how MOVES2014 adjusts exhaust emissions of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx) in response to varying levels of fuel sulfur in gasoline. MOVES2014 assumes that there is no direct impact of fuel sulfur on criteria emissions from diesel vehicles.

Fuel sulfur content has long been understood to affect the performance of emission aftertreatment catalysts in light duty vehicles, where the sulfur and/or its oxides adsorb to the active precious metal sites, reducing the catalyst's efficiency in destroying harmful pollutants. This can severely impair the effectiveness of the catalyst to convert the products of combustion, leading to increase in emissions relative to a “clean” catalyst. Because the quantity of sulfur present on the catalyst at any given time is primarily a function of its temperature and the fuel sulfur level, the effects of gasoline sulfur content are modeled as though independent of the effects of other fuel properties.

The sulfur effects modeled in MOVES2014 are based on two separate fuel effect models. The two models are MOBILE6 Fuel Sulfur Model (M6Sulf) and Tier 2 Low Sulfur Model.

The MOBILE6 Fuel Sulfur Model (M6Sulf) applies to (1) all model years for sulfur level above 30 ppm, and (2) pre-2001 model years for sulfur level equal to and below 30 ppm. Section 2 details the M6Sulf algorithm and discusses the minor changes and assumptions applied to adapt the M6Sulf model into MOVES framework.

The Tier 2 Low Sulfur Model applies only to 2001-and-later model year vehicles operating on sulfur levels equal to or below 30 ppm. Section XX describes how the results of a study specifically designed to measure sulfur effects on Tier 2 gasoline vehicles were applied in MOVES2014. Previously, in MOVES2010, only the M6Sulf model was used to model sulfur effects.

2. The MOBILE6 Sulfur Model (M6Sulf)

The M6Sulf model was developed based on the analysis of several studies examining the effect of sulfur on exhaust emissions, conducted by the US Auto/Oil Air Quality Improvement Research Program (AQIRP)[1,2,3], US Environmental Protection Agency (EPA)[4,5,6], and American Petroleum Institute (API)[7]. All data sources and the details of the analysis used to develop the M6Sulf model are documented in “Fuel Sulfur Effects on Exhaust Emissions for MOBILE6”.[8] The vehicle technologies included in the analysis were Tier 0, Tier 1, Low-Emitting Vehicles (LEVs), and Ultra Low-Emitting Vehicles (ULEVs).

In MOVES, we apply the M6Sulf model for (1) all model years for sulfur levels above 30 ppm, and (2) pre-2001 model years for sulfur levels equal to and below 30 ppm. The M6Sulf model contains separate fuel sulfur effects (coefficients) and equations (i.e., log- log and log-linear) for “normal” and “high” emitters. In MOBILE6, a “high emitter” was defined as a vehicle emitting twice the applicable HC or NOx standards or three times the applicable CO standard.

Because MOVES does not distinguish between "normal" and "high" emitters, and because the weights applied to effects for both classes were frequently about equal, an unweighted arithmetic average of the "normal" and "high" effects was calculated and used in MOVES.

The M6Sulf algorithm as programmed into MOVES contains four separate steps.

1. Short Term Sulfur Effects
2. Long Term Sulfur Effects
3. Sulfur Irreversibility Effects
4. Effects of Sulfur geographical phase-in areas (GPA)

2.1 Short-Term Sulfur Effects

In MOVES, the M6Sulf model data are stored as a set of equation coefficients in "*sulfurmodelcoeff*" table. It has the following table structure:

pollutantID
processID
M6emitterID
sourceTypeID
fuelMYGroupID
SulfurFunctionID
SulfurCoefficient

The M6emitterID is designated as either "normal" or "high" and the SulfurFunctionID is designed as either "Log-Log" or "Log-Linear". The "Log-Log" designation refers to a model with a natural log - natural log form and the "log-linear" refers the natural log-linear model.

The Short Term Sulfur Effect estimates the short-term effects on emissions due to sulfur's adsorption onto the catalyst surface by calculating an adjustment to the base emissions as a function of the sulfur volume of the gasoline. The initial calculations use Equation 1 and Equation 2. These equations are used in cases where the log-log relationship is required (the variable SulfurFunctionID is set to 'log-log'). This relationship applies to Tier 0, and LEV+ vehicles. The variable "sulfShortTarget" ($C_{\text{short,target}}$) is the correction factor for the sulfur level of the fuel being modeled, for which the sulfur content (x_S) is expressed in ppm. The parameter, $C_{\text{short,basis}}$, is the correction factor for the base sulfur (sulfurBasis variable in "*SulfurBase*" table) level. The sulfur basis ($x_{S,\text{basis}}$) is always 30 ppm – even for model year groups that use 90 ppm sulfur as the base.

$$C_{\text{short,target}} = \exp(\beta \ln x_S) \qquad \textbf{Equation 1}$$

$$C_{\text{short,basis}} = \exp(\beta \ln x_{\text{S,basis}}) \quad \textbf{Equation 2}$$

The short-term Sulfur effects for Tier 1 vehicles (i.e. model years 1994-2000) use a log-linear algorithm as in Equation 3 and Equation 4. Again, the sulfur basis ($x_{\text{S,basis}}$) is 30 ppm. The variable SulfurFunctionID in "*sulfurmodelcoeff*" table shows which form of the equation is used.

$$C_{\text{short,target}} = \exp(\gamma x_{\text{S}}) \quad \textbf{Equation 3}$$

$$C_{\text{short,basis}} = \exp(\gamma x_{\text{S,basis}}) \quad \textbf{Equation 4}$$

The Short-term sulfur effect (SulfAdj, $A_{\text{S,short}}$) for all groups is computed using Equation 5.

$$A_{\text{S,short}} = \frac{C_{\text{short,target}} - C_{\text{short,basis}}}{C_{\text{short,basis}}} \quad \textbf{Equation 5}$$

2.2 Long Term Sulfur Effects

The Long-term Sulfur effects ($A_{\text{S,long}}$) are intended to account for the effects of prolonged exposure to sulfur in the catalyst that are reversible. The values used in MOVES are stored in the sulfurLongCoeff variable in "*M6SulfurCoeff*" table. The values for sulfurLongCoeff are a function of pollutant. They are:

HC	2.50
CO	2.36
NOx	1.47

These short-term and long-term effects are multiplied to produce the variable sulfAdj2 (A_2), as shown in Equation 6. Sulfur levels of 30 ppm or less are assumed to have no long-term sulfur effects.

$$A_2 = A_{s,short} \times A_{s,long} \quad \textbf{Equation 6}$$

2.3 Sulfur Irreversibility Effects

In this step, the permanent effects of sulfur on emissions are computed. These effects are intended to represent long-term emission impact of past exposure to high sulfur fuels, even when current fuels have lower sulfur levels. The irreversibility effects apply to only Tier 2 and later (2004+ model year vehicles), and apply only to target fuel sulfur level greater than 30 ppm sulfur. For model years 2003 and earlier and for fuel sulfur levels ≤ 30 ppm, the model does not calculate permanent effects. The same effects are applied to all three pollutants (HC, CO and NOx) and processes (start and running).

The SulfurCap is a function of model year group.

Model Year Group	SulfurCap
2004 – 2005	303 ppm
2006 – 2007	87 ppm
2008 +	80 ppm

If the fuel sulfur level is greater than 30 ppm but less than the SulfurCap ($x_{S,cap}$), Equation 7 is used to compute the “irreversible sulfur effect” ($A_{S,Irr}$, SulfIRR) effects, and the effect is applied as a function of model year group.

$$A_{S,Irr} = \exp(\phi \ln x_{S,cap}) \quad \textbf{Equation 7}$$

If the selected sulfur level is greater than the maximum sulfur level, rather than using the value of the "cap" as the sulfur level, the actual sulfur level (x_S) is input to the Equation 7 to calculate the irreversibility effect. However, sulfur levels above the maximum are not expected in normal use of the MOVES model.

2.3.1 Combining Short-Term, Long-Term and Irreversibility Sulfur Effects

Equation 8 combines all the sulfur effects described into a final sulfur effect, designated as $A_{S,3}$ or "sulfAdj3." The effect is calculated as a multiplicative adjustment, and includes the short-term effects applied to the fuel basis ($C_{\text{short,basis}}$) from Equation 2 or Equation 4, the combined short-term and long-term adjustment (A2, Equation 6) and the irreversibility effect $A_{S,\text{Irr}}$ (Equation 7). The two main terms in the expression are weighted by the factor w_{IR} (irreversibility factor), which takes a value of 0.425.[9]

$$A_{S,3} = 1.0 + \left[w_{IR} \left(\frac{A_{S,\text{Irr}} - C_{\text{short,basis}}}{C_{\text{short,basis}}} \right) + (1.0 - w_{IR}) A_2 \right] \qquad \textbf{Equation 8}$$

2.4 Sulfur Effects in Geographical Phase-In Areas (GPA)

During calendar years 2004-2006, the gasoline sulfur levels in the Sulfur "Geographical Phase-In Area" (Sulfur GPA) were allowed to be higher than elsewhere in the nation. MOVES accounts for this difference with the calculation of "Sulfur GPA Effects." The algorithm applies a maximum sulfur level of 330 ppm within designated "GPA areas," most of which are located in the Rocky Mountains and are identified in the database table "*county*," using the field "GPAFract."

The sulfur adjustments in GPA are calculated using the same process as for other areas, except that the variable for the sulfur basis is assigned a different value. A value of 330 ppm, representing a typical worst case in a GPA scenario ($x_{S,\text{GPAmax}}$), is assigned in Equation 9 in place of the actual sulfur level in the fuel to be evaluated. The result $C_{\text{short,GPA}}$ is applied in Equation 10 with $C_{\text{short,basis}}$ to give the adjustment $A_{S,\text{short,GPA}}$, as shown below:

$$C_{\text{short,GPA}} = \exp(\beta \ln x_{S,\text{GPAmax}}) \qquad \textbf{Equation 9}$$

$$A_{\mathrm{S,short,GPA}} = \frac{C_{\mathrm{short,GPA}} - C_{\mathrm{short,basis}}}{C_{\mathrm{short,basis}}} \qquad \textbf{Equation 10}$$

In this application of Equation 10, the numerator is multiplied by 0.608 to represent NOx high emitters.

As with non-GPA areas, the combined short- and long-term effect is calculated by multiplying the GPA short-term effect and the same long-term coefficient as used outside GPA areas, using Equation 11.

$$A_{\mathrm{2,GPA}} = A_{\mathrm{S,short,GPA}} * A_{\mathrm{long}} \qquad \textbf{Equation 11}$$

Then, the equivalent of the adjustment $A_{S,3}$ for the GPA area ($A_{3,GPA}$) is calculated by applying Equation 12 as shown below.

$$A_{\mathrm{3,GPA}} = 1.0 + \left(w_{\mathrm{IR}} A_{\mathrm{2,GPA}} + (1.0 - w_{\mathrm{IR}}) A_2\right) \qquad \textbf{Equation 12}$$

In years outside the phase-in, or in areas where sulfur < 30 ppm, $A_{3,GPA}$ is set equal to $A_{S,3}$. This equivalence is also assigned in cases when the assigned sulfur level is greater than sulfurGPAMax (i.e., 330 ppm).

To calculate a combined sulfur adjustment, the values of $A_{S,3}$ and $A_{3,GPA}$ are weighted by the "GPA fraction" (f_{GPA}, GPAFract) in a county being simulated, as shown in Equation 13. In the default values assigned in the database, the fraction is always 0 or 1. However, GPA fraction is a user input, allowing assignment of alternate values between 0 and 1.

$$A_{\mathrm{S,combined}} = (1 - f_{\mathrm{GPA}}) A_{\mathrm{S,3}} + f_{\mathrm{GPA}} A_{\mathrm{3,GPA}} \qquad \textbf{Equation 13}$$

2.5 Weighting for "Normal" and "High" Emitter Fractions

The original M6Sulf algorithm produces a sulfur correction for both "Normal" and "High" emitters. However, because MOVES does not attempt to distinguish "normal" and "high" emitter classes, the sets of model coefficients for "normal" and "high" emitters were regarded as independent models and assigned equal weights for consistency with the MOBILE6 model. That is, in the MOVES application, $w_{normal} = w_{high} = 0.50$. These calculations are applied to both target and base fuels, as shown in Equation 14.

$$A_{S,3}^{target} = (1 - w_{high}) A_{S,3,normal}^{target} + w_{high} A_{S,3,high}^{target}$$
$$A_{S,3}^{base} = (1 - w_{high}) A_{S,3,normal}^{base} + w_{high} A_{S,3,high}^{base}$$

Equation 14

Likewise, a composite of normal and high emitter GPAsulf adjustments are calculated using the same weights.

$$A_{3,GPA}^{target} = (1 - w_{high}) A_{3,GPA,normal}^{target} + w_{high} A_{3,GPA,high}^{target}$$
$$A_{3,GPA}^{base} = (1 - w_{high}) A_{3,GPA,normal}^{base} + w_{high} A_{3,GPA,high}^{base}$$

Equation 15

2.6 Computing the Sulfur Adjustment for Target and Base Fuels

During a model run, the calculations described to this point (sections 2.1 through 2.5) are repeated and applied for the two base fuels with 90 ppm and 30 ppm sulfur, corresponding to the two model-year groups (1960-2000 and 2001-2050), respectively. As stated earlier, the M6Sulf model applies to all sulfur levels for model year group 1960-2000, and only to sulfur levels above 30 ppm for model year groups 2001-2050. This step is taken because the final sulfur fuel adjustment is the ratio of the adjustments for the target and base fuels, as shown in Equation 11 for non-GPA and GPA areas. All calculations described are identical for the target and base fuels. All other properties of these fuels are held constant for the sulfur correction. A final sulfur adjustment for fuels containing 30 ppm sulfur resolves to 1.0 because the target fuel level is equal to the base fuel of 30 ppm. The 30 ppm sulfur level is called the *base* because the entire MOBILE6.2 Fuel Sulfur algorithm was developed based on this level. The calculation result does not equal 1.0 for the 90 ppm base sulfur.

$$A_{S,final} = \frac{A_{S,3}^{target}}{A_{S,3}^{base}}$$
$$A_{GPA,final} = \frac{A_{3,GPA}^{target}}{A_{3,GPA}^{base}}$$

Equation 16

3. Tier 2 Low Sulfur Model (T2LowSulf)

The M6Sulf model, described above, is used in MOVES to model emission effects for gasoline fuels with sulfur content greater than 30 ppm. For sulfur content less than 30 ppm in Tier 2 and later vehicles, a different algorithm, based on additional data collected since the M6Sulf model was created, is used.

Following the successful implementation of the Tier 2 sulfur standards, new research has focused on the emission reduction potential of lowering sulfur levels below 30 ppm, particularly in vehicles employing Tier 2 and newer technologies, under the hypothesis that increased reliance on the catalytic convertor would result in a higher sensitivity to fuel sulfur content. A 2005 study conducted jointly by EPA and several automakers found large decreases in NOx and HC emissions from vehicles meeting Tier 2 Bin 5 emission levels when operating on 6 ppm versus 32 ppm sulfur test fuel.[10] Another study published in 2011 by Umicore Autocat USA examined the impact of sulfur on the catalyst efficiency during repeated FTP tests using 3 and 33 ppm sulfur test fuel and observed significant reduction in emissions with lower fuel sulfur level.[11]

To gain further understanding of how such emission reductions might be reflected in the in-use fleet, EPA conducted a study assessing the state of sulfur loading (poisoning) in typical in-use Tier 2 vehicles, as well as the effect of fuel sulfur level on these vehicles during subsequent mileage accumulation.[12] The project was designed to take into consideration what was known from prior studies on sulfur build-up in catalysts over time and the effect of periodic regeneration events that can occur during higher speed and load operation in day-to-day driving.

The study sample included 81 cars and light trucks recruited from owners in southeast Michigan, covering model years 2007-9 with approximately 20,000-40,000 odometer miles. The makes and models targeted for recruitment were chosen to represent high-sales vehicles covering a range of types and sizes. Test fuels were two non-ethanol gasolines with properties typical of certification fuel, one at a sulfur level of 5 ppm and the other at 28 ppm, the higher level chosen to be representative of retail fuel available to the public in the vehicle recruiting area. All emissions data was collected using the FTP cycle at a nominal ambient temperature of 75°F.

To assess the overall in-use reduction between high and low sulfur fuel, a mixed-model analysis of the emissions data as a function of fuel-sulfur level and distance driven after cleanout was performed. The "sulfur level" data represents the emission measurements from the repeated FTP test cycles with mileage accumulation following back-to-back US06 cycle on two different fuel sulfur levels at 28 ppm and 5 ppm. Additional details on the design of the program and the statistical analysis of the data can be found in the report.

Table 1 summarizes the percent reduction in emissions from the analysis for NOx, THC, CO, and PM, which are the most relevant pollutants in MOVES context. The percent reductions were estimated for the complete dataset with all Tier 2 certification bin levels included, and for a dataset including only the vehicles certified to Tier 2 Bin 8. The p-values represent the statistics from the Type III F test. Unlike the gaseous pollutants, there was no effect of sulfur level found for PM. A plausible explanation is that the majority of PM as measured in this program (that is, from normal-emitting Tier 2 vehicles operated at low and moderate loads) was soot produced shortly after cold start (bag 1)[13], and the destruction of soot by the catalyst may be minimal regardless of its relative efficiency. As a result, sulfur would not be expected to have a significant effect on directly-emitted PM (other than very small amounts of sulfate).

Table 1. Emission Reductions from 28 to 5 ppm Sulfur

Tier 2 Cert Bin	Process	Pollutant			
		NO_x (p-value)	THC (p-value)	CO (p-value)	PM
B4, B5, B8	Hot-running[1]	59.2% (< 0.0001)	48.8% (< 0.0001)	–	–
	Cold Start[2]	–	5.2% (0.0063)	4.3% (0.0689)	–
B8 only	Hot-running[1]	66.3% (< 0.0001)	36.8% (< 0.0001)	22.1% (< 0.0001)	–
	Cold Start[2]	–	–	–	–

[1] Measured on the hot-running Phase of the FTP cycle (Bag 2).
[2] Measured as the difference between the cold-start and hot-start phases on the FTP cycle (Bag 1 – Bag 3).

The results shown in Table 1 were applied to model year 2001-and-later gasoline vehicles to estimate the sulfur effects when modeling fuel sulfur levels below 30 ppm. In applying the results from the study of Tier 2 vehicles to model year as early as 2001, it was assumed that NLEV vehicles are more similar to upcoming Tier 2 vehicles than the Tier 1 vehicles.

The T2LowSulf model is applied multiplicatively in conjunction with other gasoline fuel effects in MOVES, and applies only for sulfur levels equal to and below 30 ppm. For sulfur levels above 30 ppm, and for all pre-2001 model year vehicles, the M6Sulf model is used, as described in Section 2. Equation 17 shows the generic form of the Tier 2 Low Sulfur model.

$$A_S = 1.0 - \beta_S\left(S_{base} - x_S\right) \qquad \textbf{Equation 17}$$

The Tier 2 Low Sulfur coefficients (β_S) were developed by linearly interpolating between emission levels at 28 to 5 ppm, corresponding to the reductions in emissions shown in Table 1, and standardizing to base sulfur level of 30 ppm. The sulfur coefficient simply represents the slope of the interpolated line. The emission reductions from FTP bag 2 and FTP bag1-bag3 were used to calculate the sulfur coefficients for running exhaust and start exhaust, respectively. The percent reduction estimates from all Tier 2 certification bin levels were used to develop the T2LowSulf coefficients for passenger cars, passenger trucks, and light commercial trucks. For all other gasoline vehicles types, the estimates of percent reduction from Tier 2 Bin 8 vehicles only were used to develop the T2LowSulf coefficients, assuming that the catalyst response of heavier gasoline trucks to fuel sulfur level is closer to Tier 2 Bin 8 vehicles than others. Table 2 shows the specific values of the sulfur coefficients used in MOVES by pollutant, process, and vehicle type.

The sulfur base (S_{base}) in the T2LowSulf model varies as a function of model year group. For model year group 2001-2016, the sulfur base is unchanged at 30 ppm. However, for model year group 2017-2050, since the Tier 3 emission rates in MOVES assume that Tier 3 vehicles run on 10 ppm sulfur, the sulfur base is set at 10 ppm to prevent double-counting of benefits of low levels of sulfur in fuels for Tier 3 vehicles.

Table 2. Tier 2 Low Sulfur Coefficients by Vehicle Type, Process and Pollutant.

Vehicle Type	**THC**		**CO**		**NO_X**		**PM**	
	Starts	*Running*	*Starts*	*Running*	*Starts*	*Running*	*Starts*	*Running*
Motorcycle	0	0	0	0	0	0	0	0
Passenger Car, Passenger Truck & Light Commercial Truck	0.002568	0.018126	0	0	0	0.021582	0	0
All other Vehicle Types	0	0.015488	0	0.009436	0	0.027266	0	0

Equation 17 has been applied using the coefficients in Table 2 in the database table that stores fuel effect equations in the MOVES database ("*generalFuelRatioExpression*"). This table consolidates the two sulfur models (M6Sulf and T2LowSulf) for MYG 2001-2016 and 2017-2050, and the other fuel effect models (i.e., EPAct model), and allows the MOVES model to compute fuel effects based on the fuel properties of any fuel contained in the "*fuelSupply*" and "*fuelFormulation*" database tables. The detailed description of the "*generalFuelRatioExpression*" table is documented in Section 4 of the "Fuel Effects for Vehicles certified to Tier-2 Standards" Chapter.

4. Results: Sulfur Effects in MOVES2014

Trends of emissions in relation to fuel sulfur levels are shown in Figure 1 through Figure 4 for the 2017+, 2001-2016, 1996 and 1988 model years, respectively. The effects are 'net fuel effects' from the MOVES model. They were produced by eight separate MOVES runs using a constant fuel formulation and varying the fuel sulfur level from 4 ppm sulfur to 500 ppm sulfur. The 1988 model year represents the fuel effects on Tier 0 vehicles, and the 1996 model year represents the Tier1 and LEV standards, applying log-log and log-linear relationships within the M6Sulf model, as previously described (Equation 1 to Equation 16), the 2001-2016 model year represent Tier 2 vehicles, and the 2017+ model years represent Tier 3 vehicles.

The fuel effects are normalized to 90 ppm sulfur for model years 1988 and 1996, to 30 ppm sulfur for model years 2001 to 2016, and to 10 ppm sulfur for model years 2017 and later. In this context, 'normalization' means the correction factor is set to 1.0 at the specified level. For this example, the other fuel parameters were set at Base Fuel levels (6.9 psi RVP, 0% Ethanol volume, 26.1% aromatic content, 5.6% olefin content, 1.0% benzene content, 218F T50 and 329 F T90).

Figure 1. Relative Fuel Sulfur Effect for Running Exhaust Emissions for MYs 2017 and later

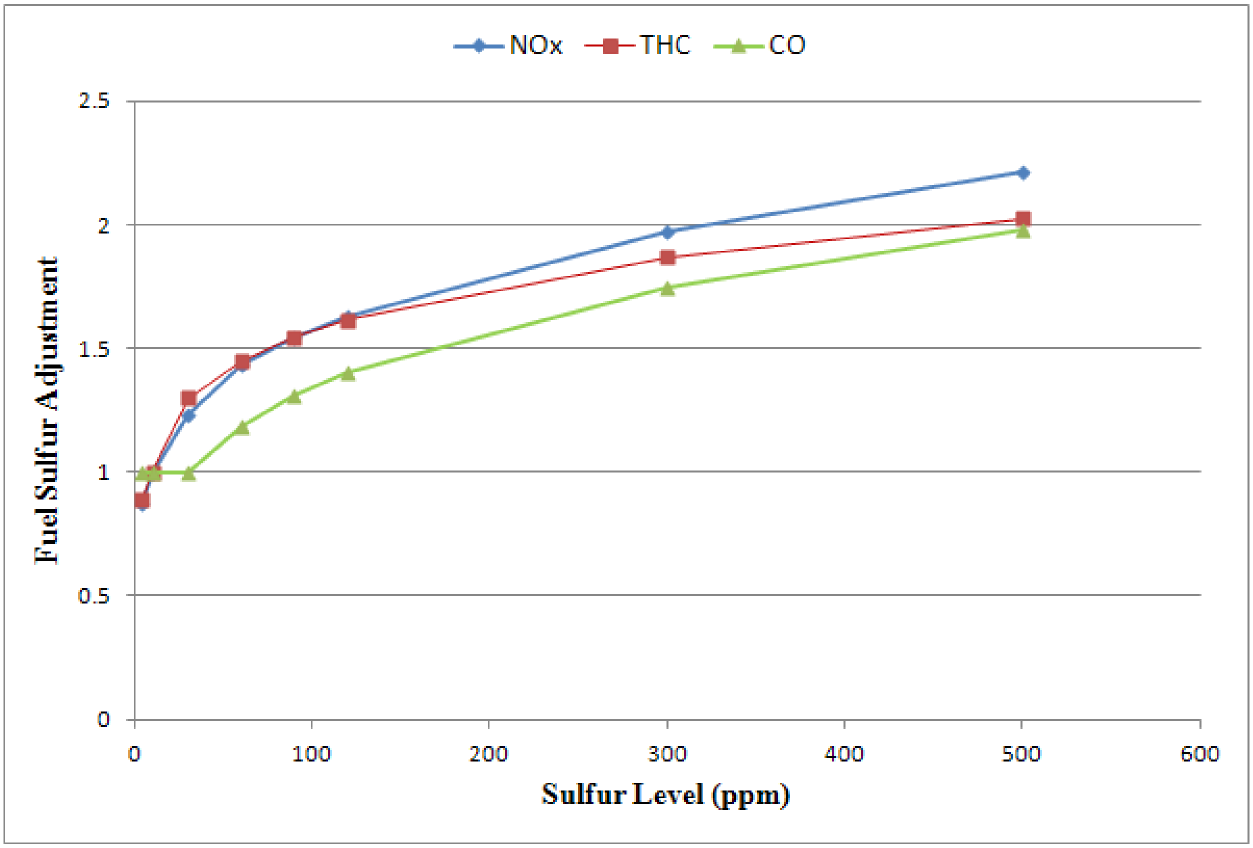


Figure 2. Relative Fuel Sulfur Effect for Running Exhaust Emissions for MYs 2001 to 2016

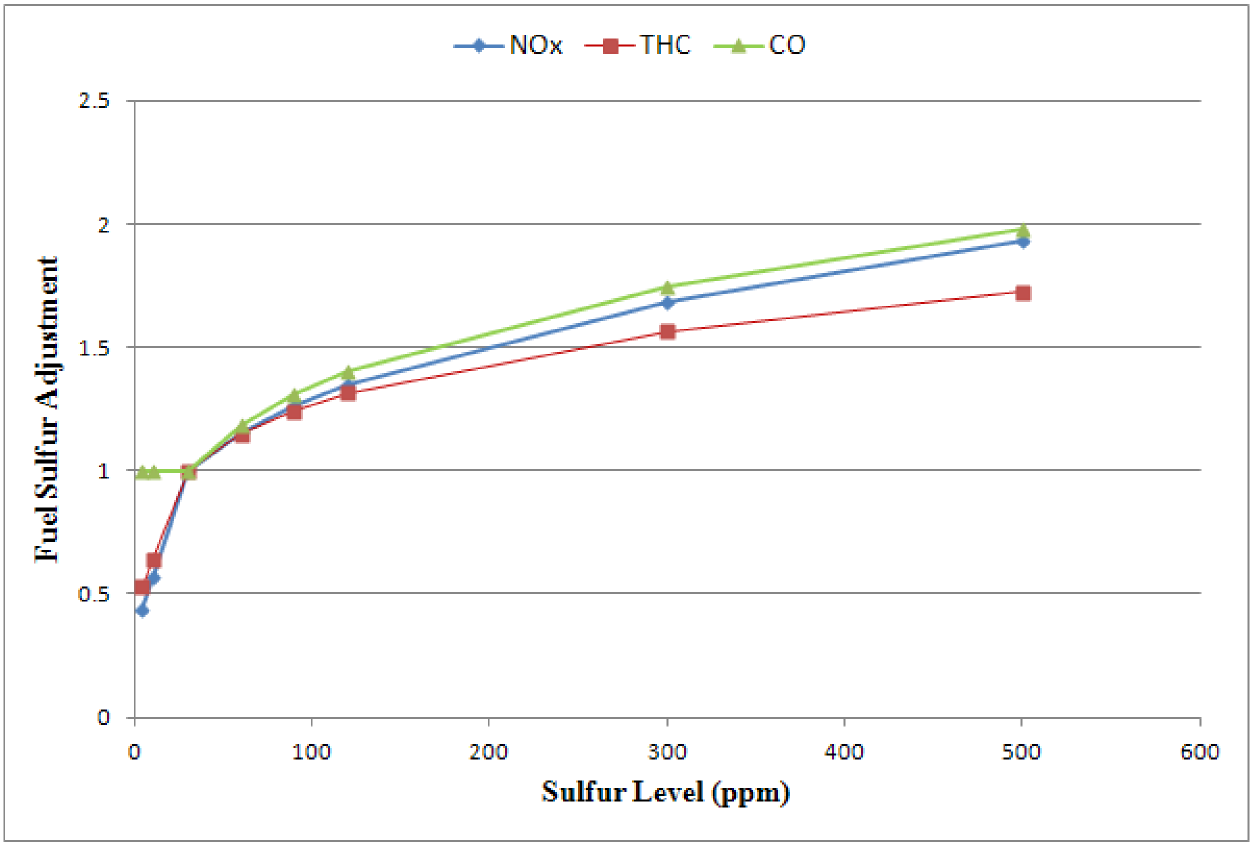


Figure 3. Relative Fuel Sulfur Effect for Running Exhaust Emissions for MY 1996

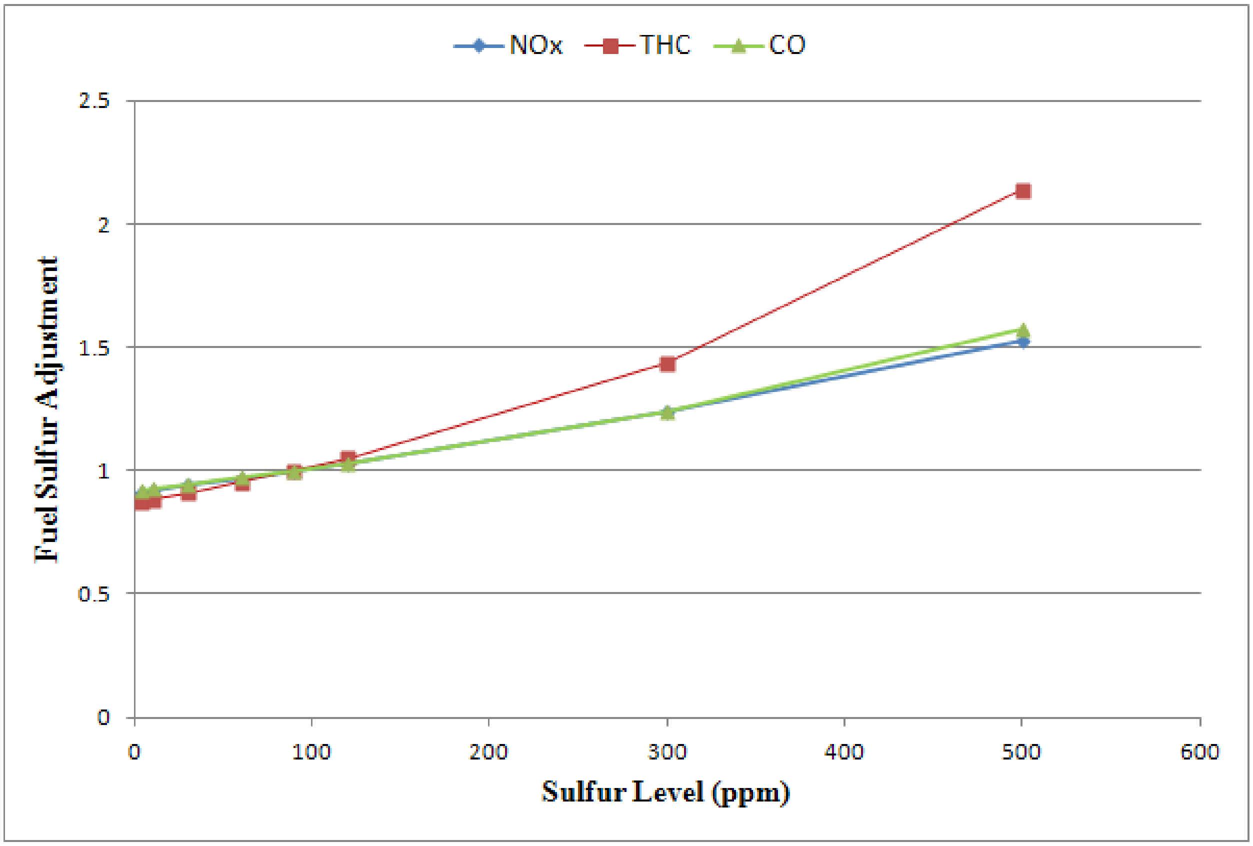
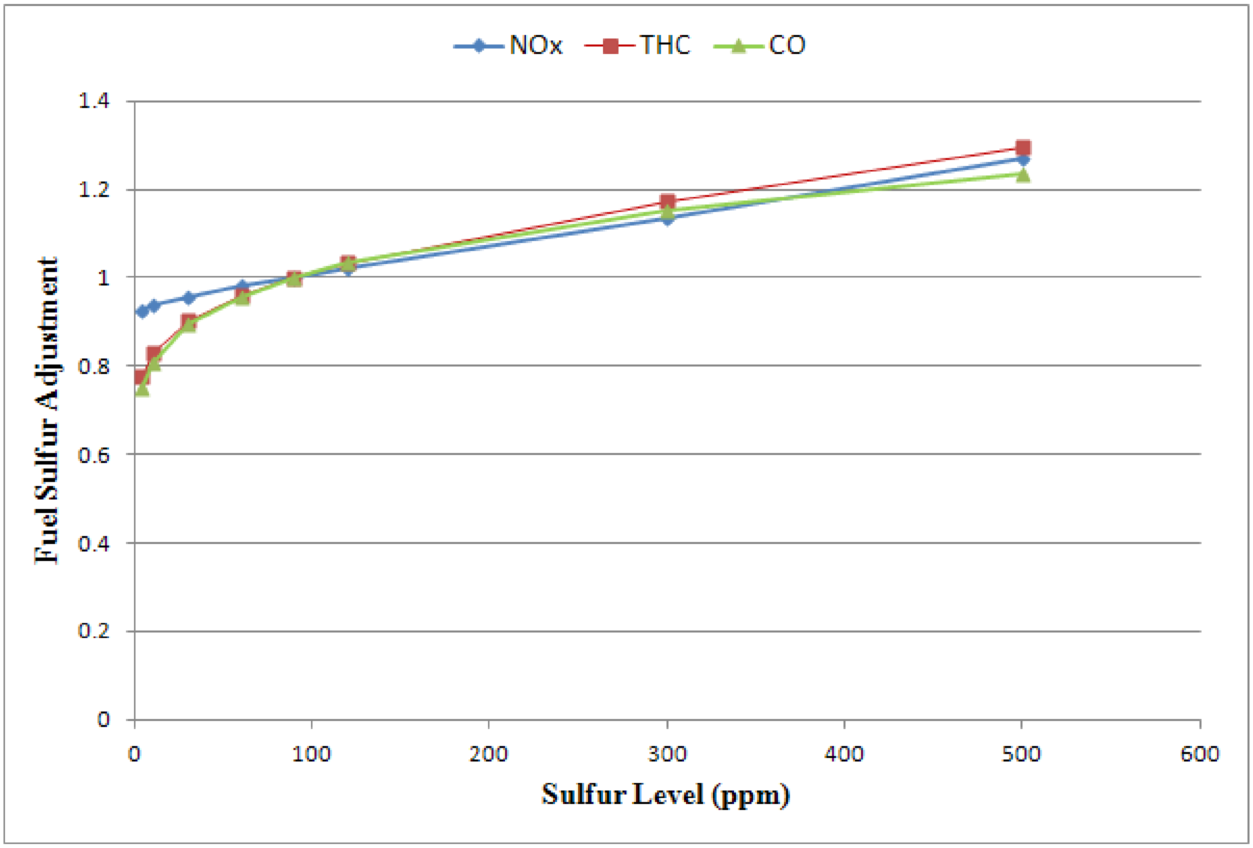


Figure 4. Relative Fuel Sulfur Effect for Running Exhaust Emissions for MY 1988



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