United States Environmental Protection Agency Air and Radiation

EPA420-P-99-008 M6.FUL.001 March 1999



# Fuel Sulfur Effects on Exhaust Emissions



### **Fuel Sulfur Effects on Exhaust Emissions**

### **Recommendations for Mobile 6**

Venkatesh Rao Assessment and Modeling Division Office of Mobile Sources U.S. Environmental Protection Agency

### NOTICE

This technical report does not necessarily represent final EPA decisions or positions. It is intended to present technical analysis of issues using data which are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position, or regulatory action.

### **Objective**

This document describes EPA's effort to estimate empirical relationships between fuel sulfur content and exhaust emissions of hydrocarbons (HC), non-methane hydrocarbons (NMHC), nitrogen oxides (NOx), and carbon monoxide (CO) as a function of vehicle technology and vehicle emitter classification for gasoline-powered vehicles. MOBILE6 will use these relationships to adjust exhaust emission rates in response to fuel sulfur levels input by the user. The vehicle technologies addressed in this analysis include: Tier 0, Tier 1, Low-Emitting Vehicles (LEVs), and Ultra Low-Emitting Vehicles (ULEVs). Where possible, the vehicle technology data are further stratified by passenger car (PC), Light-Duty Truck Class 1 (LDT1), and heavier Light-Duty Truck classifications (LDT2/LDT3/LDT4). Table 1 below defines the weight classifications for the different truck classes.

Truck Category	Gross Vehicle Weight in lbs. (GWVR)	Loaded Vehicle Weight in lbs (LVWR)
LDT1	0-6000	0-3750
LDT2	0-6000	3751-5750
LDT3	6001-8500	3751-5750
LDT4	6001-8500	5751-8500

 Table 1

 Light-Duty Truck Weight Definitions

Wherever possible, normal and high emitters are also addressed and analyzed separately. Dieselpowered heavy-duty vehicles are not considered in this analysis as very little data exists to describe sulfur's effect on emissions from these vehicles.

#### **Background**

Since the early 1970s it has been recognized that gasoline sulfur levels impact the conversion efficiency of automotive three way catalysts. A significant amount of test data has been generated in the recent past to investigate this phenomenon. Data were collected first during the development of EPA's Complex Model, and more recently in response to questions about the in-use performance of advanced technology (i.e., low-emission and Tier 2) vehicles. The Complex Model was constructed in response to the Clean Air Act's Reformulated Gasoline (RFG) requirements and is used to certify reformulated gasolines. The Complex Model is an empirical model designed to predict emissions as a function of fuel properties. The exhaust portion of the Complex Model is based solely on data from a number of different emission testing programs and includes the effect of aromatics, olefins, RVP, distillation characteristics, sulfur, and oxygen content on emissions of VOC, NOx, and air toxics. The exhaust Complex Model also applies strictly to only "1990 technology" vehicles (which are, in general, vehicles of Model Year 1987-1992). The reader is referred to the RFG web site

(http://www.epa.org/oms/reformulated gasoline) for further information on the RFG regulations and the Complex Model. In this report, any reference to the "Complex Model" will only refer to the exhaust portion.

Many studies have been conducted on the effects of fuel sulfur levels on vehicle exhaust emissions. In 1991, the US Auto/Oil Air Quality Improvement Research Program (AQIRP) published the first<sup>1</sup> of its six studies on the effects of sulfur. The first study concluded that reducing sulfur levels from 450 to 50 ppm reduced exhaust emissions in 1990 Tier 0 technology vehicles by 16, 13, and 9% respectively, for total hydrocarbon (THC), carbon monoxide (CO), and nitrogen oxide (NOx) emissions. A subsequent study was published by the US AQIRP in 1993.<sup>2</sup> This study confirmed the previous studies' results for emission benefits accrued from reducing sulfur from 450 to 50 ppm and also investigated effects of reducing sulfur down to 10 ppm. In 1995, the US AQIRP published a study<sup>3</sup> investigating sulfur's effect on emissions from vehicles certified to Tier 1 standards. In addition, EPA has conducted several studies to investigate sulfur's effect on emissions<sup>4,5,6</sup>. Recently, the American Petroleum Institute also sponsored a "Sulfur Reversibility" study<sup>7</sup> which examines sulfur's effect on exhaust emissions from newer vehicles. All data sources used in this analysis are described below in more detail in the "Data Sources" section.

Based on much of this data, EPA proposes to include an adjustment for in-use gasoline sulfur levels in the next version of its highway motor vehicle emission factors model, MOBILE6. Consistent with the new start/running methodology<sup>11</sup> being implemented in MOBILE6, this report will present separate estimates for the impacts of gasoline sulfur levels on running exhaust emissions and start emissions. MOBILE6 will use these start and running emission rates to calculate composite effects when necessary. However, to facilitate comparisons to results from previous studies and other existing emission models, estimates have been developed for FTP/composite (the composite emissions calculated from appropriate weighting of bag data) emissions directly from the data. FTP/composite emissions will be identified by "FTP emissions" in the remainder of this report. It should be noted that all FTP emissions correlations shown and discussed in this paper are for illustrative purposes only; sulfur correction factors in MOBILE6 will be solely based on the correlations developed for start and running emissions.

The structure of this report is as follows:

- Brief overview of EPA's previous sulfur adjustment proposal made at 10/1/97 MOBILE6 workshop
- Summary of major comments received on the proposal made at 10/1/97 workshop
- EPA's proposed final methodology for MOBILE6
  - Data sources
- Analysis of sulfur data
  - Definition of emitter classes
  - Data sources

- Regression methodology and mathematical fits
- Start, running, and FTP emissions
- Analysis of Tier 0 normal emitters
- Analysis of Tier 1 normal emitters
- Analysis of LEV and ULEV normal emitters
- Analysis of high emitters
- Valid sulfur range
- Summary

.

### EPA Preliminary Proposal for MOBLE6 on 10/1/97

As a first-cut approach to model the impacts of fuel sulfur content on exhaust emissions, EPA first segregated all available vehicle data on the effects of sulfur on exhaust emissions (mostly Auto/Oil and EPA testing data) into normal and high emitter categories. High emitters were defined, as they were in the Complex Model, as vehicles emitting more than two times the particular vehicle's HC standard on a base fuel (0.82 grams/mile for Tier 0 vehicles). Vehicles were not grouped by fuel injection technology as the type of fuel injection was shown not to heavily effect sulfur's impact on emissions. For each data set, an average gram/mile value was calculated at each individual sulfur level. Then, a nonlinear curve of the following form was fit through the resulting averages:

Emissions =  $A^* \ln(Sulfur) + B$ 

This fit was used for all vehicle technologies, emitter classifications, emission categories, and pollutants. In this initial analysis for the 10/1/97 MOBILE6 workshop, the effects of sulfur on start emissions were found to be small in magnitude and statistically insignificant in most cases when compared to FTP emissions and running emissions effects. So, the effect of sulfur on start emissions was assumed to be zero in all cases. The reader is referred to the 10/1/97 workshop presentation materials and handouts for the exact correlations developed based on the relationship between sulfur and exhaust emissions shown above. Table 2 below illustrates the effects calculated from the correlations developed using the above equation:

Emis- sions Mode	Vehicle Tech	Percent Reduction in HC Emissions when Sulfur (in ppmW) Changed From:		Percent Reduction in NOx Emissions when Sulfur (in ppmW) Changed From:		Percent Reduction in CO Emissions when Sulfur (in ppmW) Changed From:				
		700-> 400	400-> 200	200-> 50	700–> 400	400-> 200	200-> 50	700-> 400	400-> 200	200-> 50
FTP	Tier 0	4.8	6.0	12.8	1.64	2.08	4.20	5.28	6.92	14.8
	Tier 1	2.8	3.4	7.1	1.87	2.40	4.80	7.50	5.23	11.1

 Table 2

 Sulfur Reductions Based on Correlations Presented at 10/1/97 MOBILE6 Workshop

	RFG Model*	14.0	9.9	7.5	2.90	5.70	7.40	14.4	9.60	7.26
running	Tier 0	8.6	11.7	26.3	2.66	3.38	7.00	7.80	10.5	23.3
	Tier 1	10.1	13.4	32.5	1.84	2.30	4.71	7.20	9.72	21.4
				Н	igh Emitter	ſS				
FTP	Tier 0	0.55	0.72	1.43	0.45	0.55	1.10	0.85	1.10	2.20
	RFG Model*	-1.60	-1.00	-0.80	7.00	4.80	3.60	11.8	6.90	6.10
running	Tier 0	4.00	5.04	10.8	2.91	3.70	7.66	5.37	6.97	15.2

\* "RFG Model" refers to EPA's Complex Model for certifying reformulated gasolines. The Complex Model applies strictly only to "1990 technology" vehicles. The numbers in the "RFG model" rows are for comparison purposes only.

After the workshop, EPA received comments indicating that the methodology used to compute the correlations and obtain the results shown in Table 1 may not be the most accurate way to model sulfur's effect on emissions for this set of data. The following concerns were identified:

- modeling sulfur impacts as a non-linear effect for all pollutants may not be appropriate in all cases;
- a simpler approach should be used for modeling higher emitters since the data available is so sparse and comes from different test programs;
- statistical techniques that adjust for the different fleets and base fuels used in the testing programs must be employed;
- the definition of a high emitter should be re-examined (it is not clear that the Complex Model definition of 0.82 g/mi HC is appropriate for MOBILE6);
- an approach should be developed that allows sulfur effects to be estimated for both conventional gasoline and reformulated gasoline (RFG) areas.

Based on these comments, and on additional test data from Tier 1, LEV, and ULEV vehicles that has become available since the workshop, EPA now proposes a revised methodology to estimate sulfur's effect on exhaust emissions for gasoline-powered vehicles.

### EPA's Final Proposed Methodology for MOBILE6

### **Data Sources**

<u>Auto/Oil Phase I Sulfur Study</u><sup>1</sup>–In this portion of this extensive testing program, ten 1989 model year light-duty gasoline vehicles (representing a subset of the "Current" fleet (Tier 0 vehicles) tested in all the other Auto/Oil studies) were tested using two fuels with sulfur levels of 466 and 49 ppm (other fuel parameters were held constant). The results of that testing indicated that overall HC, CO, and NOx emissions were reduced by approximately 16%, 13% and 9%, respectively, when fuel sulfur content was reduced from 466 to 49 ppm.

<u>Auto/Oil Phase II Sulfur Study</u><sup>2</sup>–This portion of the testing expanded on the Phase I study by testing the same "Current" fleet vehicles over a wider range of sulfur levels with more intermediate points. This was done to determine non-linear trends in the data. Two fuel sets were used. The first, termed "Part I", was a five-fuel set ranging from a nominal sulfur level of 450 ppm down to 50 ppm in increments of 100 ppm. The second, termed "Part II", was a three-fuel set having sulfur levels of 50 ppm to 10 ppm in increments of 20 ppm. This study confirmed the results of the Phase I study and further found that reducing fuel sulfur from 50 ppm to 10 ppm, resulted in a reduction in HC of 6% and CO of 10%; there was no statistically significant effect on NOx emissions in this range.

<u>T50/T90/Sulfur Study</u><sup>3</sup>–Testing in this part of the Auto/Oil program was designed to investigate possible non linear impacts of the fuel distillation parameter  $T_{90}$ , interactive impacts of fuel distillation parameters  $T_{50}$  and  $T_{90}$ , and sulfur on emission from light-duty vehicles. Three vehicle fleets were tested: the Current fleet assessed in the Phase I and Phase II Studies (10 vehicles), a Federal Tier 1 fleet (consisting of six vehicles), and an Advanced Technology fleet (six production type LEV and ULEV vehicles). Only the Current and Tier 1 fleets were tested to investigate the impact of fuel sulfur on exhaust emissions: a low  $T_{90}$  set and a high  $T_{90}$  set with approximate sulfur levels of 33 and 317 ppm.

<u>API Extension Fuel Set<sup>8</sup></u>–In this program, the 10-vehicle "Current" fleet from the Auto/Oil program was tested at sulfur levels of 450 and 900 ppm to investigate the impact of the higher levels of fuel sulfur observed in U.S. gasoline. Results from this program showed very modest emission reductions as a result of reducing sulfur from 900 to 450 ppm (5% HC, 2% CO, and 3% NOx).

<u>EPA RFG Phase I Study</u><sup>4</sup>–Phase I was an initial investigation of the impacts of oxygenates, volatility, distillation properties, and sulfur on emissions. Vehicles included in this program represented 1990 model year or equivalent technology(Tier 0 vehicles). Two fuels examined in this program had differing sulfur levels (112 ppm and 371 ppm) with other fuel parameters at approximately constant levels. Results indicated that decreasing sulfur from 371 ppm to 112 ppm caused an approximate 5% reduction in HC emissions, a 7% reduction in NOx emissions, and a 9% reduction in CO emissions in the fleet tested.

<u>EPA RFG Phase II Study</u><sup>5</sup>–Phase II was a continuance of Phase I investigating further the effects of oxygen content, oxygenate type, volatility, sulfur, olefins, and distillation parameters. Relevant testing included fuels with sulfur levels of 59 and 327 ppm. Again, vehicles with 1990 model year or equivalent technology were tested. For the fleet tested, the results indicated that a reduction in sulfur from 327 to 59 ppm caused an approximate 7% reduction in HC, a 5% reduction in NOx emissions, and a 8% reduction in CO emissions.

<u>API "Reversibility" Study</u><sup>7</sup>- API tested a series of vehicles in response to the issue of sulfur reversibility in LEV and advanced technology vehicles. Sulfur has an almost immediate effect

on catalyst performance, with the sulfur level of the fuel primarily impacting the speed with which the catalyst is affected. One tankful of fuel containing high levels of sulfur will inhibit catalyst performance to essentially the same degree as several tankfuls of fuel with somewhat lower sulfur content. However, the return of catalyst performance upon refueling on low sulfur fuel is not as prompt with the higher sulfur fuel. Therefore, the potential "reversibility" of the sulfur effect could have substantial consequences for the design of a commercial sulfur control program. That being the case, API undertook this study to begin to investigate this phenomena. When this EPA report was being drafted, only very few vehicles had finished testing. Only one of the vehicles tested that had accumulated 100K mileage (Ford Taurus–VIN #). This vehicle was used in this analysis as part of the LEV emissions data set (all of which had approximately 100K mileage). The other vehicles in this test program were not included in the analysis either because: 1) they did not have the 100K mileage accumulation or, 2) the testing was not completed in the time frame during which the analysis for this report was completed. See discussion below on why only vehicles with 100K mileage were thought to me most appropriate for the purposes of this EPA report.

<u>CRC Sulfur/LEV Study</u><sup>9</sup>– This testing involved 6 LDV models certified for sale in California as LEVs in 1997. Two vehicles from each model type were tested on 7 fuels. Two fuel sets were investigated: one fuel set was a California RFG with two sulfur levels (nominally 40 ppm and 150 ppm); the other set of five fuels consisted of a base, conventional fuel with five different sulfur levels (nominally 40, 100, 150, 330, and 600 ppm). The same base gasoline was used for all five of these fuels and the sulfur levels were varied by adding representative sulfur-containing hydrocarbons. The vehicles were first tested in an "as-received" condition (average vehicle mileage of 10,000 miles) and with the catalysts bench-aged to simulate 100,000 miles of operation (although the oxygen sensors were original, low mileage sensors). The 10,000 mile emissions data will hereafter be referred to as the "10K data" and the 100,000 data will be referred to as the "100K data." The conclusions from this study included:

- For the 10,000-mile catalysts, reducing sulfur from 600 to 40 ppm resulted in a fleet emission FTP composite emission reduction in NMHC of 46%, in NOx of 63%, and in CO of 57%.
- For the aged 100,000-mile catalysts, reducing sulfur from 600 to 40 ppm resulted in a fleet emission FTP composite emission reduction in NMHC of 32%, in NOx of 61%, and in CO of 46%.
- The fleet response to fuel sulfur changes was found to be linear for the 10,000-mile catalysts and nonlinear for the 100,000-mile catalysts. With the aged catalysts, the effect of sulfur was more pronounced at lower sulfur levels.

In this EPA analysis, only the 100K data was used (since the other major LEV/ULEV testing program only tested vehicles with aged components to simulate 100,00 miles of driving–see the next section below). Emissions data from both fuel sets (conventional and RFG gasoline) were used in this analysis.

AAMA/AIAM Sulfur/LEV Study<sup>10</sup>-This study tested 21 vehicles, each of different design: 9

LEV LDVs, 1 LEV LDT1, 7 LEV LDT2s, and 4 ULEV LDVs. Some of the vehicle designs have been certified for sale in California, while others were designs which were deemed ready for certification and production. The vehicles were equipped with emission control components that were aged to mimic 100,000 miles of on-road driving. The base fuel used in the program was a California RFG with a nominal sulfur level of 40 ppm. The base fuel was then doped with sulfur compounds to obtain nominal sulfur levels of 100, 150, 330, and 600 ppm. Based on the 21-vehicle fleet, AAMA/AIAM reached the following conclusions:

- The emissions benefits of low-emission vehicle hardware are diminished as fuel sulfur level is increased above 40 ppm;
- The LEVs and ULEVs tested in this program showed a larger detrimental effect from fuel sulfur increases than the Tier 0 or Tier 1 vehicles tested in the Auto/Oil program; and
- The emissions response of LEVs and ULEVs to fuel sulfur is non-linear for all pollutants and is more pronounced at lower sulfur levels.

<u>Valid Sulfur Range</u>--The range of sulfur data available for this analysis varied from 10 ppm to 900 ppm. Table 3 summarizes the range of actual data available to estimate sulfur's effect on emissions by vehicle category:

Vehicle Technology/Type	Studies Available	Approximate Sulfur <sup>*</sup> Range for which Data is Available and Over which Regressions were Based
Tier 0/Normals/LDVs	Auto/Oil, EPA RFG, and API Extension-Set Studies	10–>900 ppm
Tier 1/Normals/LDVs	Auto/Oil T50/T90 Study	30–>350 ppm
LEV/Normals/LDVs	AAMA/AIAM , CRC, and API Reversibility Studies	30–>600 ppm
LEV/Normals/Trucks	AAMA/AIAM Study	30–>600 ppm
High Emitters (Data Available only for Tier 0 Vehicles)	EPA RFG Studies	40–>450 ppm

 Table 3

 Range of Available Sulfur Data by Vehicle Technology and Type

\* All sulfur values in the databases are "actual" sulfur values (as opposed to "nominal" values)

While the regressions were based on all the data, the valid range for MOBILE6 will be limited to 30 ppm on the low end and 600 ppm on the high end. The main reasoning for these limits is that LEV emissions data is only available over that range. Because LEV emissions are most sensitive to sulfur fluctuations, it was thought that extrapolations would be both speculative and possibly very inaccurate, especially below 30 ppm. Thus, in MOBILE6, sulfur's effect on emissions will be limited to a range of 30 ppm on the low end and 600 ppm on the high end. For consistency within MOBILE6 and for ease of use, this valid range will apply to all vehicle

technologies and emitter classifications.

### Analysis of Sulfur Data

### **Definition of Emitter Classes**

Several comments since the October 1, 1997 MOBILE6 workshop have indicated that sulfur's effect on emissions is a strong function of emission levels of individual vehicles and that the Complex Model definitions of emitter classes are too broad and are based on hydrocarbon emissions only. The comments further suggested that predictive equations based on normal emitters with relatively low emissions (e.g., vehicles in the Auto/Oil program) may not be directly applicable to the entire fleet of vehicles with HC emissions below the Complex model normal-emitter definition of  $\leq 0.82$  grams/mile HC. Some of the suggestions further indicated that a "moderate emitter" category be established<sup>12</sup>. While this type of approach has merit in estimating the effect of sulfur control on emissions, MOBILE6 is structured with only two emitter classes, normals and highs due to lack of data. Thus, for this work, emitter categories are defined in the following manner and are slightly different than the original proposal made at the 10/1/97 workshop:

### Table 4Emitter Categories

Normal	≤ Two times the emission standard for NOx, and HC, and ≤ Three times the emissions standard for CO
Highs	> Two times the emission standard for either NOx, or HC, or > Three times the emission standard for CO

Table 5 below shows the number of vehicles in each category that are normal and high emitters according to the definition in Table 4. Note that there are no Tier 1 or LEV high emitters (as defined in Table 4) in the database.

Table 5
Distribution of Number of Vehicles in Each of the Emitter Categories
Defined in Table 3 for Studies Used in this Analysis

Study	Number of Normal Emitters	Number of High Emitters
All Auto/Oil (all Tier 0 Vehicles)	10	0
EPA RFG Phase I (all Tier 0 Vehicles)	20	19
EPA RFG Phase II (all Tier 0 Vehicles)	24	15
Tier 1 T50/T90 Study (all Tier 1 Vehicles)	б	0
CRC Sulfur/LEV Study (LEV and ULEV Vehicles)	12	0
AAMA/AIAM Sulfur/LEV Study (LEV and ULEV Vehicles and Trucks)	21	0
TOTALS:	93	34

#### **Regression Methodology and Mathematical Fits**

Unless otherwise specified, all data sets were analyzed using the following regression methodology. Individual fuel/vehicle data points were analyzed using a regression procedure in SAS termed "ABSORB." Please consult the SAS manual for details on this procedure. Dummy variables were used to absorb the vehicles' effect on emissions thereby allowing the fuel sulfur effect to be isolated and better approximated. This approach is rather similar to the approach used in the development of the reformulated gasoline Complex model in which a "dummy" variable was created for each vehicle in the data set. Repeat tests on vehicles (and for the same vehicle(s) used in different testing programs) at a given sulfur level were averaged to represent one data point. Emissions were regressed against raw sulfur values (all sulfur values in this report are in ppmW).

In all cases, two different mathematical fits were used to represent the emissions vs. sulfur data: a log-linear fit {ln(emissions(in grams/mile)) = (Regression Coefficient) \* S (in ppm) + Constant}, and a log-log fit {ln (emissions(in grams/mile) = (Regression Coefficient) \* ln (Sulfur (in ppm)) + Constant}. The final decision on which fit to use in the different sulfur regimes were based on accuracy of fit, previous knowledge of how sulfur affects emissions in the regime being considered, quantity of data available, and other published work. Some of the comments (resulting from the methodology proposed at the workshop on 10/1/97) suggested use of a polynomial (quadratic) fit seemed to represent the emissions data. However, quadratic fits and the non-linear logarithmic fits shown above yielded nearly the same level of accuracy and fit, thus polynomial regressions were not included in the final analysis. The correlations developed

in this analysis relating sulfur to emissions for use in MOBILE6 will be used only to estimate percent changes in emissions when changing sulfur from one level to another. Whenever a tabular entry in this report indicates "Ln-Ln" fit, it refers to the following relationship:

ln(Emissions (g/mile)) = [(Regression Coefficient) \* ln (S (in ppm))]+ C

Whenever an entry indicates a "Ln-Linear" fit, the corresponding mathematical relationship is:

ln(Emissions (g/mile)) = [(Regression Coefficient) \*S (in ppm)]+ D

Note that C and D in the above equations are constants but are never used in the calculations. As discussed previously, all regressions in this report can only be used for comparing emission effects (i.e., percent change in emissions resulting from sulfur variation) and not for estimating absolute or relative g/mile numbers.

### Start, Running, and FTP-Composite Emissions

Start and running emissions were calculated from bag data using the methodology outlined in the MOBILE6 EPA report entitled "The Determination of Hot Running and Start Emissions from FTP Bag Emissions." It is report number M6.STE.002 and can be found on the MOBILE6 web site<sup>11</sup>. Though this report used only Tier 0 vehicle data to generate the bag-to-emissions mode correlations, the correlations were used for Tier 0, Tier 1, and LEV vehicles and trucks (for both normal and high emitters) in this analysis. For regression purposes, FTP-composite emissions were used as reported in the individual databases.

In most cases, the effect of sulfur on start emissions was statistically insignificant; however, the magnitude of the effect, especially for NOx emissions, was similar to the sulfur effect for running emissions. Since MOBILE6 will use start and running emissions to recalculate FTP emissions whenever necessary, it is very important that these start effects be included. Thus, regressions for start emissions will be developed and used for all vehicle technologies and pollutants. It should be noted that, in a few cases, the sulfur effect on start emissions is negative. While this is counterintuitive, it is supported by the data and assures that the composite emissions are not too high.

### Analysis of Tier 0 Normal Emitters

The sulfur impacts for normal-emitting Tier 0 vehicles will be based on analysis of the entire Auto/Oil database, the API extension fuel set, and the EPA Phase I and Phase II RFG data sets. The "ABSORB" procedure was applied to the Tier 0 data and regressed using the two non-linear schemes discussed above. It was found that the log-log fit was consistently better than the log-linear fit. The resulting correlations are shown below in Table 6 and the emission effects resulting from these correlations are shown in Table 7:

Pollutant	Emissions Mode	Type of Regression Fit	Regression Coefficient	R <sup>2</sup>
НС	Composite	Ln-Ln	0.06126	0.963
NMHC	Composite	Ln-Ln	0.05502	0.959
СО	Composite	Ln-Ln	0.07596	0.950
NOx	Composite	Ln-Ln	0.03077	0.939
НС	Running	Ln-Ln	0.15262	0.947
NMHC	Running	Ln-Ln	0.15187	0.918
СО	Running	Ln-Ln	0.19086	0.886
NOx	Running	Ln-Ln	0.02083	0.944
НС	Start	Ln-Ln	0.0027436	0.959
NMHC	Start	Ln-Ln	0.0037181	0.961
СО	Start	Ln-Ln	-0.01792	0.860
NOx	Start	Ln-Ln	0.04772	0.862

Regression Analysis for Tier 0 Normal Emitting Vehicles

Table 7Emission Effects from Varying Sulfur for Tier 0 Normal Emitting Vehicles

Pollutant	Emissions Mode	% Increase in Emissions when Sulfur is Increased from 30 ppm to:				
		75	150	330	600	
НС	Composite	5.77	10.4	15.8	20.1	
NMHC	Composite	5.17	9.26	14.1	17.9	
СО	Composite	7.21	13.0	20.0	25.6	
NOx	Composite	2.86	5.08	7.66	9.66	
НС	Running	15.0	27.8	44.2	58.0	
NMHC	Running	14.9	27.7	43.9	57.6	
СО	Running	19.1	36.0	58.0	77.1	
NOx	Running	1.93	3.41	5.12	6.44	
НС	Start	0.25	0.44	0.66	0.83	
NMHC	Start	0.34	0.60	0.90	1.12	

СО	Start	-1.63	-2.84	-4.21	-5.23
NOx	Start	4.47	7.98	12.1	15.4

The continuum of composite emission effects from the regression equations in Table 6 are shown in graphical format in Figure 1 in Appendix A. The Tier 0 analysis summarized in Tables 6 and 7 will apply to all normal emitters of Tier 0 or earlier (pre-Tier 0) categorization (all vehicles equipped with a catalyst) since very little data is available to support an individual evaluation of sulfur's effect on pre-Tier 0 vehicles. Pre-catalyst vehicles cannot be considered because sulfur will have no direct effect on exhaust emissions from those vehicles.

As a comparison, Table 8 shows estimated emission effects of reducing sulfur from 450–>50 ppm using the regressions listed in Table 6 for Tier 0 normal emitters and the effects computed from the Complex Model<sup>12</sup> for normal emitters. The results are similar for CO but the HC and (especially the) NOx effects estimated in this EPA analysis are smaller when compared to the NOx and HC effects predicted by the Complex Model. This is most likely due to inclusion of the T50/T90 heavy-hydrocarbon Auto/Oil data set in this analysis. The T50/T90 heavy-hydrocarbon Auto/Oil data set in the Complex Model was constructed. Inspection of the T50/T90 heavy-hydrocarbon data shows muted somewhat muted HC effects and much lower NOx effects for sulfur variations. Thus, the overall HC and NOx effects of reducing sulfur are much lower in this analysis than that estimated by the Complex Model.

Table 8Comparison of Composite Emission Effects for Normal EmittingTier 0 vehicles estimated from this Analysis to those Estimated from the ComplexModel when Sulfur is Reduced from 450 to 50 ppm

Approach Percent Reduction in		Percent Reduction in NOx	Percent Reduction in CO*
This EPA Analysis	13.0	6.6	15.4
Complex Model*	19.0	13.6	18.5

\* CO emissions were not part of the original RFG Complex Model. The CO model estimates are based on the CO model developed separately (using the same statistical techniques used to construct the RFG Complex Model) from the RFG rulemaking and discussed in SAE paper 961214<sup>13</sup>.

### Analysis of Tier 1 Normal Emitters

Only one set of data<sup>3</sup> has examined the effects of sulfur on emissions from certified Tier 1 vehicles. Two sulfur data points were tested in this analysis (~ 30 ppm and ~ 330 ppm) at high and low levels of T90. Because only two sulfur data points were available, the log-linear version of the fits were chosen to represent the data. Semi-log regressions were run using the procedures outlined earlier and the regression coefficients and effects obtained are shown respectively in Tables 9 and 10. It is interesting to note from comparing Tables 7 and 10 that Tier 1 emission benefits (in percentage reduction space) from reducing sulfur are generally larger than Tier 0 for CO and HC and about the same for NOx.

Pollutant	Emissions Mode	Type of Regression Fit	Regression Coefficient	R <sup>2</sup>
НС	Composite	Ln-Linear	8.053E-4	0.765
NMHC	Composite	Ln-Linear	7.223E-4	0.748
СО	Composite	Ln-Linear	6.295E-4	0.907
NOx	Composite	Ln-Linear	3.181E-4	0.903
НС	Running	Ln-Linear	2.457E-3	0.818
NMHC	Running	Ln-Linear	2.897E-3	0.785
СО	Running	Ln-Linear	1.746E-3	0.911
NOx	Running	Ln-Linear	6.337E-4	0.853
НС	Start	Ln-Linear	9.516E-5	0.941
NMHC	Start	Ln-Linear	9.172E-5	0.936
СО	Start	Ln-Linear	-2.338E-4	0.820
NOx	Start	Ln-Linear	8.023E-4	0.692

Table 9Regression Analysis for Tier 1 Normal Emitting Vehicles

Table 10Emission Effects from Varying Sulfur for Tier 1 Normal Emitting Vehicles

Pollutant	Emissions Mode	% Increase in Emissions when Sulfur is Increased from 30 ppm to:			m 30 ppm to:
		75	150	330	$600^{*}$
НС	Composite	3.69	10.1	27.3	34.8
NMHC	Composite	3.30	9.05	24.2	30.7
СО	Composite	2.87	7.85	20.8	26.6
NOx	Composite	1.44	3.89	10.0	12.6
НС	Running	11.7	34.3	109.0	143.0
NMHC	Running	13.9	41.6	138.5	181.7
СО	Running	8.17	23.3	68.8	91.4
NOx	Running	2.90	7.90	20.9	26.3
НС	Start	0.43	1.15	2.90	3.65
NMHC	Start	0.41	1.11	2.79	3.47
СО	Start	-1.05	-2.77	-6.77	-8.41

NOx Start 3.68 10.1 27.2 34.6
-------------------------------

\* Please see explanation below about how the effects at 600 ppm were estimated.

Since the available Tier 1 data only extends to 330 ppmW sulfur, it would be inaccurate to use the semi-logarithmic regression equations listed in Table 6 all the way out to 600 ppm, which will be the valid high end of the sulfur range in MOBILE6. Instead, the regressions listed in Table 6 will be applicable only for sulfur values between 30 and 330 ppm; and, for any sulfur level above 330 ppm, the following equation will be used to estimate Tier 1 effects for a given pollutant and a given emissions mode:

Tier 1 Effect at any sulfur level "X" above 330 ppm =  $[(TierO_X)/(TierO_{330})]^*(TierI_{330})$ 

where,

 $TierO_X = Tier 0$  percent effect at level X using a 30 ppm as baseline (can be estimated from Table 4)

 $\text{Tier}O_{330} = \text{Tier 0}$  percent effect at 330 ppm using 30 ppm as baseline (available in Table 5)

Tier $1_{330}$  = Tier 1 percent effect at 330 ppm using 30 ppm as baseline (available in Table 7)

For example, the Tier 1 effect of increasing sulfur to 600 ppm from 30 ppmw on running HC emissions according to the above equation would be: (58.0%/44.2%)\*109.0% = 143.0%. The values 58.0% and 44.2% were obtained from Table 7 and 109.0% was obtained from Table 10. The continuum of composite emission effects from the regression equations in Table 9 and the approach described here are shown in graphical format in Figure 2 in Appendix A.

### Analysis of LEV and ULEV Normal Emitters

As discussed in the "Data Sources" section above, 100K data from the recently completed AAMA/AIAM and CRC testing programs will be used to develop sulfur impacts for LEVs and ULEVs. Emissions from both the conventional and RFG set of fuels in the CRC testing program were used in this analysis. The CRC 10K data was omitted because: (1) it was felt that is was not representative of true in-use conditions and, (2) there was no accurate way to combine the 10K with the 100K data common to both testing programs. Because the AAMA/AIAM testing program contained data on trucks, the impacts will be stratified by light-duty vehicles (passenger cars and light trucks) and LDT2 trucks. This combination of passenger cars and LDT1 trucks will be referred to as Light-Duty Vehicles (LDVs) hereafter. Emissions data from passenger cars and LDT1 trucks were combined due to the technical similarities in their catalyst systems that result in similar emission responses. Past EPA analyses<sup>14</sup> have also traditionally combined these two categories of vehicles. As suggested by the authors of the CRC and AAMA/AIAM reports, log-log fits were found to be better for most of the pollutants and emission modes. Tables 11 and 12 show the regression statistics and the emission effects of changing sulfur for LDVs,

respectively:

Pollutant	Emissions Mode	Type of Regression Fit	Regression Coefficient	$\mathbb{R}^2$
НС	Composite	Ln-Ln	0.16845	0.947
NMHC	Composite	Ln-Ln	0.13992	0.944
СО	Composite	Ln-Ln	0.23746	0.917
NOx	Composite	Ln-Ln	0.35392	0.889
НС	Running	Ln-Ln	0.42809	0.879
NMHC	Running	Ln-Ln	0.49561	0.859
СО	Running	Ln-Ln	0.48626	0.915
NOx	Running	Ln-Ln	0.57085	0.904
НС	Start	Ln-Ln	0.05067	0.958
NMHC	Start	Ln-Ln	0.05552	0.954
СО	Start	Ln-Ln	0.04847	0.941
NOx	Start	Ln-Ln	0.11240	0.723

 Table 11

 Regression Analysis for LEV and ULEV Normal Emitting LDVs

Pollutant	Emissions Mode	% Increase in Emissions when Sulfur is Increased from 30 ppm to:			m 30 ppm to:
		75	150	330	600
НС	Composite	16.7	31.1	49.8	65.6
NMHC	Composite	13.7	25.3	39.9	52.1
СО	Composite	24.3	46.5	76.7	103.6
NOx	Composite	38.3	76.8	133.6	188.7
НС	Running	48.0	99.2	179.1	260.5
NMHC	Running	57.5	122.0	228.2	341.4
СО	Running	56.1	118.7	220.9	329.2
NOx	Running	68.7	150.6	293.1	453.0
HC	Start	4.75	8.50	12.9	16.4
NMHC	Start	5.22	9.35	14.2	18.1
СО	Start	4.54	8.11	12.3	15.6
NOx	Start	10.8	19.8	30.9	40.0

 Table 12

 Emission Effects from Varying Sulfur for LEV & ULEV Normal Emitting LDVs

Note that Table 12 shows ULEV and LEV normal emitting vehicles to have a much stronger emissions response to sulfur changes than did Tier 1 vehicles (Table 10) or Tier 0 vehicles (Table 7). The continuum of composite emission effects upon changing sulfur on LEV LDVs are shown in Figure 3 in Appendix A.

While the Tier 0 and Tier 1 analysis is based only on LDV data, truck data on the effect of sulfur on emissions were also available in the AAMA/AIAM study. A total of 7 LDT2 trucks were tested in the AAMA/AIAM program in addition to the testing conducted on LDVs. These data were analyzed in the exact same manner as described above using "ABSORB" in SAS to arrive at the regression analysis and emission effects shown in Tables 13 and 14, respectively:

Pollutant	Emissions Mode	Type of Regression Fit	Regression Coefficient	R <sup>2</sup>
НС	Composite	Ln-Ln	0.12549	0.985
NMHC	Composite	Ln-Ln	0.08956	0.983
СО	Composite	Ln-Ln	0.15084	0.980
NOx	Composite	Ln-Ln	0.14625	0.951
НС	Running	Ln-Ln	0.31818	0.939
NMHC	Running	Ln-Ln	0.25326	0.960
СО	Running	Ln-Ln	0.38379	0.887
NOx	Running	Ln-Ln	0.29491	0.934
НС	Start	Ln-Ln	0.02551	0.990
NMHC	Start	Ln-Ln	0.02846	0.989
СО	Start	Ln-Ln	0.07030	0.968
NOx	Start	Ln-Ln	0.04130	0.901

 Table 13

 Regression Analysis for LEV and ULEV Normal Emitting LDT2 Trucks

 Table 14

 Emission Effects from Varying Sulfur for LEV & ULEV Normal Emitting LDT2 Trucks

Pollutant	Emissions Mode	% Increase in Emissions when Sulfur is Increased from 30 ppm to:			m 30 ppm to:
		75	150	330	600
НС	Composite	12.2	22.4	35.1	45.6
NMHC	Composite	8.55	15.5	24.0	30.8
СО	Composite	14.8	27.5	43.6	57.1
NOx	Composite	14.3	26.5	42.0	55.0
НС	Running	33.8	66.9	114.5	159.4
NMHC	Running	26.1	50.3	83.5	113.5
СО	Running	42.1	85.5	151.0	215.7
NOx	Running	31.0	60.7	102.8	141.9
НС	Start	2.36	4.19	6.31	7.94
NMHC	Start	2.64	4.68	7.05	8.89
СО	Start	6.65	12.0	18.4	23.4
NOx	Start	3.86	6.88	10.4	13.2

Note that the sensitivity of emissions to changes in sulfur is much lower for LEV trucks than for LEV LDVs. Figure 4 in Appendix A shows the emissions response to changes in sulfur for LEV trucks.

### Analysis of High Emitters

The emissions criteria for high emitters are listed in Table 3. Actual data on the effects of sulfur on emission from high emitters is available only for Tier 0 vehicles as indicated in Table 4. These data were used to determine regression coefficients for high emitters. A log-linear fit was used since the amount of high emitter data available was small and only two sulfur levels were tested in the EPA RFG programs. The regression coefficients for high emitters are shown in Table 15 and the corresponding emission effects are shown in Table 16.

Pollutant	Emissions Mode	Type of Regression Fit	Regression Coefficient	R <sup>2</sup>
НС	Composite	Ln-Linear	3.727E-5	0.997
NMHC	Composite	Ln-Linear	3.727E-5	0.997
СО	Composite	Ln-Linear	6.317E-6	0.997
NOx	Composite	Ln-Linear	3.046E-4	0.996
НС	Running	Ln-Linear	1.138E-4	0.996
NMHC	Running	Ln-Linear	9.614E-5	0.996
СО	Running	Ln-Linear	1.111E-4	0.993
NOx	Running	Ln-Linear	2.848E-4	0.998
НС	Start	Ln-Linear	-2.227E-4	0.985
NMHC	Start	Ln-Linear	-1.824E-4	0.989
СО	Start	Ln-Linear	-5.336E-4	0.962
NOx	Start	Ln-Linear	2.519E-4	0.889

 Table 15

 Regression Analysis for Tier 0 High Emitting Vehicles

Pollutant	Emissions Mode	% Increase i	% Increase in Emissions when Sulfur is Increased from 30 ppm to:		
		75	150	330	600
HC	Composite	0.17	0.45	1.12	2.15
NMHC	Composite	0.17	0.45	1.12	2.15
СО	Composite	0.03	0.08	0.19	0.37
NOx	Composite	1.39	3.72	9.57	19.0
HC	Running	0.51	1.37	3.47	6.70
NMHC	Running	0.43	1.16	2.93	5.63
СО	Running	0.50	1.34	3.39	6.54
NOx	Running	1.29	3.48	8.92	17.6
HC	Start	-1.00	-2.64	-6.46	-11.9
NMHC	Start	-0.82	-2.17	-5.32	-9.87
СО	Start	-2.37	-6.20	-14.8	-26.2
NOx	Start	1.14	3.07	7.85	15.4

Table 16Emission Effects from Varying Sulfur for High Emitting Tier 0 Vehicles

The effects in Table 16 are in good agreement with the Complex Model which showed that NOx effects were much more sensitive than HC effects to sulfur variation in Tier 0 high emitting vehicles<sup>14</sup>. As an example, the Complex Model indicates that the effect of reducing sulfur from 450 to 50 ppm on high emitting vehicles to be an approximate 10% decrease in NOx emissions. This EPA analysis shows the same effect to be approximately 11%. Table 17 is a comparison of the emission effects estimated in this EPA report to the Complex Model estimates for high emitters.

# Table 17Comparison of Composite Emission Effects for High EmittingTier 0 vehicles estimated from this Analysis to those Estimated from the ComplexModel when Sulfur is Reduced from 450 to 50 ppm

Tool	Percent Reduction in HC	Percent Reduction in CO*	Percent Reduction in NOx
This EPA Analysis	1.5	0.3	11.2
Complex Model	-5.00	1.4	10.0

\* The same footnote as in Table 8 applies here

Note that in some cases, in Table 16, reducing sulfur may actually increase start emissions. Despite these counterintuitive effects, MOBILE6 will apply the start effects exactly as reported in Tables 15 and 16. This is because MOBILE6 will combine running and start emissions to estimate composite emissions whenever necessary and any manual adjustments to start emissions

(such as "zeroing out" the counterintuitive effects) would result in skewing of the composite emission estimates made by MOBILE6.

The regression coefficients shown in Table 15 will be used for Tier 0 vehicles. However, no high emitter test data relating sulfur to emissions exists for any other category of vehicles. Thus, a simple algorithm is required to estimate the emission sensitivity to sulfur changes in vehicles certified to Tier 1 and cleaner standards. The following methodology will be used to estimate high emitter effects for other-than-Tier 0 vehicles. Analysis of the Complex Model<sup>15</sup> indicates that the NOx sensitivity of high emitters is approximately 60% of the sensitivity for normal emitters in percent-emissions-change space. Thus, for vehicles and trucks certified to Tier 1 and cleaner standards (LEV, ULEV, Tier 2, etc.), this correction factor will be applied to estimate a NOx effect for high emitting vehicles. A high emitter in any given vehicle category is defined by the criteria listed in Table 3. For example, if the normal emitter NOx emissions effect of reducing sulfur from 150 to 50 ppm is 25% for Tier 1 (or LEV or ULEV) vehicles, then high emitters in this same category would get a NOx benefit of (0.6)\*(25%), or 15%.

The Complex Model does not show nearly as great or as consistent a CO or HC effect<sup>13,14</sup> and sensitivity to changes in sulfur from high emitting vehicles; thus, the high-emitter regression coefficients listed as-is for HC and CO in Table 15 will be used for all vehicle categories. Table 18 summarizes the high emitter effects to be used in MOBILE6:

Vehicle Category	Pollutant	High Emitter Effect
Tier 0–LDVs	НС	Use Appropriate Regression Coefficient listed in Table 15
Tier 0–LDVs	NMHC	Use Appropriate Regression Coefficient listed in Table 15
Tier 0–LDVs	СО	Use Appropriate Regression Coefficient listed in Table 15
Tier 0–LDVs	NOx	Use Appropriate Regression Coefficient listed in Table 15
Tier 1–LDVs	НС	Use HC Regression Coefficient listed in Table 15
Tier 1–LDVs	NMHC	Use NMHC Regression Coefficient listed in Table 15
Tier 1–LDVs	СО	Use CO Regression Coefficient listed in Table 15
Tier 1–LDVs	NOx	Use (0.60* Normal Emitter Tier 1 Effect (calculated from Table 9))
LEV & ULEV–LDVs	НС	Use HC Regression Coefficient listed in Table 15
LEV & ULEV–LDVs	NMHC	Use NMHC Regression Coefficient listed in Table 15
LEV & ULEV–LDVs	СО	Use CO Regression Coefficient listed in Table 15
LEV & ULEV–LDVs	NOx	Use (0.60* Normal Emitter LEV LDV Effect (calculated from Table 11))
LEV & ULEV–LDT2s	НС	Use HC Regression Coefficient listed in Table 15
LEV & ULEV–LDT2s	NMHC	Use NMHC Regression Coefficient listed in Table 15
LEV & ULEV–LDT2s	СО	Use CO Regression Coefficient listed in Table 15
LEV & ULEV LDT2s	NOx	Use (0.60* Normal Emitter LEV LDT2 Effect (calculated from Table 13))

Table 18Summary of High-Emitter Effects

<u>Summary</u>

Empirical relationships were developed for relating sulfur to exhaust emissions from Tier 0, Tier 1, and LEV vehicles based on available data. Separate correlations were obtained for light-duty vehicles and trucks wherever possible. Analysis was conducted on two separate emitter classifications, normal and high. The valid sulfur range for MOBILE6 was estimated to be  $30 \le$  sulfur in ppm $\le 600$ .

### **References**

- 1. Benson, J. D., et al., "Effects of Gasoline Sulfur Level on Mass Exhaust Emissions-Auto/Oil Air Quality Improvement Research Program, SAE Paper No. 912323, 1991.
- 2. Koehl, W. J., et al., "Effects of Gasoline Sulfur Level on Exhaust Mass and Speciated Emissions: The Question of Linearity–Auto/Oil Air Quality Improvement Research Program," SAE Paper No. 932727, 1993.
- 3. Rutherford, J. A., et al., "Effects of Gasoline Properties on Emissions of Current and Future Vehicles–T<sub>50</sub>, T<sub>90</sub>, and Sulfur Effects–Auto/Oil Air Quality Improvement Research Program," SAE Paper No. 952510, 1995.
- Mayotte, S. C., et al., "Reformulated Gasoline Effects on Exhaust Emissions: Phase I: Initial Investigation of Oxygenate, Volatility, Distillation and Sulfur Effects," SAE Paper No. 941973, 1994.
- 5. Mayotte, S. C., et al., "Reformulated Gasoline Effects on Exhaust Emissions: Phase II: Continued Investigation of the Effects of Fuel Oxygenate Content, Oxygenate Type, Volatility, Sulfur, Olefin and Distillation Parameters," SAE Paper No. 941974, 1995.
- 6. Korotney, D. J., et al., "Reformulated Gasoline Effects on Exhaust Emissions: Phase III: Investigation on the Effects of Sulfur, Olefins, Volatility, and Aromatics and the Interactions Between Olefins and Volatility or Sulfur," SAE Paper No. 950782, 1995.
- 7. Sulfur "Reversibility" Study on LEV-certified Vehicles. Private communication with David Lax of the American Petroleum Institute.
- 8. Sulfur "Extension" study conducted by American Petroleum Institute. Data Transmitted to EPA.
- 9. "Summary: CRC Sulfur/LEV Program," Coordinating Research Council Report, CEC Project No. E-42, December 22, 1997.
- 10. "AAMA/AIAM Study on the Effects of Fuel Sulfur on Low Emission Vehicle Criteria Pollutants," December 1997.
- 11. EPA Report Number M6-STE-002 "The Determination of Hot Running and Start Emissions from FTP Bag Emissions." Available on MOBILE6 web site.

- 12. EPA's Complex Model for certifying Reformulated Gasolines. Please consult the RFG rulemaking documents.
- 13. Rao. V., "Development of an Exhaust Carbon Monoxide Emissions Model" SAE Paper No. 961214, 1996.
- 14. EPA Final Regulatory Impact Analysis for Reformulated Gasoline, December 13, 1993.
- 15. Private communication with EPA's Rick Rykowski, National Expert, Engine Programs and Compliance Division, August 1998.

## **APPENDIX** A







