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Fuel Sulfur Effects on Exhaust Emissions

Recommendations for MOBILE6

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Introduction

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 varying fuel sulfur. 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 and light light-duty trucks (LDV) , 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.

Table 1
Light-Duty Truck Weight Definitions

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

Wherever possible, normal and high emitters are also addressed and analyzed separately. Diesel-powered and heavy-duty vehicles are not considered in this analysis as MOBILE6 is not set up to compute fuel sulfur effects for these vehicles.

The structure of this report is as follows:

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Response to Comments and Changes from Draft Report

A draft report on the proposed methodology for MOBILE6 sulfur effects was posted on the MOBILE6 web page for stakeholder comment in May 1999. Because much of this sulfur analysis was used in the Tier 2 rulemaking, stakeholder comments on the analysis were addressed as part of the Tier 2 regulation package. Readers are referred to the Tier 2 docket for detailed response to comments on the sulfur analysis detailed in this report.

Also, as part of MOBILE6's review process, this report (excluding the last section on **"**Revisions to Short-Term Effects and Inclusion of Long-Term and Irreversibility Effects") was sent our for independent, external peer review. No major comments were received on the methodologies and conclusions reached in the report.

This final report reflect the stakeholder and peer review comments, as well as additional research completed too late for incorporation in the draft report. This includes changes to take into account long-term sulfur effects and the "irreversibility" of some high sulfur effects. The new analysis was reviewed as part of the Tier 2 rulemaking process.

Technical 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 (completed as part of the Reformulated Gasoline Regulation in December 1994) is an empirical model designed to predict emissions as a function of fuel properties. The exhaust portion of the Complex Model is based 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. Also, the exhaust Complex Model only applies to "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 refer to the exhaust portion of the model only.

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 of a series of studies on the effects of sulfur.[1] 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.[2] This study confirmed the previous study's 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 investigating sulfur's effect on emissions from vehicles certified to Tier 1 standards.[3] In addition, EPA has conducted several studies to investigate sulfur's effect on emissions.[4,5,6] Recently, the American Petroleum Institute also sponsored a "Sulfur Reversibility" study[7] which examines sulfur's effect on exhaust emissions from newer vehicles. All data sources used in this analysis are described in more detail in the "Data Sources" section below.

Based on much of this data, EPA will include an adjustment for in-use gasoline sulfur levels in the newest version of its highway motor vehicle emission factors model, MOBILE6. Consistent with the new start/running methodology[11] 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 (Federal Test Procedure) /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.

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 did not greatly affect 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. (Add footnote) Table 2 below illustrates the effects calculated from the correlations developed using the above equation:

Table 2
Sulfur Reductions Based on Correlations Presented at 10/1/97 MOBILE6 Workshop

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
	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
High Emitters										
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 2 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 became available after the workshop, EPA revised the methodology to estimate sulfur's effect on exhaust emissions for gasoline-powered vehicles.

EPA's Final Methodology for MOBILE6

Data Sources

EPA's sulfur analysis relied on the following data sources:

Auto/Oil Phase I Sulfur Study[1]–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.

Auto/Oil Phase II Sulfur Study[2]–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.

T50/T90/Sulfur Study[3]–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 for their response to changes in sulfur levels. Two fuel sets tested in this program can be used 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.

API Extension Fuel Set[8]–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).

EPA RFG Phase I Study[4]–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.

EPA RFG Phase II Study[5]–Phase II was a continuation 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.

API "Reversibility" Study[7]- API tested a series of vehicles in response to the issue of sulfur reversibility in LEV and advanced technology vehicles. Sulfur "reversibility" refers to the ability of a vehicle to return to low emissions on low sulfur fuel after temporary use of high sulfur fuel. When this MOBILE6 analysis 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 at the time the analysis for this report was completed. See discussion below on why only vehicles with 100K mileage are thought to be most appropriate for the purposes of this EPA report.

CRC Sulfur/LEV Study[9]– 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 mile 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 change 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.

<u>AAMA/AIAM Sulfur/LEV Study</u>[10]–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:

Table 3
Range of Available Sulfur Data by Vehicle Technology and Type

Vehicle Standard/Emitter Type//Class	Studies Available	Approximate Sulfur* 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

* 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. For consistency within MOBILE6 and for ease of use, in MOBILE6 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[12]. 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. Thus, for the current sulfur analysis, emitter categories are defined in the following manner and are slightly different than the original proposal made at the October 1997 workshop:

Table 4
Emitter 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 4 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)	6	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 the SAS statistical software package called "ABSORB." The SAS manual provides 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 ("as-reported" values) 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 as shown below. The final decisions 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 on the methodology proposed at the October 1997 workshop suggested use of a polynomial (quadratic) fit 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. Whenever a tabular entry in this report indicates "Ln-Ln" fit, it refers to the following relationship:

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

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

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

Note that C and D in the above equations are constants but are never used in the calculations. The equations in this report are used only for comparing emission effects (i.e., percent change in emissions resulting from sulfur variation) and not for estimating absolute or relative g/mile numbers. Thus, the values of C and D are irrelevant.

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."[11]. 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, 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 are 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 SAS "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:

Table 6
Regression Analysis for Tier 0 Normal Emitting Vehicles

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

Table 7
Emission 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
HC	Composite	5.77	10.4	15.8	20.1
NMHC	Composite	5.17	9.26	14.1	17.9
CO	Composite	7.21	13.0	20.0	25.6
NOx	Composite	2.86	5.08	7.66	9.66
HC	Running	15.0	27.8	44.2	58.0
NMHC	Running	14.9	27.7	43.9	57.6
CO	Running	19.1	36.0	58.0	77.1
NOx	Running	1.93	3.41	5.12	6.44
HC	Start	0.25	0.44	0.66	0.83
NMHC	Start	0.34	0.60	0.90	1.12
CO	Start	-1.63	-2.84	-4.21	-5.23
NOx	Start	4.47	7.98	12.1	15.4

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 evaluation of sulfur's effect on pre-Tier 0 vehicles. Pre-catalyst vehicles are treated separately because sulfur will have no direct effect on exhaust emissions from those vehicles.

For 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[12] for normal emitters. The results are similar for CO but the HC and 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 the current analysis. The T50/T90 heavy-hydorcarbon Auto/Oil data was not available at the time the Complex Model was constructed. Inspection of the T50/T90 heavy-hydrocarbon data shows 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 those estimated by the Complex Model.

Table 8

Comparison of Composite Emission Effects for Normal Emitting Tier 0 vehicles estimated from this Analysis to those Estimated from the Complex Model when Sulfur is Reduced from 450 to 50 ppm

Approach	Percent Reduction in HC	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[13].

Analysis of Tier 1 Normal Emitters

Only one set of data[3] 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. Log-linear 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 that for Tier 1, percent change benefits from reducing sulfur are generally larger than the benefits for Tier 0 for CO and HC, and are about the same for NOx.

Table 9
Regression Analysis for Tier 1 Normal Emitting Vehicles

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

Table 10

Emission Effects from Varying Sulfur for Tier 1 Normal Emitting Vehicles

Pollutant	Emissions Mode	% Increase in Emissions when Sulfur is Increased from 30 ppm to:			
		75	150	330	600*
HC	Composite	3.69	10.1	27.3	34.8
NMHC	Composite	3.30	9.05	24.2	30.7
CO	Composite	2.87	7.85	20.8	26.6
NOx	Composite	1.44	3.89	10.0	12.6
HC	Running	11.7	34.3	109.0	143.0
NMHC	Running	13.9	41.6	138.5	181.7
CO	Running	8.17	23.3	68.8	91.4
NOx	Running	2.90	7.90	20.9	26.3
HC	Start	0.43	1.15	2.90	3.65
NMHC	Start	0.41	1.11	2.79	3.47
CO	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 log-linear 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 equations listed in Table 6 will be applicable only for sulfur values between 30 and 330 ppm; 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 (start vs. running) and emitter classification:

Tier 1 Effect at any sulfur level "X" above 330 ppm = $[(Tier0_X)/(Tier0_{330})]*(Tier1_{330})$

where,

$Tier0_X$ = Tier 0 percent emission change at level X using a 30 ppm as baseline (can be estimated from Table 6)

$Tier0_{330}$ = Tier 0 percent emission change at 330 ppm using 30 ppm as baseline (available in Table 7)

$Tier1_{330}$ = Tier 1 percent emission change at 330 ppm using 30 ppm as baseline (available in Table 10)

For example, according to the above equation, the Tier 1 effect of increasing sulfur to 600 ppmW from 30 ppmW on running HC emissions 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. A graph of the emission effects from the regression equations in Table 9.

Initial Analysis of LEV, ULEV, and Cleaner Normal Emitters

This section describes our initial analysis, as presented in our draft report. The estimated short-term effect of sulfur on LEV and ULEV emissions was revised in the time after the draft report was published, as described in the following section. EPA also revised the analysis of emission effects for the newest vehicles to account for long-term and irreversibility effects, as discussed later in this report.

As discussed in the "Data Sources" section above, 100K data from the recently completed AAMA/AIAM and CRC testing programs were 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 data with the 100K data common to both testing programs. Because the AAMA/AIAM testing program contained data on trucks, the impacts were stratified into light-duty vehicles (passenger cars and light trucks) and LDT2, LDT3, and LDT4 trucks. The 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[14] 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:

Table 11
Initial Regression Analysis for LEV and ULEV Normal Emitting LDVs

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

* Note, for the final equations used in MOBILE6, see Table 17

Table 12

<u>Initial Emission Effects from Varying Sulfur for LEV & ULEV Normal Emitting LDVs</u>

Pollutant	Emissions Mode	% Increase in Emissions when Sulfur is Increased from 30 ppm to:			
		75	150	330	600
HC	Composite	16.7	31.1	49.8	65.6
NMHC	Composite	13.7	25.3	39.9	52.1
CO	Composite	24.3	46.5	76.7	103.6
NOx	Composite	38.3	76.8	133.6	188.7
HC	Running	48.0	99.2	179.1	260.5
NMHC	Running	57.5	122.0	228.2	341.4
CO	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
CO	Start	4.54	8.11	12.3	15.6
NOx	Start	10.8	19.8	30.9	40.0

* Note, these are not the final effects used in MOBILE6.

Note that Table 12 shows ULEV and LEV normal emitting vehicles have a much stronger emissions response to sulfur changes than did Tier 1 vehicles (Table 10) or Tier 0 vehicles (Table 7).

While the Tier 0 and Tier 1 analysis is based only on LDV data, the AAMA/AIAM study also provided truck data. 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 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.

Table 13

Regression Analysis for LEV and ULEV Normal Emitting LDT2 Trucks

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

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:			
		75	150	330	600
HC	Composite	12.2	22.4	35.1	45.6
NMHC	Composite	8.55	15.5	24.0	30.8
CO	Composite	14.8	27.5	43.6	57.1
NOx	Composite	14.3	26.5	42.0	55.0
HC	Running	33.8	66.9	114.5	159.4
NMHC	Running	26.1	50.3	83.5	113.5
CO	Running	42.1	85.5	151.0	215.7
NOx	Running	31.0	60.7	102.8	141.9
HC	Start	2.36	4.19	6.31	7.94
NMHC	Start	2.64	4.68	7.05	8.89
CO	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.

Revisions to LEV and ULEV calculations

Since the draft report on sulfur was completed, several additional LEV-type light-duty vehicles were tested for sulfur sensitivity. Those that were completed in time for inclusion in this analysis (9/11/99) are listed below in Table 15. The emissions data from these 11 new vehicles and from the six CRC-10K vehicles were included in the LEV database (which previously consisted only of 100K data) and revised composite regression coefficients were estimated (using the exact same procedures used to develop regression coefficients for "short-term" effects) using SAS. The emissions data from these 17 vehicles were added to the existing LEV database and SAS was used to conduct regressions as before. The resultant composite emission regression coefficients are summarized (for comparison purposes the old regression coefficients are also listed) in Table 16.

Table 15
Additional LEV/ULEV vehicles tested for Sulfur Sensitivity

Make/Model	Test Program	Catalyst Aging (~ miles)	Only short-term exposure or short-term and long-term exposure data?
ALTIMA	API	100k	BOTH
TAURUS	API	4k	BOTH
ACCORD	API	4k	BOTH
AVALON	API	4k	BOTH
TOWN CAR	API	4k	Only Short-Term
TAURUS	CRC-1	10k	Only Short-Term
ESCORT	CRC-1	10k	Only Short-Term
HONDA	CRC-1	10k	Only Short-Term
NISSAN	CRC-1	10k	Only Short-Term
TOYOTA	CRC-1	10k	Only Short-Term
GEO	CRC-1	10k	Only Short-Term
ACCORD	EPA	50k	BOTH
CAVALIER	EPA	50k	BOTH
TAURUS	ATL	53k	Only Short-Term
WINDSTAR	ATL	43k	Only Short-Term
TAURUS	FORD	4k	Only Short-Term
EXPLORER	FORD	4k	Only Short-Term

Table 16
Revised Composite Regression Coefficients based on original and additional LEV data

Pollutant	Previous Regression Coefficient	Revised Regression Coefficient
HC	0.168	0.168
NMHC	0.140	0.160
CO	0.237	0.236
NOx	0.354	0.351

The composite regression coefficients listed in Column 3 of Table 16 are used as the MOBILE6 coefficients to determine sulfur's short-term emission effects on LEV and cleaner vehicles. Note that we were unable to get the bag data from the new testing programs to determine start and running coefficients directly from the new data. Instead, we revised the LEV running and start emission regression coefficients based on the existing LEV composite regression coefficients, as described in the next section..

Revision of LEV Running and Start Regression Coefficients

In general, start and running emissions and corrections to them are calculated using bag data and correlations between the bags and start and running emissions. However, the data that was used to develop these correlations, consisted entirely of Tier 0 emissions data. There is some question as to whether those correlations can be directly applied to LEV data. At this time, we feel the most appropriate approach for LEV and cleaner vehicles (and trucks) is to apply the composite regression coefficients to both running and start emissions.

The final regression coefficients to use for determining sulfur's short term impacts on LEV (and cleaner technology) emissions are summarized in Table 17. While unrevised, the LEV truck, Tier 0 (in Table 18), and Tier 1 (in Table 18) coefficients are also listed for completeness. The mathematical fits relating the regression coefficients to emissions for each set of vehicles remains as outlined in the draft report (i.e., as discussed in the sections preceeding this one).

Table 17
LEV Normal Emitters: Revised regression coefficients for the effects of sulfur on composite, start, and running. Emissions from LEV-and-cleaner vehicles & trucks

Pollutant	Light-Duty Vehicles			LDT2,3,4 Trucks		
	For Compos. Emissions	For Running Emissions	For Start Emissions	For Compos. Emissions	For Running Emissions	For Start Emissions
HC	0.168	0.168	0.168	0.125	0.125	0.125
NMHC	0.160	0.160	0.160	0.090	0.090	0.090
CO	0.236	0.236	0.236	0.151	0.151	0.151
NOx	0.351	0.351	0.351	0.146	0.146	0.146

Table 18
Tier 0 and Tier 1 Normal Emitters: Regression coefficients for the effects of sulfur on composite, start, and running. Emissions from Tier 0 and Tier 1 Vehicles

Pollutant	All Tier 0 Vehicles			All Tier 1 Vehicles		
	For Compos. Emissions	For Running Emissions	For Start Emissions	For Compos. Emissions	For Running Emissions	For Start Emissions
HC	0.0613	0.1526	0.0027	8.05e-4	2.46e-3	9.52e-5
NMHC	0.0550	0.1519	0.0037	7.22e-4	2.90e-3	9.17e-5
CO	0.0760	0.1909	-0.018	6.30e-4	1.75e-3	-2.34e-4
NOx	0.0308	0.0208	0.0477	3018e-4	6.34e-4	8.02e-4

Analysis of High Emitters

The emissions criteria for high emitters are listed in Table 4. Actual data on the effects of sulfur on emission from high emitters is available only for Tier 0 vehicles as indicated in Table 5. 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 19 and the corresponding emission effects are shown in Table 20.

Table 19
<u>Regression Analysis for Tier 0 High Emitting Vehicles</u>

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

Table 20

Emission Effects from Varying Sulfur for High Emitting Tier 0 Vehicles

Pollutant	Emissions Mode	% 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
CO	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
CO	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
CO	Start	-2.37	-6.20	-14.8	-26.2
NOx	Start	1.14	3.07	7.85	15.4

The effects in Table 20 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[14]. 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 21 is a comparison of the emission effects estimated in this EPA report to the Complex Model estimates for high emitters.

Table 21

Comparison of Composite Emission Effects for High Emitting Tier 0 vehicles estimated from this Analysis to those Estimated from the Complex Model 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	-5.0	1.4	10.0

* 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[13].

Note that in some cases Table 20 shows that reducing sulfur may actually increase start emissions. While this result was unexpected, MOBILE6 will apply the start effects as reported in Tables 19 and 20. We considered applying manual adjustments to the start correction factors, (such as "zeroing out" the counterintuitive effects), but we rejected this option because MOBILE6 will combine running and start emissions to estimate composite emissions whenever necessary and any changes to the start effects would skew the composite emission estimates.

The regression coefficients shown in Table 19 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 high emitters certified to Tier 1 and cleaner standards. Analysis of the Complex Model[15] indicates that the NOx sensitivity of high emitters is approximately 60 percent of the sensitivity for normal emitters. Thus, for vehicles and trucks certified to Tier 1 and cleaner standards (LEV, ULEV, Tier 2, etc.), a 60 percent correction factor will be applied to estimate a NOx effect for high emitting vehicles. 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[13,14] for normal emitters or a conistent sensitivity to changes in sulfur from high emitting vehicles; thus, the regression coefficients listed for HC and CO in Table 19 will be used as is for all vehicle categories. Table 22 summarizes the high emitter effects to be used in MOBILE6:

Table 22
Summary of High-Emitter Effects

Vehicle Category	Pollutant	High Emitter Effect
Tier 0–LDVs	HC	Use Appropriate Regression Coefficient listed in Table 19
Tier 0–LDVs	NMHC	Use Appropriate Regression Coefficient listed in Table 19
Tier 0–LDVs	CO	Use Appropriate Regression Coefficient listed in Table 19
Tier 0–LDVs	NOx	Use Appropriate Regression Coefficient listed in Table 19
Tier 1–LDVs	HC	Use HC Regression Coefficient listed in Table 19
Tier 1–LDVs	NMHC	Use NMHC Regression Coefficient listed in Table 19
Tier 1–LDVs	CO	Use CO Regression Coefficient listed in Table 19
Tier 1–LDVs	NOx	Use (0.60* Normal Emitter Tier 1 Effect (calculated from Table 9))
LEV & ULEV–LDVs	HC	Use HC Regression Coefficient listed in Table 19
LEV & ULEV–LDVs	NMHC	Use NMHC Regression Coefficient listed in Table 19
LEV & ULEV–LDVs	CO	Use CO Regression Coefficient listed in Table 19
LEV & ULEV–LDVs	NOx	Use (0.60* Normal Emitter LEV LDV Effect (calculated from Table 17))
LEV & ULEV–LDT2s	HC	Use HC Regression Coefficient listed in Table 19
LEV & ULEV–LDT2s	NMHC	Use NMHC Regression Coefficient listed in Table 19
LEV & ULEV–LDT2s	CO	Use CO Regression Coefficient listed in Table 19
LEV & ULEV-- LDT2s	NOx	Use (0.60* Normal Emitter LEV LDT2 Effect (calculated from Table 17))

Long-Term and Irreversibility Effects

After the draft report was completed, additional sulfur effect data collection and analysis was done to support the EPA's Tier 2 rulemaking, including work to address the long-term effects of fuel sulfur levels and to the effects of temporary exposure to high sulfur fuels. We felt it was important to incorporate this analysis into MOBILE6.

Since only LEV data were used to evaluate the irreversibility and long-term exposure effects, the long-term exposure effects will only apply to LEV and cleaner categories of vehicles and trucks. Irreversibility effects will only be applied to 2004-and-later vehicles since the data used were SFTP-compliant data. Both the long term exposure and irreversibility effects will be applied in conjunction with the short term effects estimated in the sections preceeding this one in this report.

<u>Background for Long-Term and Irreversibility Effects</u>

Fuel sulfur impacts vehicle emissions in three basic ways: 1) short-term effects due to sulfur's adsorption onto the catalyst surface, 2) longer-term effects due to sulfur's penetration into the precious metal layer of the catalyst and oxygen-storage material in the catalyst, and 3) a more lasting impact, referred to as irreversibility. Generally, items 1 and 2 are referred to as "sulfur sensitivity" and item 3 is referred to as "sulfur irreversibility."

The immediate impact (or "short-term" effects) of sulfur on emissions (item 1 above) is discussed in the previous sections of this report. From the "short-term" effects it was shown that operation on typical conventional gasoline containing 330 ppm sulfur increases exhaust VOC and NOx emissions from LEV and Tier 2 vehicles, on average, by 40% and 139% respectively compared to operation on 30 ppm sulfur fuel. New data generated since the draft version of this report was completed on similar LEVs and ULEVs show that when these vehicles were driven on high sulfur (330 ppm) fuel for a few thousand miles, the NMHC and NOx emission increase due to high sulfur fuel increased by a greater margin than what was estimated with the "short-term" data; these effects are referred to as "long-term" effects. These new data will be used to generate new estimates (both for "short-term" and "long-term" effects) for sulfur-sensitivity of LEV, ULEV, and cleaner vehicles.

Sulfur's irreversibility on LEV/ULEV vehicles also affects emissions. Sulfur "irreversibility" refers to the decreased ability of a vehicle to return to low emissions on low sulfur fuel after temporary use of high sulfur fuel. 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. This could have substantial consequences for the design of a commercial sulfur control program. For this reason API carried out a study to begin to investigate this phenomena. Our analysis of the API data and the approach that will be used to incorporate these findings into MOBILE6 are described in the final section of this report.

Long-term Sulfur Effects

As discussed above, in addition to adsorbing onto the surface of the catalyst and acting as a poison, sulfur can also penetrate into the precious metal layer, especially into palladium (the metal of choice for LEV catalysts), and into the oxygen storage material and poison the catalyst further. Full penetration may not have occurred during the very few miles of operation prior to short term emission testing on high sulfur fuel. The short-term exposure in the test programs (evaluated previously) typically consisted only of running several emission tests (FTP or LA4). Since each FTP is approximately 18 miles in length, short-term exposure usually amounted to just under 100 miles of operation, all of which was in a controlled laboratory environment.

To address this concern, API and EPA conducted test programs on a total of six light-duty vehicles (see Table 15 for listing of the vehicles) for sulfur sensitivity after both short-term and long-term exposure to sulfur. The long-term exposure consisted of between 1,500 and 4,000 miles of in-use operation over urban, rural, and highway roads. Two of the vehicles were 1999 models, while the other four were all 1998 models. All six were either LEV or ULEV vehicles. As listed in Table 15, three of the vehicles were equipped with catalyst systems aged to either 50,000 or 100,000 miles. The other three vehicles had low mileage catalyst systems aged to only about 4,000 miles.

All of the vehicles were tested for short-term exposure prior to the long-term testing. Each vehicle was tested using a FTP baseline tested on low sulfur fuel (30 or 40 ppm). The number of tests used to establish the baseline varied from two to four. The vehicles were then tested with the high sulfur fuel (EPA @ 350 ppm, API @ 540 ppm). Sulfur sensitivity was determined by calculating the percent increase in average emissions with the high sulfur fuel compared to the average emissions with the low sulfur fuel. Table 23 lists both the short-term and the long-term sulfur sensitivity data for all six vehicles.

Table 23
Vehicle-by-Vehicle Short-Term vs. Long-Term Sulfur Sensitivity

Vehicle	Sulfur Aging	Sulfur Level	Exhaust Tailpipe Emissions (g/mi)			Sulfur Sensitivity (%)		
			NMHC	CO	NOx	NMHC	CO	NOx
Accord	Short	30	0.031	0.351	0.092	12.0	36.3	69.4
		350	0.035	0.478	0.155			
	Long	30	0.033	0.330	0.09	21.7	121.1	158.5
		350	0.040	0.731	0.234			
Cavalier	Short	30	0.070	1.778	0.068	49.3	127.7	347.0
		350	0.105	4.048	0.303			
	Long	30	0.070	1.778	0.068	216.	306.4	411.8
		350	0.223	7.224	0.324			
Altima	Short	40	0.041	0.788	0.061	43.9	34.3	83.6
		540	0.059	1.058	0.112			
	Long	40	0.041	0.788	0.061	39.0	25.3	116.4
		540	0.057	0.987	0.132			
Taurus	Short	40	0.033	0.522	0.075	54.5	59.4	34.7
		540	0.051	0.832	0.101			
	Long	40	0.033	0.522	0.075	121.2	151.0	56.0
		540	0.073	1.310	0.117			
Accord	Short	40	0.029	0.285	0.100	10.3	4.9	92.0
		540	0.032	0.299	0.192			
	Long	40	0.029	0.285	0.100	41.4	63.2	145.0
		540	0.041	0.465	0.245			
Avalon	Short	40	0.040	0.406	0.068	52.5	33.3	70.6
		540	0.061	0.541	0.116			
	Long	40	0.040	0.406	0.068	50.0	80.8	108.8
		540	0.060	0.734	0.142			

In order to quantify the difference between short-term and long-term exposure, a fleet average emission rate was determined for both low and high sulfur fuels for each pollutant, for both long-term and short-term exposure. The percent change in emissions between low and high sulfur fuels was calculated, and the ratio of long-term sensitivity to the short-term sensitivity was then determined. Table 24 shows the percent increases from short-term to long-term were quite large, especially for hydocarbon emissions. Statistical tests to determine whether this observed increase in sulfur sensitivity was significant are discussed in Appendix B of the Tier 2 Regulatory Impact Analysis.

Table 24
Percent Difference Between Short-Term vs. Long-Term Sulfur Sensitivity

Average	Sulfur Sensitivity (%)			Ratio of long-term to short-term sensitivity		
	NMHC	CO	NOx	NMHC	CO	NOx
Short-Term	40.2	75.7	111.3	2.50	2.36	1.47
Long-Term	100.3	178.7	163.4			

The ratio of long-term to short-term sensitivity is was then multiplied by the short term sensitivities from the larger vehicle database to arrive at a total sulfur sensitivity effect. Numbers and ratios for HC emissions will be assumed to be the same as those for NMHC.

For MOBILE6, the most important numbers for long-term sulfur effects are the ratios developed above, so they are re-state in Table 25 below (for easy reference).

Table 25
Ratio of long-term to short-term Sulfur Sensitivity for LEV and Cleaner Vehicles

Pollutant	Ratio to be Applied
NMHC	2.50
HC	2.50
CO	2.36
NOx	1.47

To calculate an overall sulfur sensitivity for LEV and cleaner vehicles in MOBILE6, the revised LEV regression coefficients in Table 17 is used to determine short-term percent increase in emissions when sulfur is increased from one level to another. The short-term percent change is then multiplied by the ratio in Table 25. The product is the total sulfur sensitivity for a given emission model for increasing sulfur from one level to another, except for 2004-and-later model year vehicles, where an irreversibility effect is also applied.

The following should be remembered when applying these new factors:

- The long-term exposure effects applies only to LEV and cleaner vehicles and trucks. Tier 0 and Tier 1 vehicles and trucks only have short-term sulfur effects.

- For high emitting LEV vehicles and trucks the long-term factors listed in Table 25 are used as written, but as explained in the discussion of high emitters, above, the short-term effects are reduced.

Sulfur Irreversibility

In addition to the sulfur sensitivity (short and long term emission effects) issue discussed above, fuel sulfur can also impact vehicle emissions in a more lasting fashion, ranging from 20 or more miles to potentially permanent. This lasting effect of sulfur on emissions is termed irreversibility, referring to the fact that the emission impact of high sulfur fuel does not reverse when low sulfur fuel is used. The EPA Staff Paper on Gasoline Sulfur Issues (U.S. EPA, May 1998, EPA420-R-98-005) summarizes conditions required to remove sulfur from the catalyst once a vehicle has been exposed to high sulfur fuel.

In particular, the results of a number of studies have shown that generally high temperatures (in excess of 700 F) are required to remove sulfur from both the surface of the catalyst and from the internal catalyst matrix. In addition to high temperature, a rich exhaust (absence of oxygen coupled with presence of HC and CO, or a low air-to-fuel ratio) or an alternating sequence of rich and lean exhaust is often needed to fully regenerate the catalyst.

However, the two changes in conditions necessary to reverse sulfur poisoning--hotter catalyst temperatures and variable air-to-fuel ratios--both run counter to other design criteria aimed at achieving stringent emission standards in-use. Thus, EPA believes that sulfur reversibility effects should be included when assessing sulfur's total impact on exhaust emissions in MOBILE6.

The incorporation of sulfur irreversibility effects into the MOBILE6 model is similar to the steps used in the Tier 2 model[16]. As in the Tier 2 model, MOBILE6 applies a sulfur correction to 2004-and-later vehicles that is based on the vehicle's maximum sulfur level exposure, as well as the short- and long-term corrections for the current sulfur level. However, for MOBILE6, the Tier 2 methodology was simplified, as follows:

- In the Tier 2 model, there were a total of 7 fuel sulfur phase-in categories. It was felt that three major categories will suffice for most of the fuel-sulfur modeling scenarios that MOBILE6 will be used for. These three regions are: East Conventional Gasoline, West Conventional Gasoline, and Reformulated Gasoline. The average and cap (or "maximum") sulfur levels for these three different fuel categories can be found in reference 16 (for both the Tier 2 and no Tier 2 cases). Maximum levels are determined by whichever (summer vs. winter) is the maximum for a given year.

- For calendar years 2000 through 2015, average and cap sulfur levels were developed for each region with and without Tier 2. The sulfur levels are based on the methodology in reference 16, with the additional step of aggregating the SBREFA and non-SBREFA sulfur levels for the Conventional Gasoline areas. The aggregations were done based on projected fuel volumes[16].

- For a given 2004+ model year light-duty vehicle or truck, two sulfur levels are calculated in MOBILE6: "current" (or "average") and "maximum" exposure.

- The emission impacts of the "current" sulfur effects are calculated using the "current" sulfur level in the modeled calendar year by using the "short-term" sulfur coefficients, and, as necessary, multiplying the result by the long-term factors (discussed above).

- The emission impacts of the "maximum" sulfur effects are calculated using the short-term sulfur correction coefficients with the "maximum" sulfur level for the vehicle. Because sulfur levels are decreasing with time, the maximum sulfur level for a vehicle is the maximum sulfur level allowed in the year the vehicle was first driven, ie, the vehicle's model year. Long-term effects are not applied

- The average sulfur effect, including short-term, long-term and irreversibility is then calculated as a weighted average of the "current" and "maximum" based on the irreversibility factors (IR) developed in reference 16. The irreversibility factors are 0.15 (or 15%) for LEVs and 0.425% (or 42.5%) for Tier 2. The equation used to determine the average sulfur effect is:

  Average Factor = [IR * Maximum Effect] + [(1-IR) * Current Effect]

- Note that in MOBILE6, emissions for all post-2004 cars and trucks are calculated with irreversibility effects. However, in cases where post-2004 trucks are not subject to LEV or Tier 2 standards, the emissions for post-2004 trucks are calculated to have no long-term sulfur effects.

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_{50}, T_{90}, and Sulfur Effects–Auto/Oil Air Quality Improvement Research Program," SAE Paper No. 952510, 1995.

4. 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 in electronic format.

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 (www.epa.gov/otaq/m6.htm).

11a. Rao, Venkatesh. "Effects of Sulfur on Exhaust Emissions: A Proposal for MOBILE6," October 1, 1997. Available on MOBILE6 web site (www.epa.gov/otaq/m6.htm)

12. EPA's Complex Model for certifying Reformulated Gasolines. This model is available on the web at http://www.epa.gov/otaq/rfg.htm#models.

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.

16. Memorandum to Air Docket A-97-10, "Development of Light-Duty Emission Inventory Estimates in the Final Rulemaking for Tier 2 and Sulfur Standards," John W. Koupal,

OMS, December 15, 1999.

17. EPA Staff Paper on Gasoline Sulfur Issues (U.S. EPA, May 1998, EPA420-R-98-005)