Meszler
Engineering Services
906 Hamburg Drive, Abingdon, Maryland 21009

To: Coralie Cooper, NESCAUM
Christopher Porter, Cambridge Systematics

From: Dan Meszler

Subject: EPA's Treatment of Gasoline Sulfur Effects on Exhaust Emissions

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In followup to our discussion of late Thursday, I have examined the EPA's documentation describing the treatment of gasoline sulfur impacts on exhaust emissions predicted by MOBILE6.[1] Please keep in mind when considering the comments that follow, that my review of the EPA material was necessarily cursory given the available time constraints and that further investigation would undoubtedly yield a better understanding of the propriety of the EPA adjustments. In fact, for the most part, my comments are generally best interpreted as an outline of areas of further investigation that I would consider appropriate in developing a complete assessment of the EPA adjustments -- rather than as affirmative determinations of the propriety of those adjustments. Nevertheless, there is at least one significant area where I believe the fuel sulfur treatment employed by the EPA is clearly deficient and other areas where I believe that additional technical justification for the magnitude of the statistical relations developed by the EPA is warranted.

Normal Emitters: For normal emitters, the EPA MOBILE6 sulfur adjustment for a particular technology type follows one of the following two statistical relationships:[2]

$$\ln(\text{g/mile}) = a \times \ln(\text{ppm S}) + b$$

or

$$\ln(\text{g/mile}) = a \times (\text{ppm S}) + b$$

where a and b are determined through linear regression. In normal space, these relations are:

$$\text{g/mile} = (\text{ppm S})^a \times e^b \text{ and g/mile} = e^{a(\text{ppm S})} \times e^b \text{ respectively.}$$

[1] *Fuel Sulfur Effects on Exhaust Emissions, Recommendations for MOBILE6*, EPA420-R-01-039, U.S. Environmental Protection Agency, July 2001.

[2] Note that I have not actually examined the MOBILE6 source code to verify that the suggested relations are, in fact, encoded as indicated, but rather am relying on the cited technical documentation and assuming that the described adjustments are implemented as indicated therein. Nevertheless, based on the examination of several MOBILE6 output files, it is clear that the model responds as the documented adjustments would suggest.

For convenience, I will refer to the former relationship as the ln-ln (logarithm-logarithm) relationship and the latter as the ln-lin (logarithm-linear) relationship. It is perhaps important to note that the logarithmic form of both relations is important as it allows multiplicative adjustments to be developed without influence from the additive regression offset term b. For example, relations based on the ln-ln regression are developed as:

$$\begin{aligned}(\text{g/mile})_{\text{actual}}/(\text{g/mile})_{\text{base}} &= ((\text{ppm S})^{a} \times e^{b})_{\text{actual}}/((\text{ppm S})^{a} \times e^{b})_{\text{base}} \\ &= ((\text{ppm S})^{a})_{\text{actual}}/((\text{ppm S})^{a})_{\text{base}}\end{aligned}$$

Similarly, relations based on the ln-lin regression are developed as:

$$\begin{aligned}(\text{g/mile})_{\text{actual}}/(\text{g/mile})_{\text{base}} &= (e^{a(\text{ppm S})} \times e^{b})_{\text{actual}}/(e^{a(\text{ppm S})} \times e^{b})_{\text{base}} \\ &= (e^{a(\text{ppm S})})_{\text{actual}}/(e^{a(\text{ppm S})})_{\text{base}}\end{aligned}$$

EPA has determined the regression coefficient "a" to be as follows:[3]

Technology	Form	HC	NMHC	CO	NO_x
Tier 0	Ln-Ln	0.06126	0.05502	0.07596	0.03077
Tier 1	Ln-Lin	0.0008053	0.0007223	0.0006295	0.0003181
LEV-a	Ln-Ln	0.16845	0.13992	0.23746	0.35392
LEV-b	Ln-Ln	0.16800	0.16000	0.23600	0.35100
LEV-LDT2	Ln-Ln	0.12549	0.08956	0.15084	0.14625

LEV-a indicates the relationship for low emission vehicles (including Tier 2 vehicles) before a reanalysis was performed to consider additional data. LEV-b is the final relationship for low emission vehicles.

The Tier 1 relation is based on data only through 330 ppm sulfur.

Note that all relations are based on the ln-ln regression format except those for Tier 1 vehicles. This is quite important and, in my opinion, an unquestionable error that serves (for practical purposes) to improve the performance of Tier 1 vehicles relative to LEVs. The rationale behind this belief can best be understood by examining the various relations in a graphical format. The following Figures 1 through 4 present the EPA adjustment factors for HC, NMHC, CO, and NO_x relative to a base 30 ppm sulfur gasoline. Note that I have graphed the Tier 1 relationship in three formats. The first two, denoted as "Tier 1-Extrap" and "Tier 1-Final," depict relationships based on the EPA regressions. The third, denoted as "Tier 1-ln/ln," is a relationship I developed based on the EPA data. The differences between the three are critical to assessing the MOBILE6 treatment of Tier 1 vehicles.

[3] Throughout this memorandum, I utilize the regression coefficients presented by the EPA for the composite FTP cycle. Although MOBILE6 actually utilizes separate relations for start and running emissions, the issues raised in this memorandum apply equally to both and are simply easier to illustrate in a single composite FTP format.

Figure 1. MOBILE6 Gasoline Sulfur Adjustments for HC

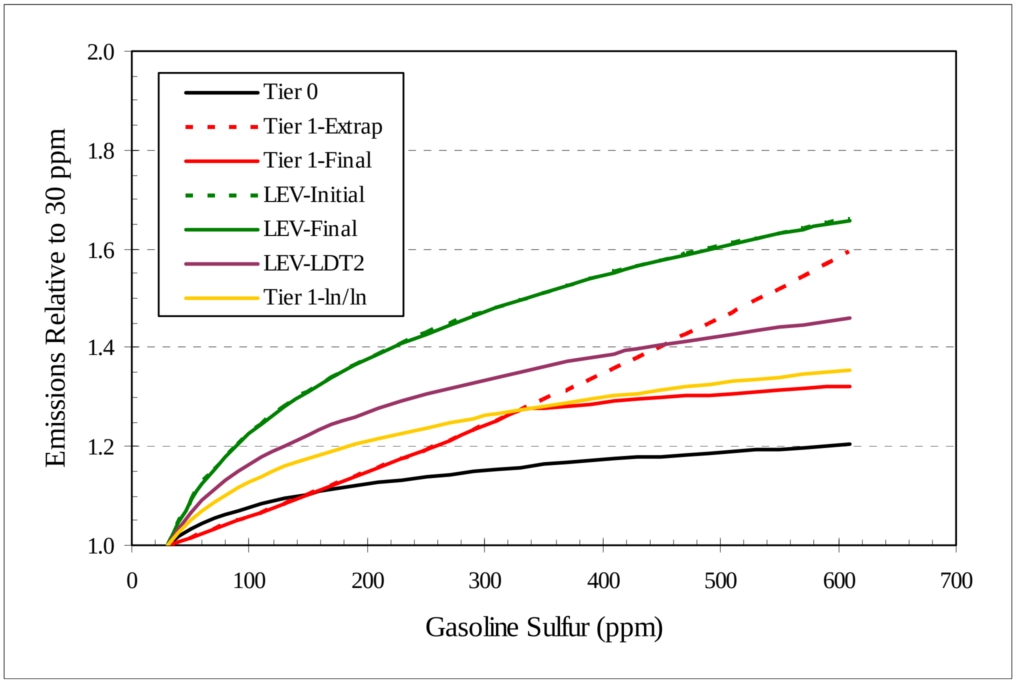


Figure 2. MOBILE6 Gasoline Sulfur Adjustments for NMHC

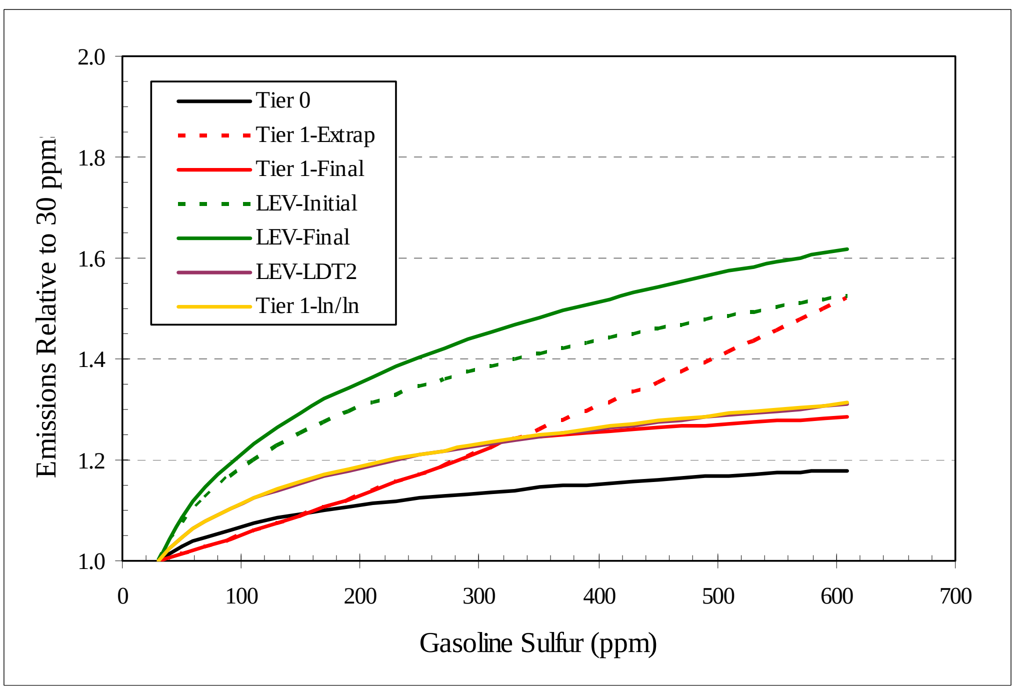


Figure 3. MOBILE6 Gasoline Sulfur Adjustments for CO

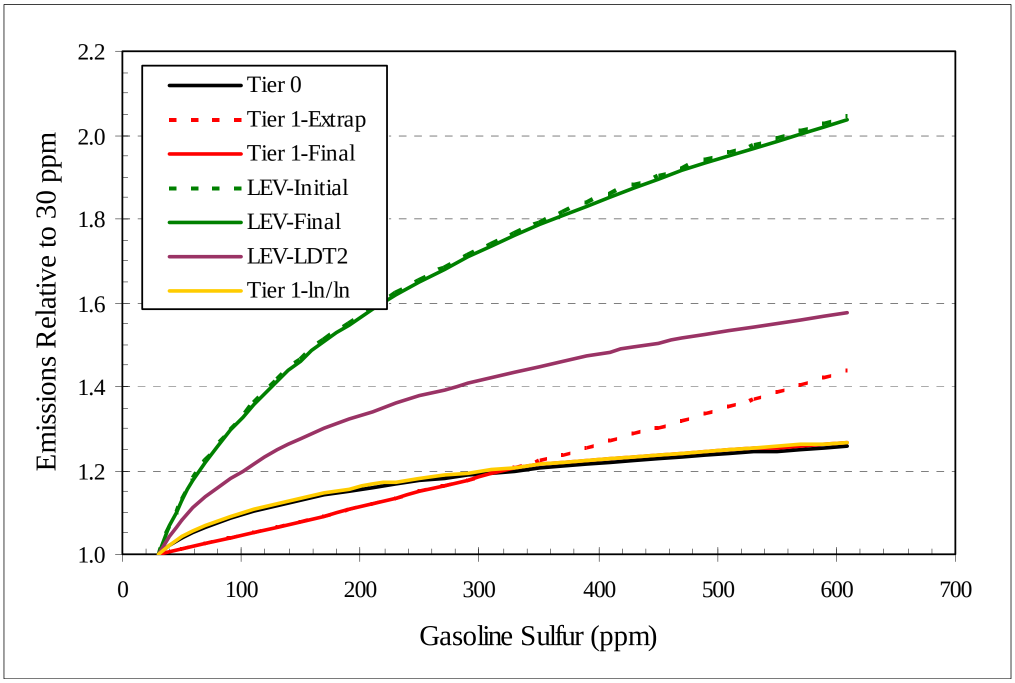
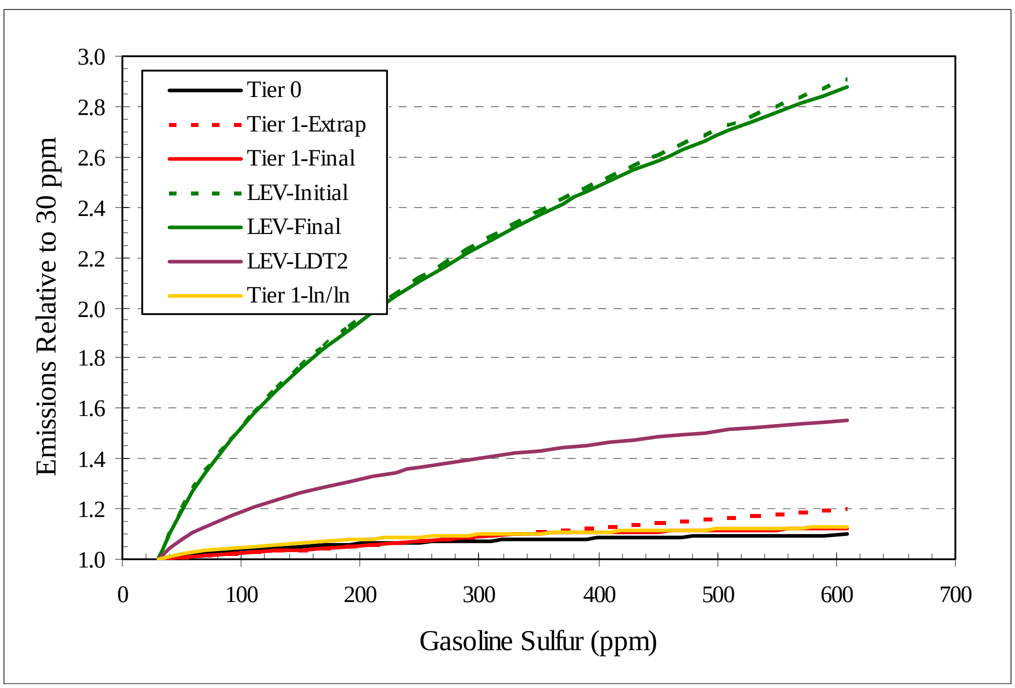


Figure 4. MOBILE6 Gasoline Sulfur Adjustments for NO_x



The “Tier 1-Extrap” curve is the actual EPA regression relation, the coefficients for which are depicted in the table presented above. However, because the Tier 1 relation is based on data that includes sulfur only to about 330 ppm, EPA does not utilize the relation beyond 330 ppm, but rather treats sulfur above 330 in accordance with the Tier 0 relation for sulfur above 300 ppm. Essentially, they multiply the Tier 1 adjustment at 330 ppm by the ratio of the Tier 0 adjustment at the target sulfur level to the Tier 0 adjustment at 330 ppm.

There is a fundamental problem with this approach. Selecting the ln-lin regression form for the Tier 1 regression effectively results is an initially lower emission factor impact relative to the other technology types as one moves away from 30 ppm sulfur. The impact relative to other technology types increases rapidly as one moves above 330 ppm sulfur, but the EPA has effectively eliminated this portion of the relation by adjusting this portion of the Tier 1 relation to mimic that of the Tier 0 relation. The net effect is that impacts between 30 and 330 ppm are muted for Tier 1 vehicles relative to impacts for the other technology types.

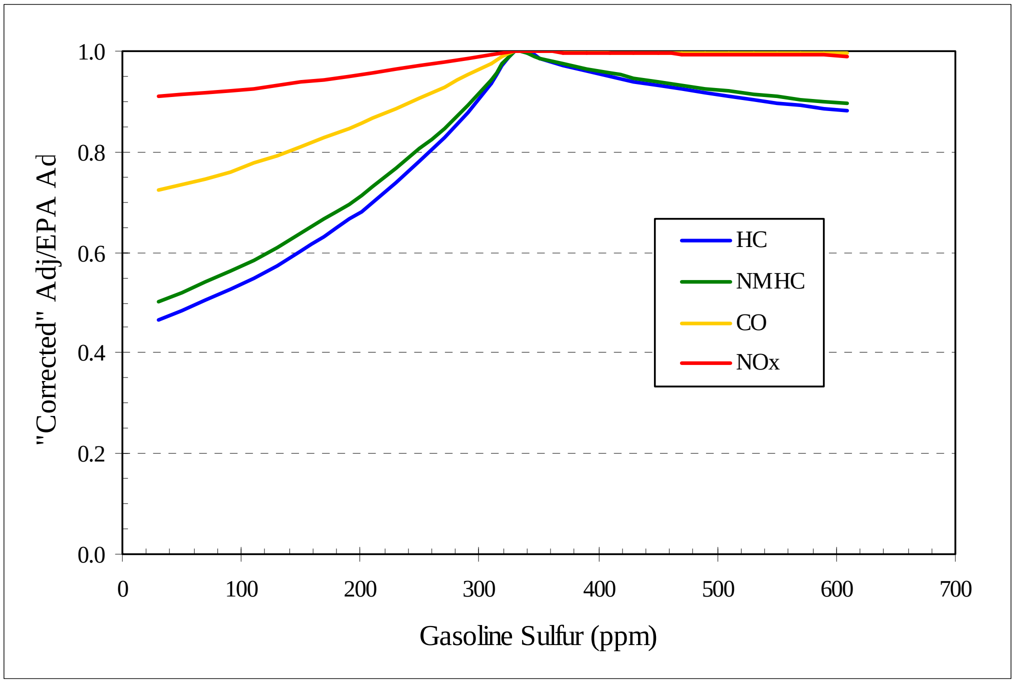
The EPA justifies the decision to construct the Tier 1 relation in ln-lin space “because only two sulfur data points were available.” The most logical regression structure for two data points would of course be lin-lin, but ln-lin approaches lin-lin (ignoring extrapolations) and allows the regression offset (i.e., intercept) to be ignored for relative adjustments. However, given that all other available data indicates that the most appropriate form of the sulfur impact relationship is ln-ln, the decision to utilize a ln-lin relationship for Tier 1 is at best myopic and at worst intentionally designed to minimize the impact of fuel sulfur on Tier 1 vehicles up to 330 ppm. In either case, the net effect is such that MOBILE6 will implement adjustments to Tier 1 vehicles in the 30 to 330 ppm sulfur range that are muted relative to the adjustments implemented for other technologies at the same sulfur content.

To approximate the magnitude of the muted response, I re-constructed the Tier 1 regression relationship in ln-ln space.[4] The resulting regressions are depicted in Figures 1 through 4 by the curves denoted as “Tier 1-ln/ln.” It is easily observed that the sulfur impacts in the 30 to 330 ppm range for this curve substantially exceed those predicted by the corresponding ln-lin curve. Moreover, given that the EPA concluded that ln-ln relations were universally the best fit approach for all technology types for which data for more than two sulfur levels were available, it is simply not reasonable to assume that the “default” best fit relation for Tier 1 technology would be anything other than a similar ln-ln relation.

Figure 5 graphically depicts the effect that would accrue if this inconsistency were corrected. The relationships presented in the figure show the differentials between the MOBILE6 LEV technology adjustments relative to both the “uncorrected” (i.e., ln-lin based Tier 1 adjustments) and “corrected” (i.e. ln-ln based Tier 1 adjustments). For example, for NMHC, the figure shows

[4] Note that I do not have the actual data utilized by the EPA to develop their regression, but rather constructed my regression utilizing the predictions of the EPA ln-lin regression. Assuming their regression is, in fact, the best fit ln-lin regression for their underlying data, this approach should yield the best fit ln-ln regression for the same data.

Figure 5. "Corrected" LEV to Tier 1 Sulfur Adjustment Ratio Relative to EPA LEV to Tier 1 Sulfur Adjustment Ratio



that at 100 ppm sulfur, the corrected sulfur adjustment differential between LEV and Tier 1 technology is only about 55 percent of the uncorrected differential.

As indicated, the degree to which the Tier 1 sulfur impact on CO and NO_x is muted is considerably reduced relative to that for HC. This results not from any difference in the way Tier 1 CO and NO_x impacts are determined, but rather from the fact that the differential between LEV CO and NO_x response and Tier 1 CO and NO_x response is considerably larger than that for HC, so that the significance of the Tier 1 CO and NO_x error is reduced in comparison to the difference between LEV and Tier 1 sulfur response (see Figures 3 and 4).

The significantly larger magnitude of the CO and NO_x sulfur impacts for LEV technology begs further investigation, but there is, unfortunately, no quick mechanism available to validate the underlying data. The cited EPA report includes neither the raw data upon which the impact relations are based nor an evaluation of the chemistry that would support such large distinctions between Tier 1 and LEV response. That is not to say that the responses are not plausible, or that the supporting chemistry is not well understood. There may well be a body of supporting material that clearly demonstrates the mechanisms at work, but I have not had an opportunity to investigate further in the timeframe available. Nevertheless, given the magnitude of the LEV sulfur impacts for CO and NO_x and in consideration of the observations that follow, I believe it would have been prudent for the EPA to have included an engineering support discussion to bolster the statistical relationships for CO and NO_x before their incorporation in MOBILE6.

Before presenting my rationale for an expanded evaluation of the CO and NO_x responses, let me again state that responses of the magnitude indicated (i.e., up to a doubling of NO_x emissions at 300 ppm sulfur and a tripling of NO_x emissions at 600 ppm sulfur) are plausible from a catalyst efficiency standpoint (although the 600 ppm response is approaching the limits of plausibility for all but the most efficient catalysts). Table 1 shows how catalyst efficiency would have to change in response to fuel sulfur to observe specific emissions increases. It is easily observed that as initial catalyst efficiencies approach 100 percent, the change in efficiency required to double or triple emissions is small. However, much larger efficiency drop-offs are required to double or triple emissions as initial efficiencies decrease below 98 percent or so.

That said, there are several reasons why an engineering explanation for the magnitude of the CO and NO_x response would be helpful in validating the statistical relationships employed for estimating LEV emissions. The following are a sample of such reasons:

- Sulfur response for LEVs is most pronounced for NO_x, followed by CO, followed by HC. The “original” Auto/Oil sulfur studies showed exactly opposite characteristics. What elements of advanced catalyst design support a major shift toward NO_x sensitivity?

- What are the elements of catalyst design that allow such divergent HC and CO sulfur response for LEVs? For Tier 0 and Tier 1 vehicles, both HC and CO seem to respond similarly to the compromised oxygen storage characteristics of the sulfur affected catalyst, but the relationship is stronger for CO with LEV technology. What is the additional aspect of LEV catalyst design that allows HC to be less affected than CO?

- What is the rationale behind the substantial differential in sulfur response for passenger car and LDT1 LEV technology and LDT2 LEV technology? Assuming the differences in emission standards for the two groups reflect only the relative differences in engine out emissions and would necessitate similar catalyst efficiencies (and, by extension, catalyst designs), why is the sulfur response for LDT2 LEV technology muted?

- Why do the increased cell density (surface area), catalyst loading, and improved catalyst distribution features of advanced technology catalysts not impart a degree of sulfur “tolerance?” Tolerance in this context is not meant to imply that fuel sulfur does not chemically and physically affect the advanced catalyst through the same mechanisms as a “conventional” catalyst, simply that a lesser percentage of active conversion sites should be affected by a given quantity of sulfur in the advanced catalyst?

Certainly, catalyst and associated air/fuel cycling technology has evolved to allow LEV technology vehicles to meet more stringent emission standards. This evolution has included catalyst formulation changes (e.g., increased palladium usage) that could well have affected fuel sulfur response. However, many of these same changes were necessitated by the introduction of

Table 1. Final Converter Efficiency for Given Initial Efficiency and Emissions Increase

Initial Converter Efficiency	Emissions Increase …					
	10%	20%	50%	100%	150%	200%
85%	83.5%	82.0%	77.5%	70.0%	62.5%	55.0%
86%	84.6%	83.2%	79.0%	72.0%	65.0%	58.0%
87%	85.7%	84.4%	80.5%	74.0%	67.5%	61.0%
88%	86.8%	85.6%	82.0%	76.0%	70.0%	64.0%
89%	87.9%	86.8%	83.5%	78.0%	72.5%	67.0%
90%	89.0%	88.0%	85.0%	80.0%	75.0%	70.0%
91%	90.1%	89.2%	86.5%	82.0%	77.5%	73.0%
92%	91.2%	90.4%	88.0%	84.0%	80.0%	76.0%
93%	92.3%	91.6%	89.5%	86.0%	82.5%	79.0%
94%	93.4%	92.8%	91.0%	88.0%	85.0%	82.0%
95%	94.5%	94.0%	92.5%	90.0%	87.5%	85.0%
96%	95.6%	95.2%	94.0%	92.0%	90.0%	88.0%
97%	96.7%	96.4%	95.5%	94.0%	92.5%	91.0%
98%	97.8%	97.6%	97.0%	96.0%	95.0%	94.0%
99%	98.9%	98.8%	98.5%	98.0%	97.5%	97.0%
99.9%	99.89%	99.88%	99.85%	99.80%	99.75%	99.70%

the Supplemental Federal Test Procedure, so it is not clear to what extent basic catalyst technology, as distinct from catalyst loading and surface area, varies between vehicles designed to federal versus California standards.

The bottom line to this whole discussion for normal emitters is that the ln-lin relationship assumed for Tier 1 vehicles is clearly incorrect and should be revised. The remainder of the sulfur response relationships are plausible, but several merit further investigation beyond the scope of this limited review.

High Emitters: EPA bases the MOBILE6 adjustments for high emitters entirely on data for Tier 0 vehicles. A regression approach identical to that described above for normal emitters is employed and since data are available for only two sulfur levels, EPA relies on a ln-lin fit. The potential problems with such a fit are described in detail above, but at least for HC and CO, the emissions increase is so small as to be negligible (0-2 percent emissions increase at 600 ppm sulfur). The effects for NO_x are larger, but for non-Tier 0 vehicles EPA employs an alternative approach for NO_x that simply assumes that the sulfur impact for high emitters is 60 percent of the impact assumed for normal emitters. Thus, each of the concerns described above regarding NO_x impacts translates directly to high emitters as well. In addition to the concerns already described for normal emitters, one must reconsider the plausibility of NO_x impacts given that a substantial fraction of high emitters may well have a catalyst that is already compromised from an efficiency standpoint. For example, doubling NO_x emissions from a catalyst operating at a compromised efficiency of 85 percent will require an additional drop-off in efficiency to 70 percent. Thus, it is not clear that advanced technology high emitters will suffer the additional emissions increases assumed by EPA through the application of a "static" 60 percent adjustment factor. At best this factor should be viewed as arbitrary.

Long Term Effects: All of the material presented above details the EPA's treatment of short term sulfur impacts (with short term meaning essentially immediate impacts observed over less than 100 miles). Short term effects are dominated by simple adsorption of sulfur onto the catalyst surface. Longer term effects (impacts observed over 1000-plus miles), which include impacts due to sulfur penetration into the catalyst, are treated separately and *are only applied to LEV technology vehicles* (including Tier 2 vehicles). This restriction is based on the fact that only data for six LEV vehicles was used to estimate long term effects, but there is no demonstration that similar impacts would not accrue for other technology types.

The EPA essentially calculates an impact multiplier to adjust short term impacts to equivalent long term impacts on the basis of data for the six test vehicles. The resulting multipliers are:

$$HC = 2.50,$$
$$NMHC = 2.50,$$
$$CO = 2.36, \text{ and}$$
$$NO_x = 1.47$$

So, in effect, short plus long term impacts are applied to all LEV technology vehicles and are equal to the short term impacts described above multiplied by the long term adjustment factor. For example, a normal emitting LEV vehicle operating on a 300 ppm sulfur gasoline would have a short term emissions increase of about 120 percent and a long term emissions increase of about 175 percent (1.2 times 1.47).

Irreversibility Effects: Finally, the EPA sulfur impact methodology also includes a permanent sulfur degradation effect that is applied only to LEV technology (including Tier 2) vehicles. This irreversibility effect appears to only be implemented for 2004 and later model years, so that its impact on LEVs and Tier 2 vehicles should be modest given the fact that gasoline sulfur levels are controlled during this period. Given this model year restriction, I am deferring further review here, but can provide additional followup material if you so desire.