

# Remote Sensing of Ammonia and Sulfur Dioxide from On-Road Light Duty Vehicles

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This study reports the largest data set of on-road, fuel-based mass emissions of ammonia and sulfur dioxide from vehicles of known make, model year, and fuel type. Ammonia is the first pollutant observed for which the emissions decrease with increasing fleet age from 10 to 20 years. The fixed nitrogen emission ratio is 15.0% by mass and 24.7% by mole, larger than current models predict. Diesel fueled vehicles emit more SO<sub>2</sub> than gasoline, and unexpectedly, gasoline SO<sub>2</sub> emissions decrease continuously with newer model year vehicles.

## Introduction

Particulate matter smaller than 2.5 μm in diameter (PM<sub>2.5</sub>) is of concern due to its possible association with increased human morbidity and mortality (1, 2), and its contribution to decreased visibility (3, 4). In the Los Angeles area PM<sub>2.5</sub> is 14–17% ammonium (NH<sub>4</sub><sup>+</sup>) and 9–18% sulfate by mass (5). Therefore, these two species are important to inventory since they compose up to 35% of the PM<sub>2.5</sub>. Ammonia (NH<sub>3</sub>) is the primary atmospheric base and through secondary atmospheric reactions forms ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Major ammonia emission sources include livestock waste, fertilizers, sewage treatment, and biological processes in soil (3). Vehicle NH<sub>3</sub> emission contributions are small in rural areas but mobile source NH<sub>3</sub> emission contributions in urban areas are larger and not well-known. In an aerosol modeling study of southern California, NH<sub>3</sub> was under predicted compared to monitoring results by 34% (6). The mean normalized error was 55–63% and the authors cite one cause due to “quite uncertain” NH<sub>3</sub> emissions both for absolute amounts and the spatial distribution. It is estimated that mobile sources contribute nearly 18% of the NH<sub>3</sub> inventory in the south coast air basin in California (7) but this estimate is based on the NH<sub>3</sub> measurements from a tunnel study thirteen years ago (3).

The mobile source NH<sub>3</sub> contribution arises from the chemistry over three-way catalysts (TWC), now equipped on all new gasoline powered light duty vehicles (8–10). The chemistry is complex and has been suggested to either proceed through the intermediate isocyanic acid (HNCO) or directly through adsorbed nitrogen and hydrogen atoms (11, 12). Ammonia emissions from tunnel studies have been reported before the widespread introduction of 3-way catalysts both in the U.S. (13) and in Europe (14). These emission estimates were lower than reported from tunnel studies in 1993 (3) and 1999 (15) when the majority of the

fleet contained 3-way catalysts. Ammonia emission estimates have also been reported by dynamometer (16), remote sensing (17), and recently by a chase vehicle (18). Results from these studies vary, possibly because, until now, the sample size has been relatively small. Apart from the tunnel studies, which do not characterize fuel type, catalyst usage, or vehicle age, this paper reports more vehicle NH<sub>3</sub> measurements than all other data combined.

Sulfur compounds in gasoline combust in the engine to form sulfur dioxide (SO<sub>2</sub>) which adsorbs somewhat reversibly onto the TWC, poisoning it and impeding proper functioning (19, 20). Proposed use of pollution control technology such as diesel particulate filters also necessitates the use of low sulfur fuel (21). To this end the U.S. Environmental Protection Agency (EPA) has adopted legislation to reduce fuel sulfur content. Tier II federal standards require gasoline to be reduced from 2004 levels of 300 parts per million by weight (ppmw) to 30 ppmw starting January 1, 2006 (22). Tier II standards also phase in during 2006: the use of ultralow sulfur diesel fuel containing 15 ppmw to help facilitate the stringent 2007 diesel engine emission requirements. These reductions will be measured by testing refinery and retailer fuel sulfur levels but no on-road verification of these reductions are scheduled. Very few in-use, on-road vehicle SO<sub>2</sub> emissions have been reported (23, 24). This paper reports the largest sample of individual, in-use, on-road vehicle SO<sub>2</sub> emissions to date and provides baseline data before the Tier II standards are implemented.

## Experimental Section

**Apparatus.** The remote sensing instrumentation and measurement technique (FEAT, Fuel Efficiency Automobile Test) has been discussed previously for light-duty vehicles (25–27). Recently, FEAT measurement capabilities have been expanded beyond carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrocarbons (HC), and nitric oxide (NO) with the addition of three new species, SO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub> (28). The FEAT system consists of a collinear UV/IR light source on one side of the road and on the other, a detector with nondispersive infrared detection of CO, CO<sub>2</sub>, and HC and dispersive UV detection of NO, SO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub>. UV absorption spectroscopy of NO, SO<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub> has been shown to have temperature and nonlinearity effects (29, 30), but fortunately, these are not significant at the ambient temperatures or column densities as measured behind a passing vehicle. The instrument calibration is also carried out under identical conditions to the vehicle measurement. The UV spectra from three of these pollutants are in the same spectral range but individual peaks are isolated without interference for analysis (28). Vehicles with large hydrocarbon emissions absorb in the same spectral region but the spectral feature is broad and does not interfere. The instrument is calibrated at least twice daily with the use of three certified gas mixtures (Scott Specialty Gases, Longmont, CO) containing 6% CO, 0.6% propane, 6% CO<sub>2</sub>, and 0.3% NO in N<sub>2</sub>; 1000 ppm SO<sub>2</sub> and 15% CO<sub>2</sub> in N<sub>2</sub>; 1000 ppm NH<sub>3</sub> and 6000 ppm propane in N<sub>2</sub>. The FEAT remote sensor measures ratios of pollutants to CO<sub>2</sub>, from which grams of pollutant per kilogram of fuel burned can be calculated (31). Accuracy is achieved by comparison to the certified cylinders which have reported uncertainties of ± 5% or better. The reported standard deviations of multiple measurements of an uncontaminated gas puff for the new species reported in this paper are 0.24 g SO<sub>2</sub>/kg and 0.26 g NH<sub>3</sub>/kg for individual vehicles (28).

**Field Measurements.** In this study, the emissions from in-use vehicles were measured in Denver, CO in June and

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**TABLE 1. Average Reported Vehicle NH<sub>3</sub> and SO<sub>2</sub> Emissions in Denver and Tulsa by Fuel Type (g/kg Fuel Consumed).<sup>a</sup>**

	NH <sub>3</sub>		SO <sub>2</sub>	
	Denver (n)	Tulsa (n)	Denver (n)	Tulsa (n)
gasoline	0.47 ± 0.02 (3534)	0.51 ± 0.01 (18 329)	0.25 ± 0.01 (3547)	0.24 ± 0.01 (18 362)
diesel	-0.04 ± 0.01 (133)	0.00 ± 0.01 (381)	0.56 ± 0.03 (133)	0.72 ± 0.03 (382)

<sup>a</sup> The (n) is the number of measurements used to determine the average and uncertainties. Uncertainties are the standard errors of the means.

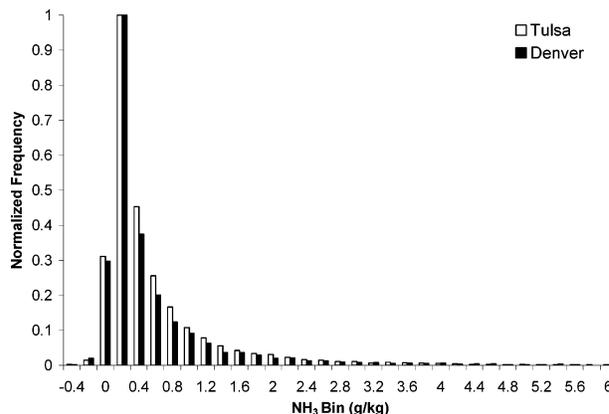
Tulsa, OK in September, 2005. These sites were chosen because they coincided with other measuring campaigns and have been used previously with the Coordinating Research Council's E-23 remote sensing project. The Denver site included 2-hour measurements each morning of June 1–3, 2005 at the interchange ramps of 6th Ave and I-25. Vehicles were measured heading uphill onto westbound 6th Ave. from northbound I-25 for the first 2 days and then eastbound 6th Ave. from southbound I-25 on the third day. The Tulsa measurements were conducted during September 19–23, 2005 on the uphill interchange ramp from westbound US 64 (Broken Arrow Expressway) to southbound US 169. All three sites include traffic freely flowing on ramps from either interstate highways or limited access state highways. License plates were recorded by video camera. The transcribed plates were submitted to the States of Colorado and Oklahoma which provided registration information including vehicle identification numbers (VIN). The State of Oklahoma did not provide fuel type with the registration information so diesel vehicles were later separated by decoding individual vehicle VINs (32). Table 1 lists the numbers of valid measurements obtained at each site and the breakdown between gasoline and diesel fuel use. The emissions and vehicle data for this paper are available at our website, www.feat.biochem.du.edu.

## Results and Discussion

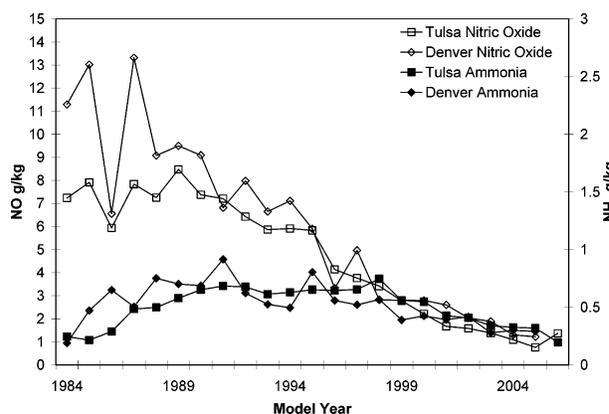
Table 1 provides the mean emissions of NH<sub>3</sub> and SO<sub>2</sub> by fuel type at the two different sites. Emissions for both pollutants from gasoline vehicles are the same between the two sites with 95% confidence. The reported fleet average NH<sub>3</sub> emission for the diesel vehicles are below the reported limit of detection for the instrument as expected (31). The Denver diesel mean NH<sub>3</sub> value should be zero and the reported slight negative value indicates that the prototype software has a slight negative bias when measuring negligible levels of NH<sub>3</sub>. There is, however, a significant difference in SO<sub>2</sub> emissions from diesel vehicles between the two sites. This could be due in part to higher refinery sulfur levels in Tulsa than in Denver. Another possibility is that, during the Tulsa measurement campaign, non-road diesel fuel, with higher allowed sulfur levels, was allowed to be sold as on-road fuel to alleviate shortages arising from hurricane Katrina (33).

**Ammonia.** Figure 1 illustrates the skewed nature of NH<sub>3</sub> emissions. Baum et al. showed a similar distribution from a smaller data set in Los Angeles 5 years ago (17). Both Denver and Tulsa exhibit the same skewed distribution with individual measurements as high as 12 g/kg (Figure 1 was truncated at 6 g/kg). The Baum et al. Los Angeles study reported the mean NH<sub>3</sub> fleet emissions to be 257 mg/L whereas this paper reports a higher mean NH<sub>3</sub> fleet emission level for the two sites combined of 370 mg/L (0.502 ± 0.006 g/kg and assuming the density of gasoline to be 0.74 kg/L).

Figure 2 shows that on-road NH<sub>3</sub> emissions decrease at the same relative rate as NO emissions for the newest vehicles



**FIGURE 1. Normalized distributions illustrate the skewed nature of on-road NH<sub>3</sub> emissions in both Tulsa and Denver from gasoline powered vehicles. Negative values do not suggest a cleaning of ambient air; rather, they are indicative of instrument noise.**



**FIGURE 2. Average NH<sub>3</sub> and NO emissions from gasoline vehicles by model year from the Denver and Tulsa sites. Note that the right-hand y-axis for NH<sub>3</sub> is 5× smaller scale than the left-hand axis for NO in order to show the overlap in the newest ~10 model years. The joining lines are only to guide the eye.**

when plotted as mass of NO and mass of NH<sub>3</sub> per kilogram of fuel consumed. By plotting the NO on a scale 5 times greater than NH<sub>3</sub> it is apparent that this trend is consistent for the 10 most recent model years. Furthermore, this trend exists at both the Denver and Tulsa sites, although the Denver data are noisier due to the smaller number of measurements. Approximately 10-year old and older vehicles deviate by emitting a lower NH<sub>3</sub>/NO ratio as would be expected with a less effective catalyst of that age. NH<sub>3</sub> is the first vehicle pollutant that we have observed that actually decreases from vehicles older than 10 years.

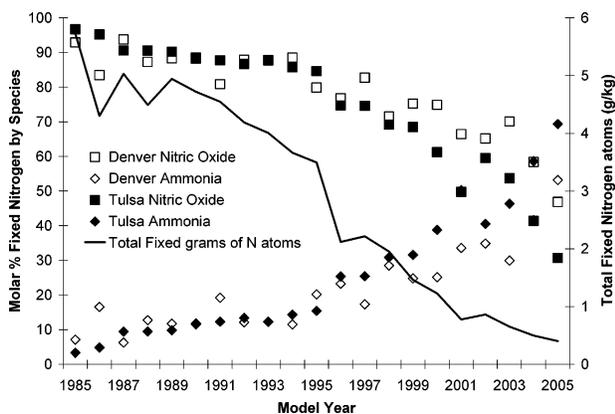
For the fleet and driving modes measured, the average emissions from gasoline powered vehicles, NH<sub>3</sub> accounts for 15.0% of the fixed nitrogen emissions by mass or 24.7% of the fixed molar nitrogen emissions. The % nitrogen is determined by the following equation (assuming NO<sub>2</sub> emissions are negligible for gasoline vehicles (19) and neglecting any unmeasured N<sub>2</sub>O emissions):

$$\% \text{ fixed nitrogen} = \frac{100 \times N_{\text{from NH}_3}}{N_{\text{from NH}_3} + N_{\text{from NO}}} \quad (1)$$

If calculating for mass emissions, N is the grams of pollutant. If calculating for molar emissions, N is the number of moles of nitrogen either determined directly from ppm measurements or by converting gram quantities to moles. Previous studies of individual vehicles have reported data that can be

**TABLE 2. Comparison of U.S. and UK National Emissions Inventories with Data from On-Road, Remote Sensing Measurements to Account for Fixed Nitrogen Emissions from Gasoline Powered Passenger Vehicles.**

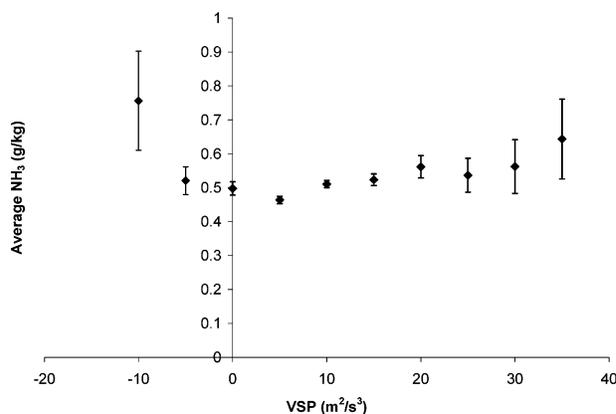
ref	source	NH <sub>3</sub> contribution	NO <sub>x</sub> (as NO <sub>2</sub> ) contribution	percentage of fixed molar nitrogen from NH <sub>3</sub>
35	mean emissions from this study predictions using remote Sensing data and U.S. Department of Energy gasoline use for 2002	0.50 (g/kg fuel) 201 (ktonnes)	2.70 (g/kg fuel) 1824 (ktonnes)	24.7% 24.7%
34	U.S. EPA National Emission Trends for light duty gasoline vehicles in 2002	251 (ktonnes)	3223 (ktonnes)	17.4%
36	UK National Atmospheric Emissions Inventory for petrol fueled vehicles in 2002	11 (ktonnes)	270 (ktonnes)	9.9%



**FIGURE 3. Average fixed nitrogen (NO and NH<sub>3</sub>) emissions from gasoline vehicles are declining by model year but the percentage of these emissions due to NH<sub>3</sub> is increasing. The diamonds represent the NH<sub>3</sub> contribution to total fixed nitrogen emissions and show that this phenomenon is true at both the Denver and Tulsa measuring sites.**

used to determine the fixed nitrogen from NH<sub>3</sub> by mole to be 6.3% from 2091 measurements made using remote sensing (17) and 20.3% for the mean of 39 vehicles on a dynamometer (16). In a tunnel study of over 67 000 vehicles in 1999, Kean et al. report NO and NH<sub>3</sub> data that account for 27% of the fixed nitrogen by moles in the form of NH<sub>3</sub> (15). Using the U.S. Environmental Protection Agency's National Emission Trends from 2002, Table 2 shows the national estimated NH<sub>3</sub> contribution to fixed molar nitrogen from gasoline on-road vehicles is 17.4% (34). The reason for this under prediction is unclear. When using national daily fuel sales available from the U.S. Department of Energy from 2002 (35) and assuming national emission factors to be the same as those in this paper for Denver and Tulsa in 2005, both NO<sub>x</sub> and NH<sub>3</sub> are over predicted by the U.S. EPA model (34). NO<sub>x</sub> emissions are over predicted by 77% (3223 ktonnes/year rather than 1824 ktonnes/year) whereas NH<sub>3</sub> emissions are over predicted by 25% (251 ktonnes/year rather than 201 ktonnes/year). The NH<sub>3</sub> fraction appears to be also under predicted in the UK using the UK National Atmospheric Emissions Inventory data (36). These data estimate the fixed molar nitrogen in the form of ammonia to be only 9.9% in 2002 for petrol (gasoline) powered cars.

The total NO<sub>x</sub> and NH<sub>3</sub> emissions are decreasing in recent model years as shown in Figure 2. The same data used in Figure 2 can be plotted to show the percent of total fixed nitrogen by species by model year. Figure 3 shows that the TWC has reduced the total fixed nitrogen (especially notice the drop between 1995 and 1996 with the introduction of OBDII) represented by the line and the right y-axis. The line is the average fixed nitrogen atom emission by model year for both Denver and Tulsa. The points show that although the total nitrogen emissions have decreased, there is an increased percentage contribution of NH<sub>3</sub>. Figure 3 shows

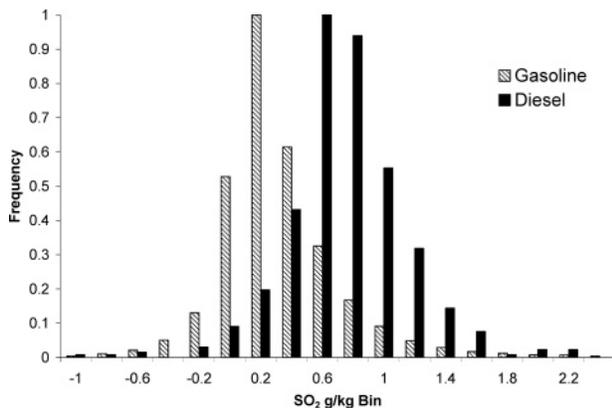


**FIGURE 4. NH<sub>3</sub> emissions versus vehicle specific power (VSP) for gasoline vehicles for both the Denver and Tulsa sites combined. Each data point is the mean of at least 50 measurements. Uncertainties are the standard errors of the mean.**

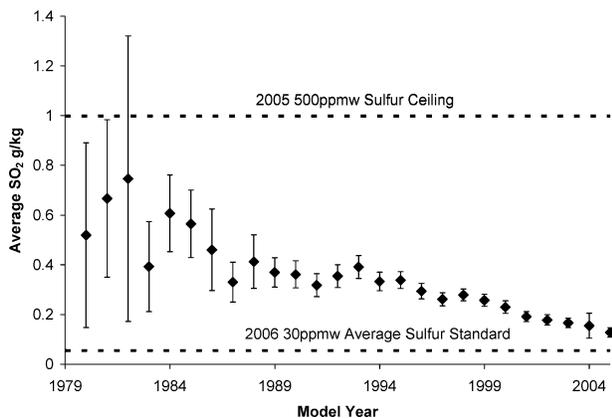
that for 2005, the most recent model year studied, over half of the fixed nitrogen emissions are NH<sub>3</sub> in both Tulsa and Denver. These data only include the gasoline powered vehicles measured at each site.

Ammonia emissions from gasoline powered vehicles possessing a TWC have been carefully studied on a dynamometer (16, 37). These studies show both that NH<sub>3</sub> emissions are highly dependent on driving mode, attributing most of the NH<sub>3</sub> production during large accelerations, and that NH<sub>3</sub> production is sporadic depending on the driving cycle just before the hard accelerations. Huai et al. correlate these NH<sub>3</sub> emission events to vehicle specific power (VSP) in an attempt to begin to model NH<sub>3</sub> emissions from mobile sources (38). They report trends in NH<sub>3</sub> emissions versus VSP, even though the same VSP can give very different emissions based on the driving behavior just before the hard accelerations. The researchers also noted that vehicles with differing certification standards had to be grouped together because in their study, only eight vehicles were tested (38). Figure 4 shows the averages of nearly 17 000 individual NH<sub>3</sub> measurements binned at 5 m<sup>2</sup>/s<sup>3</sup> increments with no point containing less than 50 readings. The VSP trend is not particularly obvious when this many measurements are plotted. For the 60 NH<sub>3</sub> measurements collected with VSP values greater than 25 m<sup>2</sup>/s<sup>3</sup>, the mean emission factor was 0.848 ± 0.204 g/kg thus making these measurements statistically the same as the other VSP bins. On-road NH<sub>3</sub> g/kg emissions do not appear to be as closely correlated to VSP as previously found on a dynamometer.

**Sulfur Dioxide.** Figure 5 shows SO<sub>2</sub> emissions to be more normally distributed than the NH<sub>3</sub> emissions in Figure 1. The gasoline fleet mean SO<sub>2</sub> emission of 0.24 g/kg is within the range measured on a dynamometer. Assuming 0.74 kg/L for gasoline and 20 mpg, the fleet mean would emit 34 mg/mi which compares to three gasoline vehicles reported



**FIGURE 5. Normalized distributions of SO<sub>2</sub> emissions by vehicle fuel type. The Denver and Tulsa data sets have been combined. The Denver fuel sample of 119 ppmw sulfur would stoichiometrically combust to produce 0.24 g/kg SO<sub>2</sub>.**



**FIGURE 6. Average SO<sub>2</sub> emissions from gasoline vehicles combined from Denver and Tulsa by model year in 2005. Uncertainty bars are  $\pm 95\%$  confidence levels about the means. The horizontal lines are for reference and represent the amount of SO<sub>2</sub> that would be emitted if the U.S. EPA 2005 and 2006 standards for gasoline sulfur levels were combusted and emitted only as SO<sub>2</sub>.**

between 0 and 230 mg/mi using fuel sulfur content ranging from 35 to 600 ppmw (39). The light duty diesel vehicle (LDDV) distribution is shifted to higher SO<sub>2</sub> emissions as expected from higher fuel sulfur content. This shift is expected to be indistinguishable at the end of 2006 when both gasoline and on-road diesel fuel sulfur levels are reduced and within 15 ppmw of each other. The LDDV SO<sub>2</sub> emission distribution is similar to that of heavy-duty diesel vehicles (HDDV) measured during the same summer (40). The HDDV mean SO<sub>2</sub> emissions are higher,  $0.85 \pm 0.01$  g/kg, than the mean LDDV SO<sub>2</sub> emissions shown in Table 1. The HDDV SO<sub>2</sub> emissions may be greater because none of these vehicles are outfitted with oxidation catalysts present in some LDDV. These catalysts can remove some SO<sub>2</sub> through adsorption but have also been shown to oxidize much of the SO<sub>2</sub> to SO<sub>3</sub>, which would be undetected by the remote sensor (41). These differences in SO<sub>2</sub> may also simply reflect fuel sulfur variability among regional distributors.

During this study, the gasoline used by the measured vehicles was, by law, not to exceed 500 ppmw sulfur. A sample of Denver gasoline was analyzed (Wyoming Analytical, Golden, CO) and contained 119 ppmw sulfur. A study by Mariq et al. reports that SO<sub>2</sub> to SO<sub>3</sub> conversion over the TWC is not significant due to the lack of excess oxygen and near stoichiometric combustion (39). They further report that a functioning TWC showed that exhaust sulfur was extremely variable over the Federal Test Procedure (FTP)

drive cycle due to storage on the catalyst. The measured sulfur in the exhaust from the Mariq et al. study of low mileage vehicles represented 10% of the consumed sulfur in the cold-start phase 1, 30% in the transient phase 2, and nearly 100% during the hot-start phase 3. The remaining stored sulfur was driven off the catalyst during high acceleration runs at the end of the FTP. Figure 6 shows model year dependence on SO<sub>2</sub> emissions for the newest vehicles. The newest vehicles presumably have more active TWCs and can thus store more of the SO<sub>2</sub> and lower its emission. H<sub>2</sub>S emissions have been suggested as a hidden problem with the use of TWC (42) undetectable by the remote sensor. The presence of H<sub>2</sub>S would lower the perceived SO<sub>2</sub> emissions but the study by Mariq et al. reports H<sub>2</sub>S emissions to be very minor (39).

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