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Multi-species On-Road Remote Sensing of Vehicle Emissions in Van Nuys, California – August 2010

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EXECUTIVE SUMMARY

The University of Denver completed an on-road remote sensing study of motor vehicle emissions for the first time at a site on eastbound Sherman Way in Van Nuys, California, about 0.4 mile west of the Van Nuys airport tunnel. Measurements were made on five consecutive days, from Thursday, August 12, through Monday, August 16, between the hours of 9:00 and 15:30. At the measurement site, Sherman Way is a divided six-lane surface street. The middle lane of the eastbound lanes was closed for approximately 2.5 blocks before the monitoring location, forcing traffic into the inside and outside lanes. The instrument was set up just east of Whitaker Ave. across a single eastbound lane that was closest to the curb. We compiled a database that contains 12,963 records for which the State of California provided registration information. All of these records contained valid measurements for at least CO and CO_2, and most of the remaining records contained valid measurements for HC, NO, SO_2, NH_3 and NO_2. After the final report is completed for the Van Nuys Tunnel Study, which was conducted in August 2010 by the Desert Research Institute, the remote sensing database will be available from our website www.feat.biochem.du.edu.

The mean CO, HC, NO, SO_2, NH_3 and NO_2 were determined to be 0.16%, 67ppm, 186ppm, -0.7ppm, 75ppm and 4ppm (19.7 g/kg, 2.5 g/kg, 2.6 g/kg, -0.03 g/kg, 0.6 g/kg and 0.09 g/kg fuel burned) respectively. The regulated fleet emissions measured in this study exhibit a gamma distribution with the minority of the measurements responsible for the majority of the emissions. The highest emitting 10% of the measurements were responsible for 86%, 90% and 72% of the CO, HC and NO emissions respectively. One particularly egregious case is a 1995 model that alone is responsible for 5.6% of the entire fleet's measured HC emissions (three HC measurements of 1.291%, 1.367% and 2.896%; for comparison the average two-stroke snowmobile measured in Yellowstone Park in 1999 averaged 2.4%). The following table details some of the emission statistics for the six species measured and for CO, HC, NO and NH_3 highlights the skewed nature of the on-road fleet's emissions distributions.

Summary of Emission Statistics from Sherman Way in Van Nuys, August 12-16, 2010.

	%CO	HC (ppm)	NO (ppm)	SO_2 (ppm)	NH_3 (ppm)	NO_2 (ppm)
Mode	0	20	1	0	3	2
Median	0.02	30	12	-0.5	26	2
Mean	0.16	67	186	-0.7	75	4
Mean Percentile*	83	68	79	11	73	56

*Percentile in which the mean emission rate is found when the fleet emissions are rank-ordered from clean to dirty.

A historical comparison between these measurements and two past measurement campaigns in the nearby Van Nuys tunnel (in 1987 by Ingalls *et al.* and in 1993 by Fraser and Cass) show large reductions in CO and HC emissions. CO and HC gram/liter emissions of 130 and 9.1 (grams of carbon) as measured in 1993 have decreased to 15 and 1.5 grams/liter as measured in

this study. CO/NO_x mass ratios have dropped from 13.3 in 1987 to 4.8 in the current work and HC/NO_x ratios have decreased from 1.7 to 0.7 for the same period. These reductions are consistent with U.S. light-duty emissions reductions reported by other researchers in the U.S.

These are the first light-duty measurements which we have collected since the large economic downturn that began in 2008. The fleet age distribution shows that relative to the 2006 and 2007 fleet fractions, the 2008 model year dropped about 10% while the 2009 model year fraction is lower by almost 40%. This undoubtedly has increased the age of the Van Nuys fleet with the average model year of 2001.5 being similar to the average model year of 2001.3 that was measured at a nearby West Los Angeles remote sensing monitoring site in March of 2008.

Unlike many of our measurements this data set includes measurements collected over a weekend. While traffic volumes were overall very similar the weekend traffic was slightly older (0.4 model years) and higher emitting for CO and HC. The NO_x emissions were not lower for the younger weekday fleet owing to the larger fraction of diesel vehicles for the week days (~1.7%) than on the weekend days (1.2% on Saturday and 0.6% on Sunday).

With this data set we report for a second time that the on-road fuel specific HC emissions of hybrid vehicles appear to be higher (almost a factor of 3 higher in this study) than similarly aged conventional vehicles. Due to the small number of hybrid vehicles (143 vehicles in this data set and 82 vehicles in the previous data set) the differences are not statistically significant, but confirmation of the previous observation (a factor of 4 higher) adds credence to there being a difference between the two fleets. Now we are not claiming that hybrid vehicles constitute a significant fraction of the fleet's HC emissions, because they do not. However, these in-use differences, if correct are important when modeling for example fleet replacement scenarios that are currently popular. In those scenarios the actual in-use HC emissions of the replacement hybrids will be understated.

Ammonia emissions are thought to be heavily influenced by driving mode, and the Sherman Way site is the first time that we have measured a cruise driving mode on a level roadway. Nearly all of our previous remote sensing measurement locations have been some type of uphill on-ramp driving. Historically the 2010 mean NH_3 emissions of 0.0075% (0.6 g/kg) are very similar to the 1993 measurements by Fraser and Cass, when scaled to account for only 76% of the 1993 fleet having catalyst. When we compare the Van Nuys measurements to recent (March of 2008) measurements at three California sites we find that the Van Nuys measurements fall between the two lowest (San Jose and Fresno of 0.49 g/kg) and the highest (West LA of 0.81 g/kg) emissions sites. The most notable differences are observed in the most recent 10 model years where the Van Nuys measurements are significantly higher than the San Jose and Fresno measurements and behave more like the ammonia emissions observed at the high load West LA site. While the cruise modes observed on Sherman Way bear no resemblance to the driving modes at the West LA site, the data bear more resemblance to the West LA data than the other two sites. A busy surface street like Sherman Way likely will result in foot on and foot off-the-throttle driving to maintain speed and spacing, and that might be a possible explanation why the NH_3 emissions are higher for the newest model years.

We also observed once again that as the reducing capacity of the catalyst starts to wane (around 15 years), driving mode becomes less important as all of the sites' ammonia emissions decrease with age at a similar rate. As NO_x emissions have decreased over the last twenty model years the amount of the total fixed nitrogen emissions have also decreased. However, the fraction of the fixed nitrogen emissions contributed by ammonia has increased.

INTRODUCTION

Many cities in the United States are in violation of the air quality standards established by the Environmental Protection Agency (EPA). Carbon monoxide (CO) levels become elevated primarily due to direct emission of the gas, and ground-level ozone, a major component of urban smog, is produced by the photochemical reaction of nitrogen oxides (NO_x) and hydrocarbons (HC). Sulfur dioxide (SO_2) is emitted when the sulfur found in fuel is oxidized. As of 2002, on-road vehicles were estimated to be the single largest source for the major atmospheric pollutants, contributing 82% of the CO, 45% of the VOC's, 5% of SO_2, and 56% of the NOx to the national emission inventory.[1] In urban locations, the contribution of on-road vehicles to the inventory is even greater.

Ammonia (NH_3), emitted from cars, is a growing concern because of its contribution to particulate matter that is smaller than 2.5μm in diameter ($PM_{2.5}$)[2-4]. In urban areas, the contribution of ammonia from car exhaust is not well known but some researchers have begun suggesting that it is a more important source than generally thought.[5,6] As traditional sources of ammonia such as livestock waste, fertilizer application, and sewage treatment have declined in many urban areas, ammonia levels have not always followed.[5]

For a description of the internal combustion engine and causes of pollutants in the exhaust see Heywood.[7] Properly operating modern vehicles with three-way catalysts are capable of partially (or completely) converting engine-out CO, HC and NO_x emissions to carbon dioxide (CO_2), water and nitrogen. If there is a reducing environment on the catalyst, ammonia can be formed as a byproduct of the reduction of NO.

Control measures to decrease mobile source emissions in non-attainment areas include inspection and maintenance (I/M) programs, reformulated and oxygenated fuel mandates, and transportation control measures, but the effectiveness of these measures remains questionable[8-10]. After nearly 50 years of mobile source regulation, many areas remain in non-attainment, and with the new 8-hour ozone standards introduced by the EPA in 1997, (and even more stringent standards being considered right now) many locations still violating the standard will have great difficulty reaching attainment.[11]

The remote sensor used in this study was developed at the University of Denver for measuring the pollutants in motor vehicle exhaust, and has previously been described in the literature.[12,13] The instrument consists of a non-dispersive infrared (NDIR) component for detecting CO, CO_2, and HC, and a dispersive ultraviolet (UV) spectrometer for measuring oxides of nitrogen (NO and NO_2), SO_2 and NH_3. The source and detector units are positioned on opposite sides of the road in a bi-static arrangement. Colinear beams of infrared (IR) and UV light are passed across the roadway into the IR detection unit, and are then focused onto a dichroic beam splitter, which serves to separate the beams into their IR and UV components. The IR light is then passed onto a spinning polygon mirror, which spreads the light across the four infrared detectors: CO, CO_2, HC and reference.

The UV light is reflected off of the surface of the dichroic mirror and is focused onto the end of a quartz fiber bundle that is mounted on the coaxial connector on the side of the detector unit. The quartz fiber bundle is split in order to carry the UV signal to two separate spectrometers. The first spectrometer was adapted to expand its UV range down to 200nm to measure the peaks from SO_2 and NH_3 and still measure the 227nm peak from NO. The absorbance from each respective UV spectrum of SO_2, NH_3, and NO is compared to a calibration spectrum in the same region to obtain the vehicle emissions. The second spectrometer measures only NO_2 by measuring an absorbance band at 438nm in the UV spectrum and by comparing it to a calibration spectrum in the same region.[14]

The exhaust plume path length and density of the observed plume are highly variable from vehicle to vehicle, and are dependent upon, among other things, the height of the vehicle's exhaust pipe, wind, and turbulence behind the vehicle. For these reasons, the remote sensor directly measures only ratios of CO, HC, NO, SO_2, NH_3 or NO_2 to CO_2. The ratios of CO, HC, NO, SO_2, NH_3 or NO_2 to CO_2, termed Q, Q', Q", Q^{SO2}, Q^{NH3} and Q^{NO2} respectively, are constant for a given exhaust plume, and on their own are useful parameters for describing a hydrocarbon combustion system. This study reports measured emissions as percentages of CO, HC, NO, SO_2, NH_3 and NO_2 in the exhaust gas, corrected for water and excess oxygen not used in combustion. The %HC measurement is a factor of two smaller than an equivalent measurement by a flame ionization detector (FID).[15] Thus, to calculate mass emissions as described below, the %HC values reported will be multiplied first by 2.0 as shown below, assuming that the fuel used is regular gasoline. These percent emissions can be directly converted into mass emissions by the equations shown below.

$$\text{gm CO/gallon} = 5506\bullet\%\text{CO}/(15 + 0.285\bullet\%\text{CO} + 2(2.87\bullet\%\text{HC})) \quad (1a)$$
$$\text{gm HC/gallon} = 2(8644\bullet\%\text{HC})/(15 + 0.285\bullet\%\text{CO} + 2(2.87\bullet\%\text{HC})) \quad (1b)$$
$$\text{gm NO/gallon} = 5900\bullet\%\text{NO}/(15 + 0.285\bullet\%\text{CO} + 2(2.87\bullet\%\text{HC})) \quad (1c)$$
$$\text{gm SO}_2\text{/gallon} = 12{,}585\bullet\%\text{SO}_2\ /(15 + 0.285\bullet\%\text{CO} + 2(2.87\bullet\%\text{HC})) \quad (1d)$$
$$\text{gm NH}_3\text{/gallon} = 3343\bullet\%\text{NH}_3\ /(15 + 0.285\bullet\%\text{CO} + 2(2.87\bullet\%\text{HC})) \quad (1e)$$
$$\text{gm NO}_2\text{/gallon} = 9045\bullet\%\text{NO}_2/(15 + 0.285\bullet\%\text{CO} + 2(2.87\bullet\%\text{HC})) \quad (1f)$$

These equations indicate that the relationship between concentrations of emissions to mass of emissions is linear, especially for CO and NO and at low concentrations for HC. Thus, the percent difference in emissions calculated from the concentrations of pollutants reported here is equivalent to a difference calculated from masses.

Another useful conversion is from percent emissions to grams pollutant per kilogram (g/kg) of fuel. This conversion is achieved directly by first converting the pollutant ratio readings to moles of pollutant per mole of carbon in the exhaust using the following equation:

$$\frac{\text{moles pollutant}}{\text{moles C}} = \frac{\text{pollutant}}{\text{CO} + \text{CO}_2 + 6\text{HC}} = \frac{(\text{pollutant/CO}_2)}{(\text{CO/CO}_2) + 1 + 6(\text{HC/CO}_2)} = \frac{(Q, 2Q', Q''\ldots)}{Q+1+6Q'} \quad (2)$$

Next, moles of pollutant are converted to grams by multiplying by molecular weight (e.g., 44 g/mole for HC since propane is measured), and the moles of carbon in the exhaust are converted to kilograms by multiplying (the denominator) by 0.014 kg of fuel per mole of carbon in fuel, assuming gasoline is stoichiometrically CH_2. Again, the HC/CO_2 ratio must use two times the reported HC (see above) because the equation depends upon carbon mass balance and the NDIR HC reading is about half a total carbon FID reading.[15]

$$\text{gm CO/kg} = (28Q/(1 + Q + 6Q'))/0.014 \qquad (3a)$$
$$\text{gm HC/kg} = (2(44Q')/(1 + Q + 6Q'))/0.014 \qquad (3b)$$
$$\text{gm NO/kg} = (30Q''/(1 + Q + 6Q'))/0.014 \qquad (3c)$$
$$\text{gm } SO_2\text{/kg} = (64Q^{SO2}/(1 + Q + 6Q'))/0.014 \qquad (3d)$$
$$\text{gm } NH_3 = (17Q^{NH3}/(1 + Q + 6Q'))/0.014 \qquad (3e)$$
$$\text{gm } NO_2\text{/kg} = (46Q^{NO2}/(1 + Q + 6Q'))/0.014 \qquad (3f)$$

Quality assurance calibrations are performed twice daily in the field unless observed voltage readings or meteorological changes are judged to warrant additional calibrations. For the multi-species instrument three calibration cylinders are needed. The first contains CO, CO_2, propane, NO and SO_2, the second contains NH_3 and propane, and the final cylinder contains NO_2 and CO_2. A puff of gas is released into the instrument's path, and the measured ratios from the instrument are then compared to those certified by the cylinder manufacturer (Praxair). These calibrations account for day-to-day variations in instrument sensitivity and variations in ambient CO_2 levels caused by local sources, atmospheric pressure and instrument path length. Since propane is used to calibrate the instrument, all hydrocarbon measurements reported by the remote sensor are reported as propane equivalents.

Studies sponsored by the California Air Resources Board and General Motors Research Laboratories have shown that the remote sensor is capable of CO measurements that are correct to within ±5% of the values reported by an on-board gas analyzer, and within ±15% for HC.[16,17] The NO channel used in this study has been extensively tested by the University of Denver, but we are still awaiting the opportunity to participate in an extensive blind study and instrument intercomparison to have it independently validated. Tests involving a late-model low-emitting vehicle indicate a detection limit (3σ) of 25 ppm for NO, with an error measurement of ±5% of the reading at higher concentrations. Appendix A gives a list of criteria for valid or invalid data.

The remote sensor is accompanied by a video system to record a freeze-frame image of the license plate of each vehicle measured. The emissions information for the vehicle, as well as a time and date stamp, is also recorded on the video image. The images are stored digitally, so that license plate information may be incorporated into the emissions database during post-processing. A device to measure the speed and acceleration of vehicles driving past the remote sensor was also used in this study. The system consists of a pair of infrared emitters and detectors (Banner Industries) which generate a pair of infrared beams passing across the road, six feet apart and approximately two feet above the road surface. Vehicle speed is calculated from the time that passes between the front of the vehicle blocking the first and the second beam. To measure vehicle acceleration, a second speed is determined from the time that passes between the rear of the vehicle unblocking the first and the second beam. From these two speeds, and the time difference between the two speed measurements, acceleration is calculated, and reported in mph/s. Appendix B defines the database format used for the data sets.

The purpose of this report is to describe the on-road measurements made on Sherman Way in Van Nuys, California in August of 2010. Measurements were made on five consecutive days, August 12-16, on eastbound Sherman Way just east of Whitaker Ave. In addition to readable plates the unreadable plates were coded for no visible plate, unreadable blue plates, motorcycles, school buses with unreadable plates, out-of-state plates and unreadable California plates.

RESULTS

We performed remote sensing measurements on five consecutive days, from Thursday, August 12, to Monday, August 16, 2010, between the hours of 9:00 and 15:30. Sherman Way is a divided six lane surface street in Van Nuys, CA. The middle lane, of the three eastbound lanes, was closed for approximately 2.5 blocks before the monitoring location, forcing traffic into the innermost and outside lanes. The instrument was set up just east of Whitaker Ave. across a single eastbound lane that was closest to the curb. A satellite picture of the measurement location is shown in Figure 1, and a photograph of the setup is shown in Figure 2. The grade at the measurement location averaged 0°. Appendix C gives temperature and humidity data for the 2010 study from the Van Nuys Airport, approximately 0.4 mile east of the measurement site. Following the five days of data collection, we read the images for license plate identification. We sent the data for plates that appeared to be in state and readable to the State of California Department of Motor Vehicles to obtain the vehicle make and model year for the vehicles belonging to those plates. The resulting database contained 12,963 records with make and model year information and valid measurements for at least CO and CO_2. Most of these records also contain valid measurements for HC, NO, SO_2, NH_3 and NO_2 as well.

These remote sensing measurements of vehicle exhaust were conducted as a part of the 2010 Van Nuys Tunnel Study, which is funded by the DOE National Renewable Energy Laboratory, and led by the Desert Research Institute. Once the final report for the Van Nuys Tunnel Study has been approved and released for public distribution, the database from this project will be available at www.feat.biochem.du.edu.

The validity of the attempted remote sensing measurements is summarized in Table 1. The table describes the data reduction process beginning with the number of attempted measurements and ending with the number of records containing both valid emissions measurements and vehicle registration information. An attempted measurement is defined as a beam block followed by a half second of data collection. If the data collection period is interrupted by another beam block from a closely following vehicle, the measurement attempt is aborted, and an attempt is made at measuring the second vehicle. In this case, the beam block from the first vehicle is not recorded as an attempted measurement. Invalid measurement attempts arise when the vehicle plume is highly diluted, or the reported error in the ratio of the pollutant to CO_2 exceeds a preset limit (see Appendix A). Other losses of data occur during the plate reading process, when out-of-state

Figure 1. A satellite view of the Sherman Way monitoring location with Whitaker Ave. on the left edge of the picture. The location of the motor home, source, detector and camera are located inside the red circle. The source generator is located to the right of the source in the closed middle lane. The traffic cones are shown as yellow dots.

vehicles and vehicles with unreadable plates (obscured, missing, dealer, out of camera field of view, etc.) are omitted from the final database. With the Van Nuys data set plate match losses are unusually small and the overall percentage of attempts that are plate matched is above average.

Table 2 provides an analysis of the number of vehicles that were measured repeatedly, and the number of times they were measured. Of the 12,963 records used in this fleet analysis, 10,436 (80.5%) were contributed by vehicles measured once, and the remaining 2,527 (19.5%) records were from vehicles measured at least twice. The percentage of repeat measurements is lower than our most recent California measurement sites which ranged between 30 to 40%.[18] Factors that could influence this difference are that the previous California sites were measured during

Figure 2. A street level view of the measurement setup on Sherman Way in Van Nuys CA. Across the road are the detector unit, dual spectrometers, speed bars, and the camera is in the road barrel located behind the motor home. The source, speed bars and generator are located in the closed middle lane, and the tire located next to the generator serves as an anti-theft device.

Table 1. Van Nuys Validity Summary.

	CO	HC	NO	SO_2	NH_3	NO_2
Attempted Measurements	14,691					
Valid Measurements	14,008	13,972	14,006	14,005	13,979	13,714
Percent of Attempts	95.4%	95.1%	95.3%	95.3%	95.2%	93.3%
Submitted Plates	13,009	12,977	13,007	13,008	12,983	12,747
Percent of Attempts	88.6%	88.3%	88.5%	88.5%	88.4%	86.8%
Percent of Valid Measurements	92.9%	92.9%	92.9%	92.9%	92.9%	92.9%
Matched Plates	12,963	12,931	12,961	12,962	12,937	12,703
Percent of Attempts	88.2%	88.0%	88.2%	88.2%	88.1%	86.5%
Percent of Valid Measurements	92.5%	92.5%	92.5%	92.5%	92.5%	92.6%
Percent of Submitted Plates	99.6%	99.6%	99.6%	99.6%	99.6%	99.7%

Table 2. Number of measurements of repeat Van Nuys vehicles.

Number of Times	Number of Vehicles	Percent of Measurements
1	10,436	80.5%
2	875	13.5%
3	171	4.0%
4	38	1.2%
5	16	0.6%
6	3	0.1%
7	2	0.1%

commuting hours, and with the exception of Fresno, did not include weekend days as did the Van Nuys measurements. In addition due to sampling configuration of the lanes, at any given time we were only able to measured roughly one-half of the fleet driving on Sherman Way.

Table 3 is the data summary for the Van Nuys measurements. For a comparison we have included the summary of the most recent measurements (collected in March of 2008) from the Coordinating Research Council (CRC) E-23 West Los Angeles (LA) site which is geographically near Van Nuys.[18,19] The average HC values here have been adjusted for comparison to remove a small systematic offset in the HC measurements. This offset, restricted to the HC channel and reported earlier in the E-23 program, is evident in the lowest emitting HC vehicles.[20] Calculation of the offset is accomplished by computing the mode and means of the newest model year vehicles, and assuming that these vehicles emit negligible levels of hydrocarbons, using the lowest of either of these values as the offset. The offset adjustment subtracts or adds this value from all of the hydrocarbon data. Since we assume the cleanest vehicles to emit little hydrocarbons, such an approximation will err only slightly towards clean because the true offset will be a value somewhat less than the average of the cleanest model year and make. This adjustment facilitates comparisons with other sites and/or different collection years for the same site. The offset has been applied where indicated in the analyses in this report, but has not been applied to the archived database. The offset for both Van Nuys and West LA 2008 is small at only 10ppm.

Figure 3 graphs the relationship between vehicle emissions of CO, HC and NO and model year for the Van Nuys and 2008 West LA data sets. The HC data have been offset adjusted as previously described for the purpose of comparison. The ages of the same model years are different for each site with the West LA vehicles being approximately 2.5 years younger than the Van Nuys vehicles. In addition the driving mode at these two sites is very different. The West LA site is a traffic light controlled on-ramp to I-10 where vehicles accelerate from a stop while the driving mode on Sherman Way is a steady cruise. The Van Nuys data set is much smaller (12,963 vs. 17,953), and that is reflected by more noise being evident in the older model year's data points.

Because emission deterioration rates are so low for late model US vehicles, as evidenced by the mean emissions for the newest 7 or 8 model years, the only noticeable emission difference between the two sites is for the NO data. The NO emissions of vehicles at the West LA site are

Table 3. Data Summary.

Study Year	2010 Van Nuys	2008 West LA
Mean CO (%) (g/kg of fuel)	0.16 (19.7)	0.17 (21.4)
Median / Mode CO (%)	0.02 / 0.00	0.02 / 0.00
Percent of Total CO from Dirtiest 10% of the Fleet	86.3%	80.7%
Mean HC (ppm)* (g/kg of fuel)* Offset (ppm)	67 (2.5) 10	50 (1.8) 10
Median / Mode HC (ppm)*	30 / 20	10 / 0
Percent of Total HC from Dirtiest 10% of the Fleet	90%	81%
Mean NO (ppm) (g/kg of fuel)	186 (2.62)	265 (3.75)
Median / Mode NO (ppm)	12 / 1	11 / 1
Percent of Total NO from Dirtiest 10% of the Fleet	72.1%	71%
Mean SO_2 (ppm) (g/kg of fuel)	-0.7 (-0.03)	2 (0.07)
Median / Mode SO_2 (ppm)	-0.5 / 0	0.2 / 0
Percent of Total SO_2 from Dirtiest 10% of the Fleet	100%	100%
Mean NH_3 (ppm) (g/kg of fuel)	75 (0.6)	99 (0.8)
Median / Mode NH_3 (ppm)	26 / 3	34 / 2
Percent of Total NH_3 from Dirtiest 10% of the Fleet	52.8%	50.8%
Mean NO_2 (ppm) (g/kg of fuel)	4 (0.09)	4 (0.08)
Median / Mode NO_2 (ppm)	2 / 2	2 / 2
Percent of Total NO_2 from Dirtiest 10% of the Fleet	100%	61.8%
Mean Model Year	2001.5	2001.2
Mean Speed (mph)	32.3	17.6
Mean Acceleration (mph/s)	0.3	1.9
Mean VSP (kw/tonne) Slope (degrees)	6.2 0°	12.2 2.0°
*Indicates values that have been HC offset adjusted as described in text.		

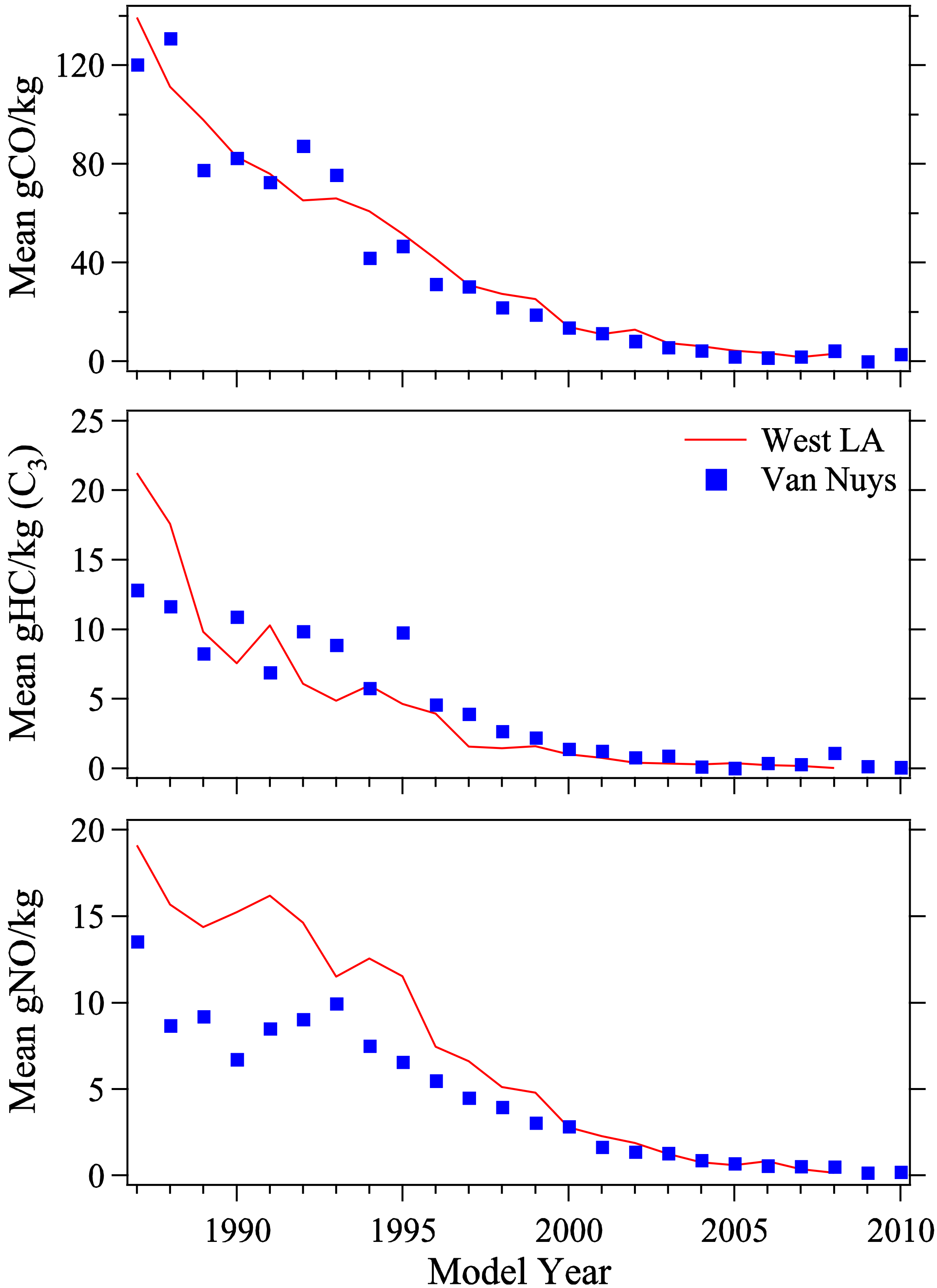


Figure 3. Van Nuys (squares) and West LA (line) mean vehicle emissions illustrated as a function of model year. HC data have been offset adjusted as described in the text. The vehicles at the West LA site are approximately 2.5 years newer than comparable model years at Van Nuys.

significantly higher beginning with the 1999 model year. While a high acceleration site should be expected to produce more NO emissions it is a testament to how well new models are able to control their NO emissions; in fact those expected increases do not show up for almost ten model years.

Figure 4 is a similar plot for the emissions species of SO_2, NH_3 and NO_2 that were collected. NH_3 shows a strong model year dependence that eventually levels out and starts to decrease in this plot. SO_2 and NO_2, within the signal to noise limits of this data set, do not appear to have any model year dependence. Both SO_2 and NO_2 emissions are expected to be very low due to the low sulfur fuels in use and the small percentage (only 1.3%) of diesel vehicles in the Van Nuys fleet.

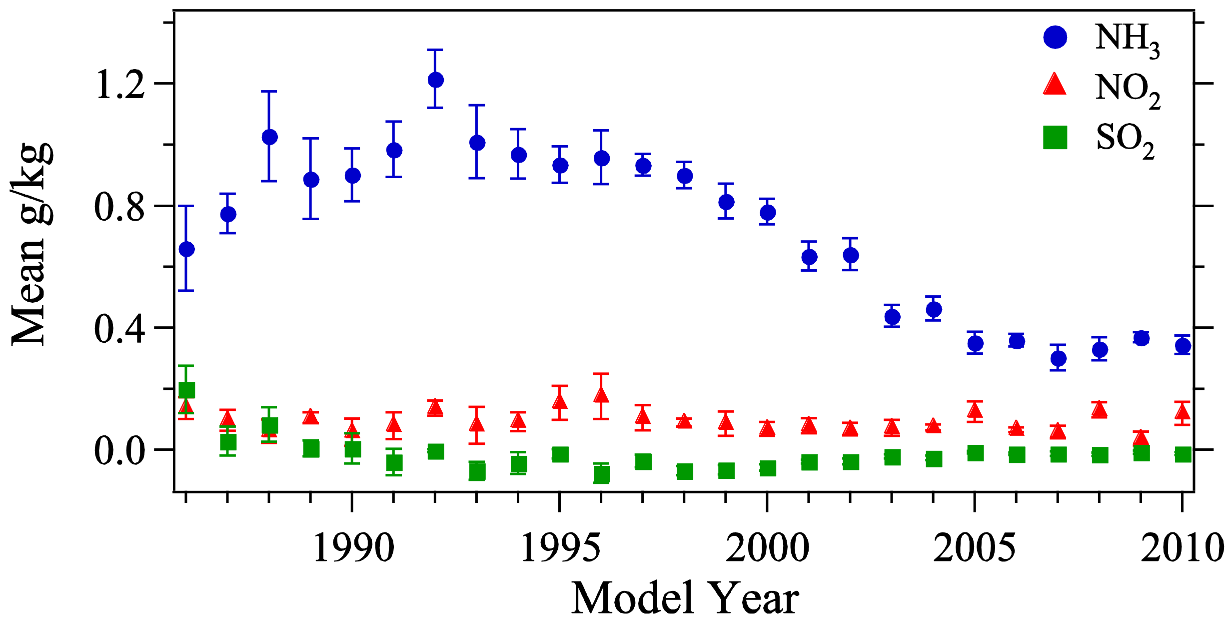


Figure 4. SO_2, NH_3 and NO_2 mean vehicle emissions of as a function of model year for the 2010 Van Nuys measurements. Errors are standard errors of the mean calculated using the daily emission values.

As originally shown by Ashbaugh *et al.*, vehicle emissions by model year, with each model year divided into emission quintiles, were plotted for the Van Nuys data.[17] This resulted in the plots shown in Figures 5 - 7. The bars in the top panel of each graph represent the mean emissions for each quintile, and do not account for the number of vehicles in each model year. This figure illustrates that the cleanest 60 to 70% of the vehicles, regardless of model year, make an essentially negligible contribution to the total fleet emissions. The inordinate contribution to the total HC fraction for the 1995 model year is the result of a single vehicle that was measured a total of 3 times with %HC readings of 1.3, 1.4 and 2.9% easily putting it on par with 2-stroke snowmobiles measured in Yellowstone National Park in the late 90's.[21]

The large accumulations of negative emissions in the first two quintiles are the result of ever decreasing emission levels. Our instrument is designed such that when measuring a true zero

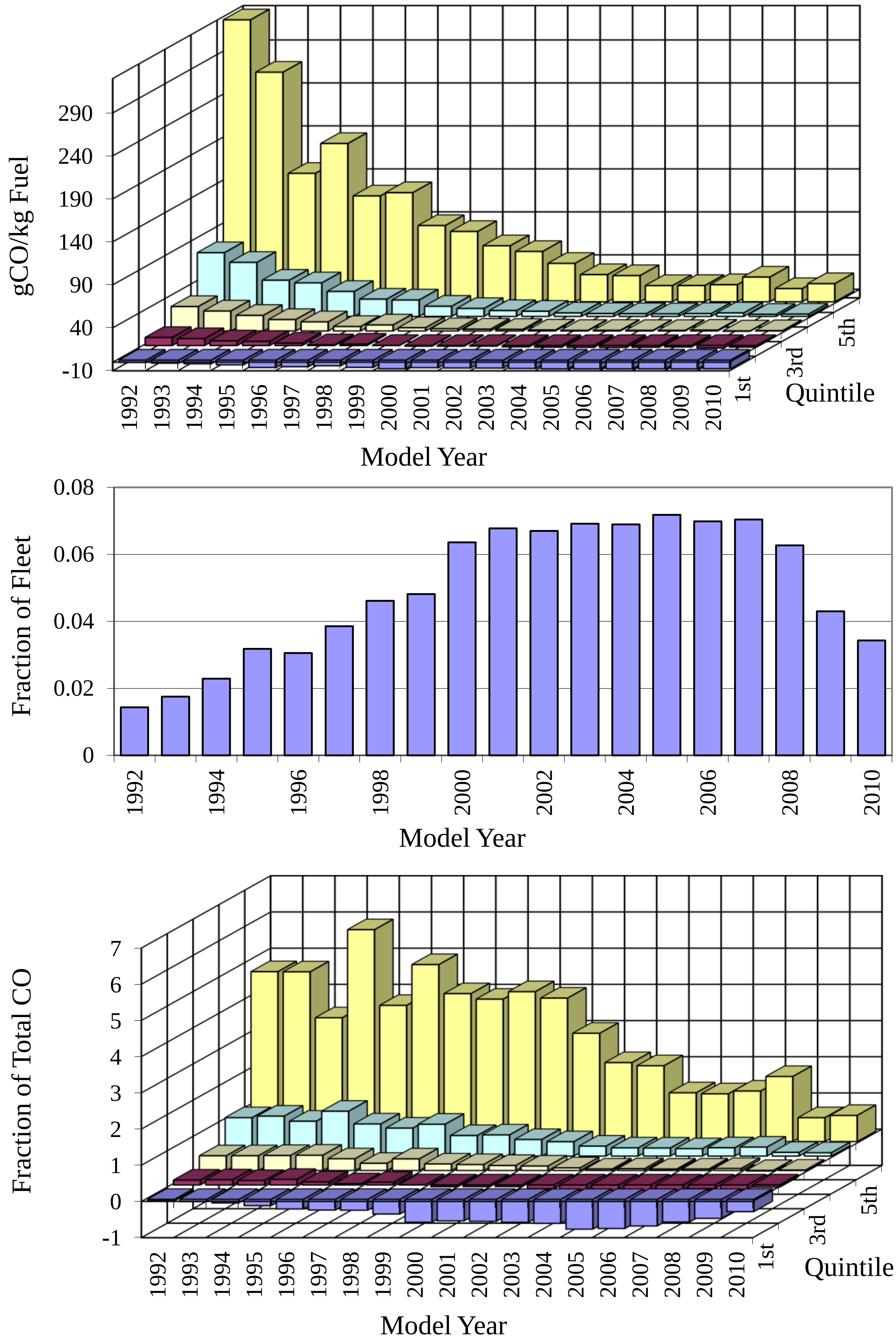


Figure 5. 2010 Van Nuys CO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional CO emissions by model year and quintile (bottom).

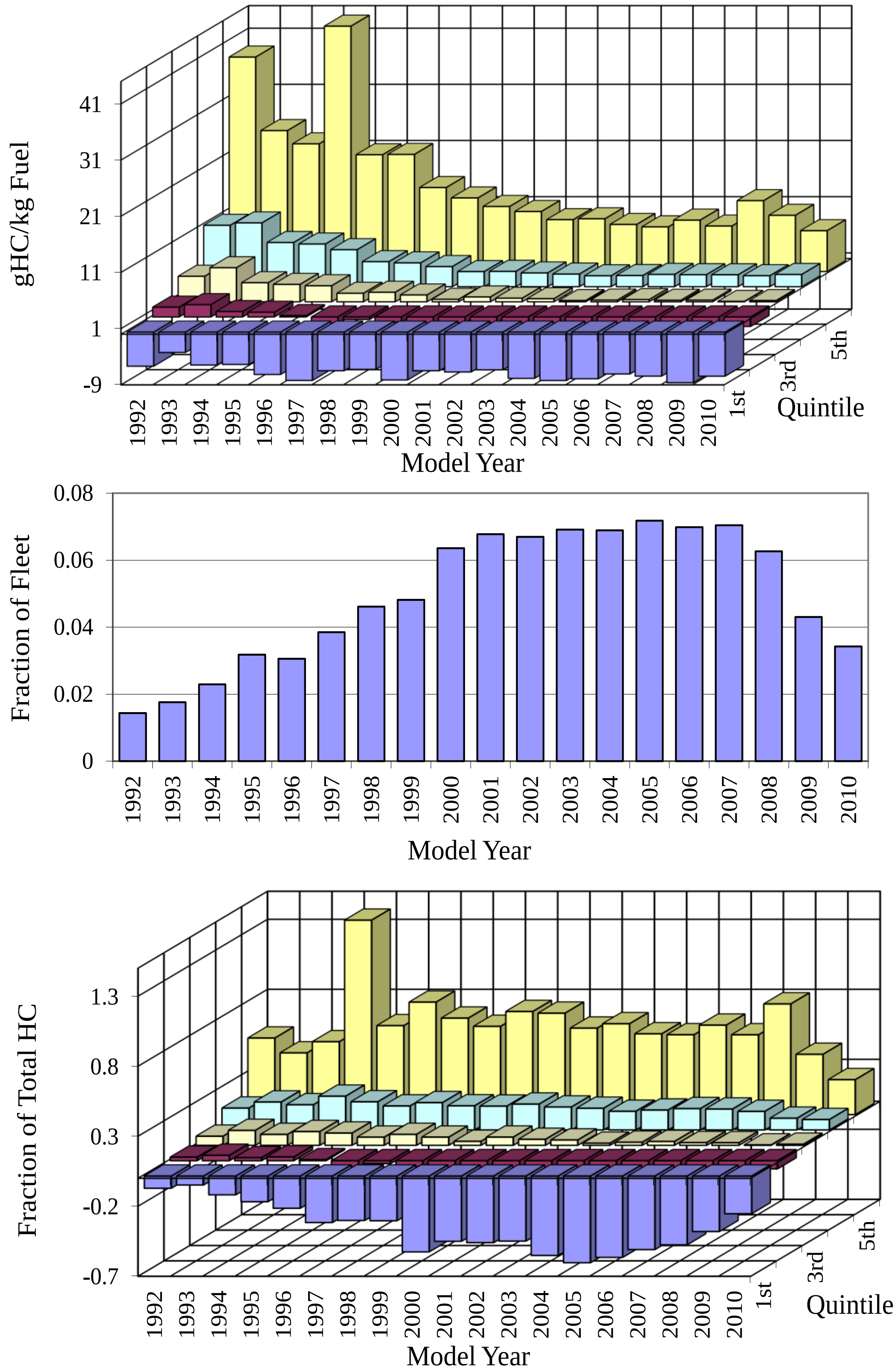
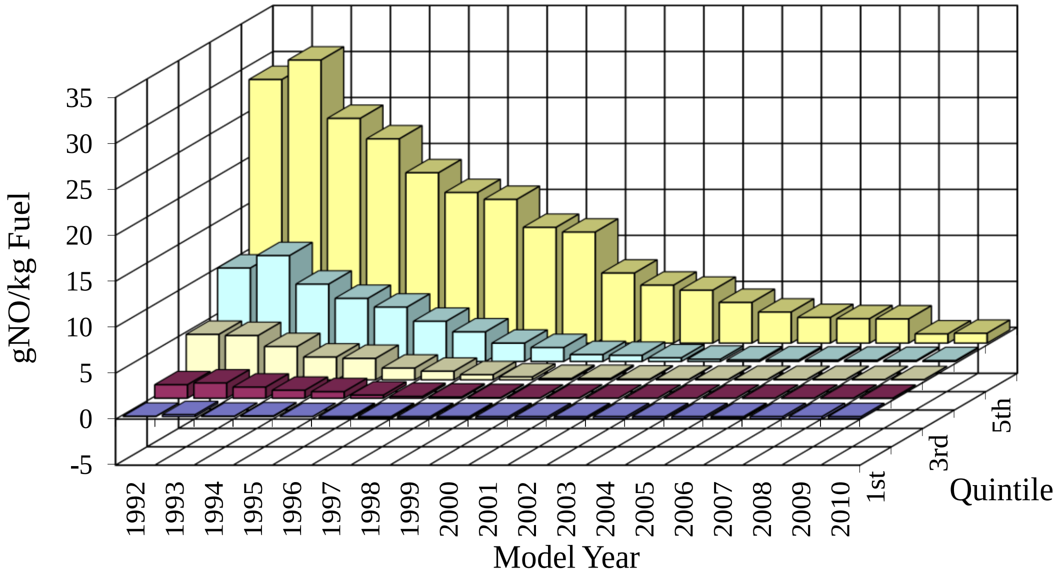
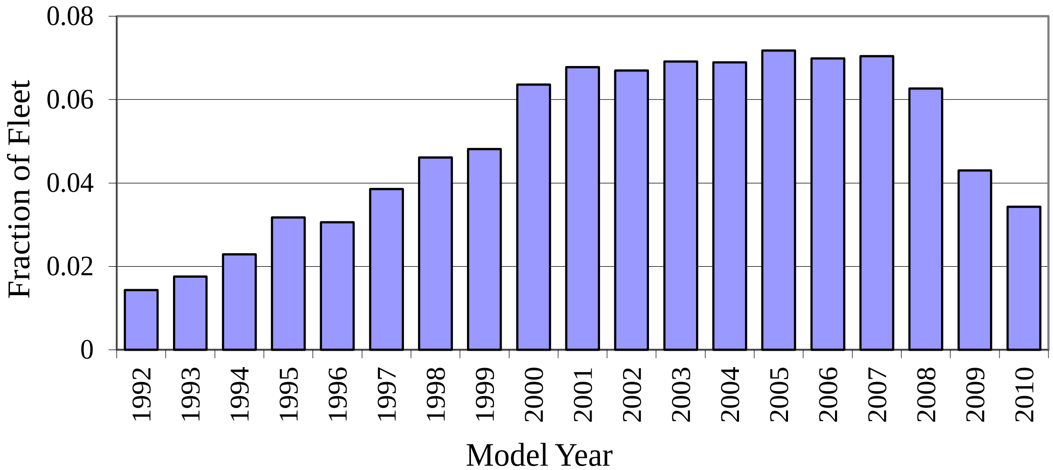


Figure 6. 2010 Van Nuys HC emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional HC emissions by model year and quintile (bottom).





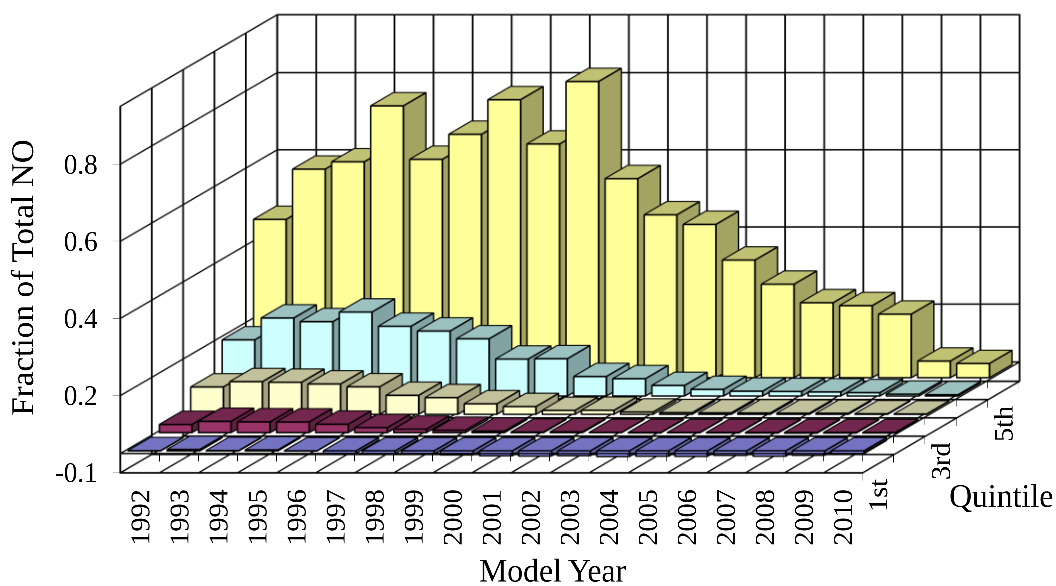


Figure 7. 2010 Van Nuys NO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional NO emissions by model year and quintile (bottom).

emission plume, half of the readings will be negative and half will be positive. As the lowest emitting segments of the fleets continue to dive toward zero emissions, the negative emission readings will continue to grow toward half of the measurements.

Figures 5 - 7 can also be used to get a picture of federal compliance standards. The on-road data are measured as mass emissions per kg of fuel. It is not possible to determine mass emissions per mile for each vehicle because the instantaneous gasoline consumption (kg/mile) is not known. An approximate comparison with the fleet average emissions shown in Figures 5 - 7 can, however, be carried out. To make this comparison, we assume a fuel density of 0.75 kg/L and an average gas mileage for all model years of 23 mpg. The Tier 1, 100,000 mile standards for CO, HC, and NO are 4.2, 0.31, and 0.6 gm/mi, respectively. With the above assumptions, these correspond to 34, 2.5, and 4.9 gm/kg fuel burned, respectively. Inspection of Figures 5 - 7 shows that significant fractions, especially of the newer vehicles, are measured with on-road, hot stabilized emissions well below these standards.

One additional observation can be made from the middle graph in Figures 5 – 7 of the fleet fraction as a function of model year. The 2001 – 2002 recession is not really noticeable at this location but the decrease in 2008 and 2009 model year vehicles in the fleet is striking. This is likely a major reason as to why the average age of the Van Nuys fleet is about 2 years older on average than the 2008 West LA fleet. The 2010 model year is likely not fully populated at the time of these measurements, given that the study was conducted in August 2010, but will still likely be lower than pre-recession levels.

An equation for determining the instantaneous power of an on-road vehicle has been proposed by Jimenez,[22] which takes the form

$$\mathrm{VSP} = 4.39 \bullet \sin(slope) \bullet v + 0.22 \bullet v \bullet a + 0.0954 \bullet v + 0.0000272 \bullet v^3 \qquad (4)$$

where VSP is the vehicle specific power in kW/metric tonne, *slope* is the slope of the roadway (in degrees), v is vehicle speed in mph, and a is vehicle acceleration in mph/s. Derived from dynamometer studies, and necessarily an approximation, the first term represents the work required to climb the gradient, the second term is the $f = ma$ work to accelerate the vehicle, the third is an estimated friction term, and the fourth term represents aerodynamic resistance. Using this equation, VSP was calculated for all measurements in the database. This equation, in common with all dynamometer studies, does not include any load effects arising from road curvature. The emissions data were binned according to vehicle specific power, and illustrated in Figure 8. All of the specific power bins contain at least 75 measurements. The HC data have been offset adjusted for this comparison.

A major characteristic of the modern, low-emission deteriorating vehicle is its emission insensitivity to VSP. With the exception of NO, where NO slowly increases with increasing VSP, the CO and HC emissions are consistently low across all of the VSP bins. The error bars included in the plot are standard errors of the mean calculated from the daily averages. These uncertainties were generated for these γ-distributed data sets by applying the central limit theorem. Each day's average emissions for a given VSP bin were assumed an independent

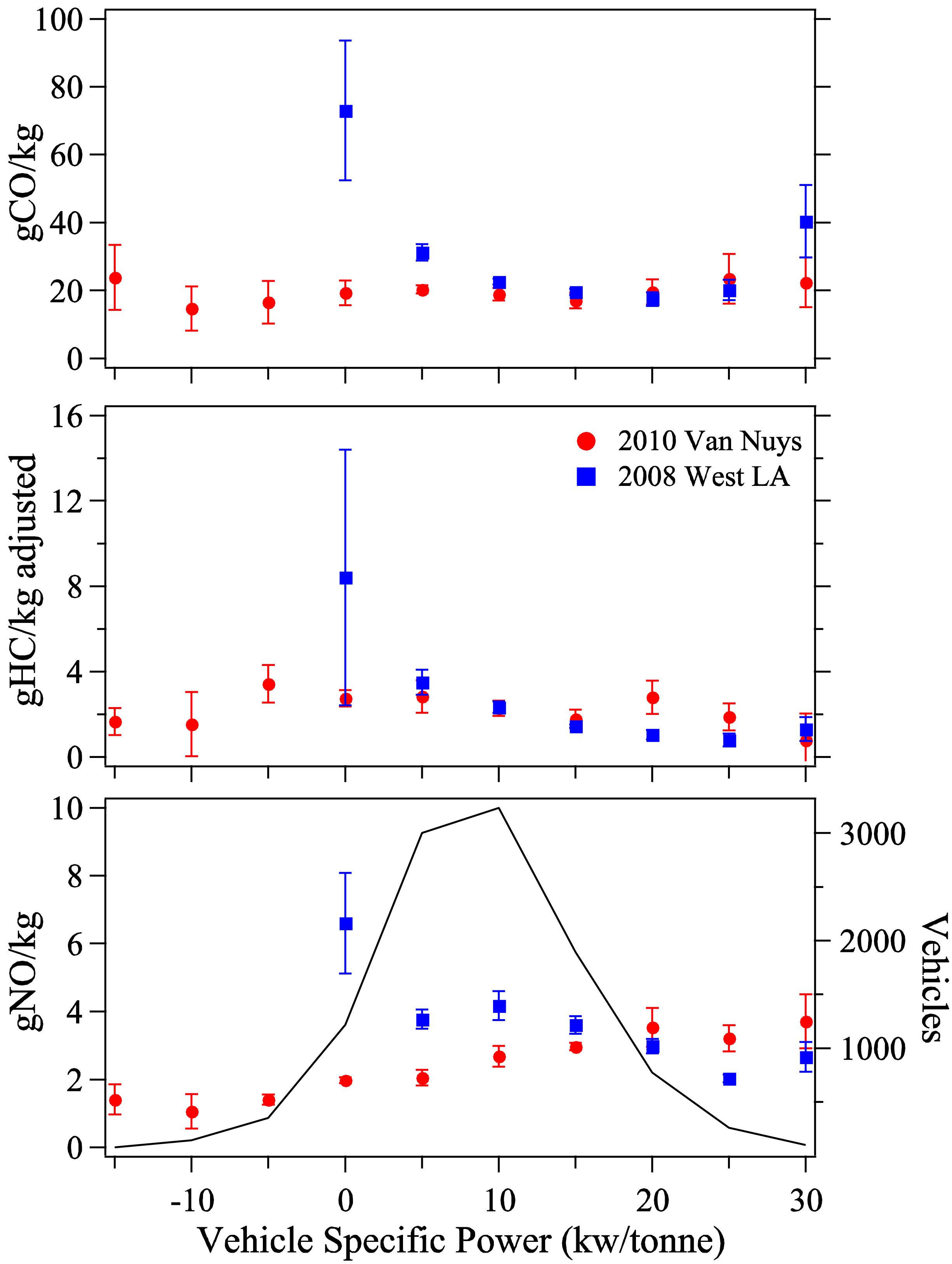


Figure 8. Vehicle emissions as a function of vehicle specific power for the 2010 Van Nuys and 2008 West LA data sets with valid speed and acceleration measurements. Error bars are standard errors of the mean calculated from daily samples and the solid line in the bottom graph is the number of vehicles in each bin for the 2010 Van Nuys data.

measurement of the emissions at that VSP. Normal statistics were then applied to these daily averages.

Figure 9 is a simlar plot of the emissions of SO_2, NH_3 and NO_2 as a function of VSP for the Van Nuys measurements. The error bars included in the plot are standard errors of the mean calculated from the daily averages. NH_3 is the only species to show any dependence on driving mode with a positive dependence on VSP very similar to that seen for NO (see Fig. 8).

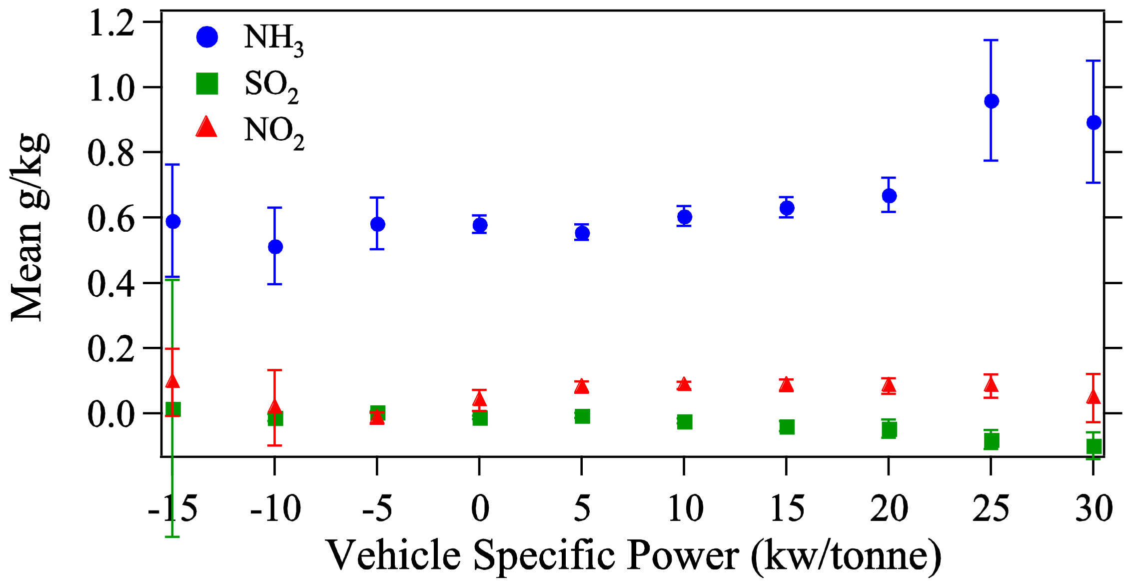


Figure 9. Van Nuys mean emissions as a function of vehicle specific power. The errors are standard errors of the means calculated from the daily means.

In the manner described in the CRC E-23 Phoenix, Year 2 report, instrument noise was measured using the slope of the negative portion of a plot of the natural log of the binned emission measurement frequency versus the emission level.[23] Such plots were constructed for all the species measured. Linear regression gave best fit lines whose slopes correspond to the inverse of the Laplace factor, which describes the noise present in the measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to fully describe the level of noise present. The Laplace factors were 5.0, 4.1, 0.1, 0.09, 0.01 and 0.2 for CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These values indicate standard deviations of 7.0 g/kg (0.06%), 5.7 g/kg (137ppm), 0.2 g/kg (12ppm), 0.13 g/kg (5ppm), 0.015 g/kg (3ppm) and 0.3 g/kg (15ppm) for individual measurements of CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These levels are consistent with the low noise level.[23] In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with averages of 100 measurements, which is the low limit for number of measurements per bin, the uncertainty reduces by a factor of 10. Thus, the uncertainties in the averages of 100 measurements reduce to 0.7 g/kg, 0.6 g/kg, 0.02 g/kg, 0.01 g/kg, 0.002 g/kg and 0.03 g/kg, respectively.

DISCUSSION

As fleet vehicle emissions levels have continued to decrease in the United States the emission distributions have become more skewed than previously reported. This has resulted in fewer and fewer vehicles being responsible for a majority of the emissions. Since it is impossible for us to successfully measure and record every vehicle that passes our sampling site we are always concerned about how representative the sample is that we are able to collect. For this study we used extra codes to tag vehicles that had unreadable plates to compare their emissions with the final data set. The category of vehicles included 1) unreadable blue or black California plates (these are the oldest California plates, though not necessarily exclusively on older vehicles since the plates can be transferred with the owner to a newer in-use model, and the yellow letters on a blue or black background are often impossible to read), 2) motorcycles, 3) vehicles with a visible plate holder and no plate (this includes a number of new and newly purchased used cars), 4) out-of-state plates, 5) school buses with unreadable plates, and 6) California-plated vehicles with unreadable plates (the plate is only partially in view but is definitely a California plate).

Table 4 tabulates the emission comparison between the matched data set, the six groups of vehicles with unreadable plates and all the valid measurements (this includes the readable plates plus the six unreadable groups). Several broad generalizations can be made from the comparison; 1) The Unreadable Blue Plates are likely older vehicles (higher CO) than the matched data set, 2) The No Plate grouping is likely much newer (all species lower) than the matched data set, 3) The Unreadable Plate grouping is likely to contain a larger fraction of diesel vehicles (NO and NO_2 higher) than the matched data set and the School Bus Unreadable appears to be a mix of natural gas (likely with three-way catalyst use as the NH_3 is elevated) and diesel while the Bus Matched group seems to have few diesels (this group contains transit buses as well as school buses). The Motorcycles group (motorcycles generally have small exhaust plumes and are not measured at the same frequency as other vehicles) generally represent uncontrolled emissions that when their higher fuel economy is taken into account likely do not represent as large an emissions source as indicated in Table 4.

One question that needs to be asked is whether any of these groups that have been left out of the Matched Plates results in a statistically significant bias in the final emission means. The standard errors of the means given for the Matched Plates range from ± 6.5% for CO to ± 30% for NO, SO_2 and NH_3. Individually the Unreadable Plates group is the only one with enough vehicle measurements to potentially affect the final means. Within that group the fraction of the final emissions are 3.6%, 3.9%, 6.9%, 4.1%, 1.3% and 21% for CO, HC, NO, SO_2, NH_3, NO_2 respectively. Only the NO_2 emissions approach a large enough fraction to be seen in the final means, however, even for this species the accompanying change is still within the standard error of the original means estimate. The All Valid Measurements grouping combines all of the unidentified vehicles and shows slight but statistically insignificant increases in most of the emission means. The reasons for the increases change depending on the species. For CO and HC the increases are driven by the inclusion of the motorcycle data, the NO and NO_2 means increase due to the inclusion of the Unreadable Plate group and its likely higher concentration of diesel vehicles. In the end this analysis shows that within the standard errors of the means reported in Table 4 the exclusion of the unidentified vehicles has not resulted in any statistically significant bias.

Table 4. Emissions comparison between vehicle subgroups and the final matched data set. Errors are standard errors of the means determined from the daily averages.

Plate Type Category	Mean gCO/kg (Count)	Mean gHC/kg (Count)	Mean gNO/kg (Count)	Mean gSO_2/kg (Count)	Mean gNH_3/kg (Count)	Mean gNO_2/kg (Count)
Unreadable Blue Plates	71.0 (34)	13.7 (34)	11.6 (34)	0.05 (34)	0.3 (33)	0.4 (33)
Motorcycle	260.1 (32)	25.4 (32)	8.5 (32)	0.2 (32)	0.5 (32)	0.3 (27)
No Plate	4.6 (347)	1.7 (346)	0.7 (347)	-0.01 (347)	0.4 (347)	0.04 (335)
Out of State	15.1 (283)	2.0 (283)	2.6 (283)	-0.03 (283)	0.6 (283)	0.1 (281)
School Bus Unreadable	32.3 (15)	13.0 (15)	5.3 (15)	0.01 (15)	1.6 (14)	1.0 (15)
Bus Matched	36.6 (32)	30.7 (31)	2.4 (31)	0.02 (31)	0.4 (31)	0.4 (29)
Unreadable Plates	32.1 (286)	5.2 (283)	8.2 (286)	-0.05 (284)	0.4 (285)	0.9 (274)
Readable Plates	19.7 (13011)	2.9 (12979)	2.6 (13009)	-0.03 (13010)	0.6 (12985)	0.09 (12749)
All Valid Measurements	20.2 ± 1.2 (14008)	3.0 ± 0.3 (13972)	2.7 ± 0.1 (14006)	-0.02 ± 0.01 (14005)	0.6 ± 0.02 (13979)	0.1 ± 0.02 (13714)
Matched Plates	19.7 ± 1.3 (12963)	2.9 ± 0.3 (12931)	2.6 ± 0.08 (12961)	-0.03 ± 0.01 (12962)	0.6 ± 0.02 (12937)	0.09 ± 0.02 (12703)

Just to the east of our measuring location on Sherman Way is a tunnel that goes under a runway at the Van Nuys Airport. This tunnel has been used on two previous occasions for measuring the emissions of vehicles traveling on Sherman Way allowing for a historical comparison with our data. Ingalls *et al.* measured gram/mile emission factors for CO, HC and NO_x in the fall of 1987 and Fraser and Cass measured gram/liter emission factors for CO, HC and NH_3 in the fall of 1993.[5,24] Table 5 compares the measured emission rates from those two studies with these measurements. The comparisons show large reductions in CO and HC emissions that have been confirmed by many other studies. Ingalls *et al*. did not measure CO_2 so the comparisons are made between mass ratios of CO and HC to NO_x. They also did not estimate a fleet age for their measurements. The reductions in those ratios are not necessarily linear because all the species have been decreasing, though not at the same rate. Fraser and Cass did not measure NO_x emissions but did measure CO_2 and report fuel-specific emissions.

The 2010 ammonia measurements show a statistically significant increase since 1993 when the fleet measured was estimated to only have 76% of the fuel burned in the tunnel by vehicles equipped with three-way catalysts. If we assume that the ammonia emissions of those vehicles would linearly scale to a fleet fully equipped with three-way catalytic convertors we would have 0.5 grams of NH_3 per liter of fuel, very similar to the 2010 measurements. Mass per mile

Table 5. Historical Sherman Way emission comparisons.

Study Year	CO/NO_x [a]	HC/NO_x [a]	gCO/liter [b]	gHC^c/liter [b]	gNO_x^a/liter [b]	gNH_3/liter [b]	Mean Model Year
1987	13.3	1.7	NA	NA	NA	NA	NA
1993	NA	NA	130	9.1	NA	0.38	1986.4
2010[d]	4.8	0.7	14.9 ± 1	1.5 ± 0.2	3.1 ± 0.4	0.46 ± 0.02	2001.5

[a] Mass ratios and moles of NO_2.
[b] Fraser and Cass assumed a carbon weight fraction of 0.87 and a gasoline density of 750 g/L.
[c] grams of carbon.
[d] Errors are standard errors of the means calculated from the daily means.

emission rates for NH_3 will depend on how the fuel consumption rates may or may not have changed along Sherman Way. While we would expect the light-duty car fleet to have increased in fuel economy the shift during the 1990s to more light-duty trucks will negate some of that increase. Recently Kean *et al.* documented NH_3 emissions decreasing at the Caldecott tunnel by 38 ± 6% since 1999.[25] Two points in time can only make a straight line but reveal nothing about the path the NH_3 emissions have followed in between leaving one to wonder whether the reductions observed at the Caldecott tunnel should be uniformly expected or are they specific to that driving mode, fleet type and age. In addition the ageing of the Van Nuys fleet, as indicated by the fleet fraction reductions of the 2008 and 2009 models, has likely resulted in an increase of NH_3 emissions at this site.

The Van Nuys data set incorporates a number of differences that set it apart from most of the remote sensing data sets that we have previously collected. The measurement site on Sherman Way is a major connector street that is not near any of the major freeways in the area. Many of our previous data sets have been collected at on- or off-ramps to major freeways. The time constraints of the County of LA permit precluded the measurements of vehicles during the morning and afternoon rush hours. This works to eliminate most commuters and generally reduces the number of repeat measurements on the same vehicle. The data in Table 2 generally bear this out. Finally we have very few data sets that contain data from the weekend days. Generally these have been viewed as lower traffic days (less commuting) and therefore our efforts have been concentrated on week days to maximize the number of vehicles measured and minimize the number of days needed to collect that data.

Because weekday and weekend traffic differences have been implicated in many metropolitan areas as being a driver for differences in resulting ozone precursor levels as part of this study we measured differences in the light-duty fleet for these days.[26] Table 6 is an emission comparison table that groups the data into week day (Thursday, Friday and Monday) and weekend (Saturday and Sunday) sets. The comparison shows that the weekend traffic is slightly older (0.4 model years) and higher emitting for CO and HC but that traffic volume is essentially identical on a per hour basis to the week day measurements. The gNO/kg fuel burned data do not follow the model year differences due to the fact that the fraction of diesel vehicles is higher for weekdays (~1.7%) than on the weekend days (1.2% on Saturday and 0.6% on Sunday), and this compensates for the lower NO emissions from the slightly newer fleet.

Table 6. Comparison of Mean Emissions for the Weekday and Weekend Data Collection.

	Mean gCO/kg	Mean gHC/kg	Mean gNO[a]/kg	Mean gSO_2/kg	Mean gNH_3/kg	Mean gNO_2/kg	Mean Model Year	Counts (hours)
Week Day	18.2	2.4	2.6	-0.04	0.6	0.1	2001.7	6757 (15)
Weekend	21.3	2.5	2.6	-0.01	0.6	0.06	2001.3	6206 (13.8)

[a] moles of NO

The matched data provided by the California DMV included fuel type which includes a special designation for hybrid drive train vehicles. Previous data from the West LA site had suggested that there might be a difference in HC emissions between hybrid and standard combustion engine vehicles.[27] Table 7 contains the mean species emissions for the hybrid vehicles in the database and age-adjusted composite emissions for the remaining vehicles identified as being fueled by either gasoline or natural gas (only 11 vehicles for this age range). The age adjustment is constructed by using the mean emissions by model year for the other vehicles and then weighting those means accorded to the age distribution of the hybrid vehicles. Although the HC and SO_2 emissions are higher for the hybrid vehicles, neither of those differences is statistically significant when using the standard errors of the mean calculated from the daily means. There still are not enough hybrid vehicles in operation to say with certainty that their on-road fuel specific HC emissions are higher than conventional vehicles. However, with this second observation of higher on-road HC emissions the likelihood that this is a correct observation increases.

Table 7. Comparison of Hybrid Vehicle Mean Emissions versus an Age Adjusted Rest of the Fleet.

Fleet	Mean gCO/kg	Mean gHC/kg	Mean gNO[a]/kg	Mean gSO_2/kg	Mean gNH_3/kg	Mean gNO_2/kg	Mean Model Year	Counts
Hybrids	-0.8 ± 0.5	0.8 ± 0.9	0.3 ± 0.07	0.002 ± 0.02	0.2 ± 0.04	0.02 ± 0.02	2007.3	143
Gasoline	2.5 ± 0.2	0.29 ± 0.03	0.3 ± 0.01	-0.01 ± 0.003	0.36 ± 0.01	0.04 ± 0.01	2007.3	7861

[a] moles of NO

The production of NH_3 emissions is contingent upon the vehicles' ability to produce NO in the presence of a catalytic convertor that has enough stored hydrogen to reduce that NO to NH_3. Without either of these species the formation of exhaust NH_3 is precluded. Dynamometer studies have shown that these conditions can be met when acceleration events are preceded by a deceleration event though not necessarily back to back.[28] Though the Sherman Way site is not typical of that driving mode, the gasoline fleet is still producing significant amounts of NH_3. Previous measurements at three locations in California in the spring of 2008 resulted in a fleet average gNH_3/kg of 0.58 ± 0.04 which is statistically identical to our Van Nuys measurements.[18,19] Figure 10 shows composite gNH_3/kg emissions as a function of model year

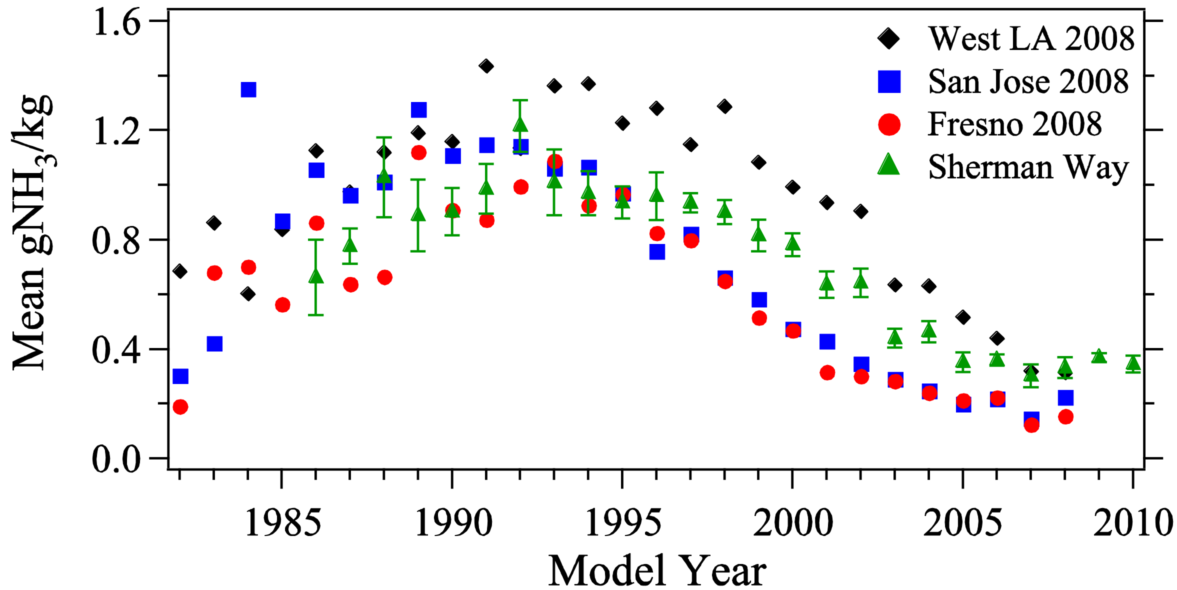


Figure 10. Mean gNH_3/kg emission averages as a function of model year comparison for the three 2008 California measurement sites and the 2010 Van Nuys measurements. Error bars are standard errors of the mean calculated from the daily measurements.

for these studies. The error bars plotted for the Van Nuys data are standard errors of the mean calculated from the daily averages.

The limited number of in-use light-duty NH_3 emissions data sets means we are likely to see slightly different model year dependence with each new location. That is the case for the Van Nuys measurements, while the shape of the model year dependence and the emissions average is very similar to the other California cities, the mean emissions of the newest model year vehicles fall between those of a very high load West LA site and the lower speed uphill cruise modes of San Jose and Fresno. The vehicles measured at the Van Nuys site are about 2.5 model years older than the same model years measured at the other California sites.

On-road ammonia emissions have been previously reported by Fraser and Cass (see previous discussion) and Baum *et al.* for a Los Angeles site of 0.35 g/kg in 1999, by Burgard *et al.* in 2005 from gasoline-powered vehicles to be 0.47 ± 0.02 and 0.51 ± 0.01 for sites in Denver and Tulsa and by Kean *et al.* from the Caldecott Tunnel in the San Francisco area in 2000 and 2006 at 0.64 ± 0.04 and 0.4 ± 0.02 g/kg.[5,25,29-31] Most recently we have reported on 2008 measurements of ammonia means of 0.49 ± 0.02, 0.49 ± 0.01 and 0.79 ± 0.02 for the three California sites of San Jose, Fresno and West LA respectively.[18,19] The Denver and Tulsa measurement sites where curved uphill interchange ramps that had similar driving modes to those observed in San Jose and Fresno.

Figure 10 shows San Jose and Fresno have peak NH_3 emissions that are very similar to those observed at Van Nuys. However, at Van Nuys the newer model year vehicles are consistently higher and less skewed than either of those sites with the newest model year emissions similar to those at the high load West LA site. After the first fifteen model years the reducing capacity of the catalyst begins to decline and the data from all of the sites, while noisy due to a shrinking number of vehicles, starts to merge and decrease at similar rates.

When the data were collected for the three previous California locations the higher emissions at the West LA site were believed to a direct result of the high load, stop-and-go driving mode at that traffic light controlled on-ramp. The Van Nuys data set suggests that there are other driving modes that result in elevated levels of NH_3 emissions. While the cruise modes observed on Sherman Way bear no resemblance to the driving modes at the West LA site, the data bear more resemblance to the West LA data than the other two sites. A busy surface street like Sherman Way will likely result in foot-on and foot-off-the-throttle driving to maintain speed and spacing, and that might be a possible explanation why the NH_3 emissions are more like the high acceleration site for the newest model years. In contrast at most of the other sites, with on-road NH_3 emissions data, the uphill nature of the sites dictates a more stable throttle position.

Figure 11 shows the mass in g/kg of NO_x and NH_3 emissions against model year for the last 22 model years. NO_x emissions have been calculated by converting the measured gNO/kg into gNO_2/kg and summing with the measured gNO_2/kg emissions. The gNO_x/kg means have been plotted on a scale that generally allows them to overlap with the gNH_3/kg emissions to highlight any similar emissions trends. Again the emission rates for NO_x and NH_3 observed at the Van Nuys site are more similar to those observed at the high load West LA site. In San Jose the NH_3 and NO_x emissions are decreasing at a similar rate over the latest 10 model years. When the reducing capabilities of the catalytic converters diminish, the NO_x emissions dominate. For all of the data sets this occurs around the 1996 – 1997 model year, though those models are 2.5 years older for the Van Nuys data.

The percent ammonia of the total fixed nitrogen was analyzed to see if the percentage of ammonia increased while the total fixed nitrogen decreased with age, as shown in the Burgard *et al.* analysis of the Tulsa and Denver fleets.[30] The gNO_x/kg was calculated by converting gNO/kg to gNO_2/kg and summing the two. The percent of ammonia in the total fixed nitrogen, in g/kg, was calculated as shown by Burgard *et al.*[30] All of the N factors were converted to mole/kg.

$$\text{Molar \% NH}_3\text{ in total fixed nitrogen} = \frac{100 \text{ x } N_{NH_3}}{N_{NH_3} + N_{NO_x}} \qquad (5)$$

Figure 12 compares the results of these calculations for the San Jose, West LA and Van Nuys sites. The molar $\%NO_x$ and $\%NH_3$ add to 100% and are percentages of the gN_2/kg values plotted by model year. The noise increases for the molar percentages in newest model years because of the diminishing amount of fixed nitrogen emissions. The total fixed nitrogen species have decreased over the last 22 model years at Van Nuys; however, the percent contributed by ammonia (the circles) has increased. While the total fixed nitrogen levels at Van Nuys are nearly identical to those observed in 2008 in San Jose how those nitrogen emissions are distributed between NH_3 and NO_x is more similar to the West LA site.

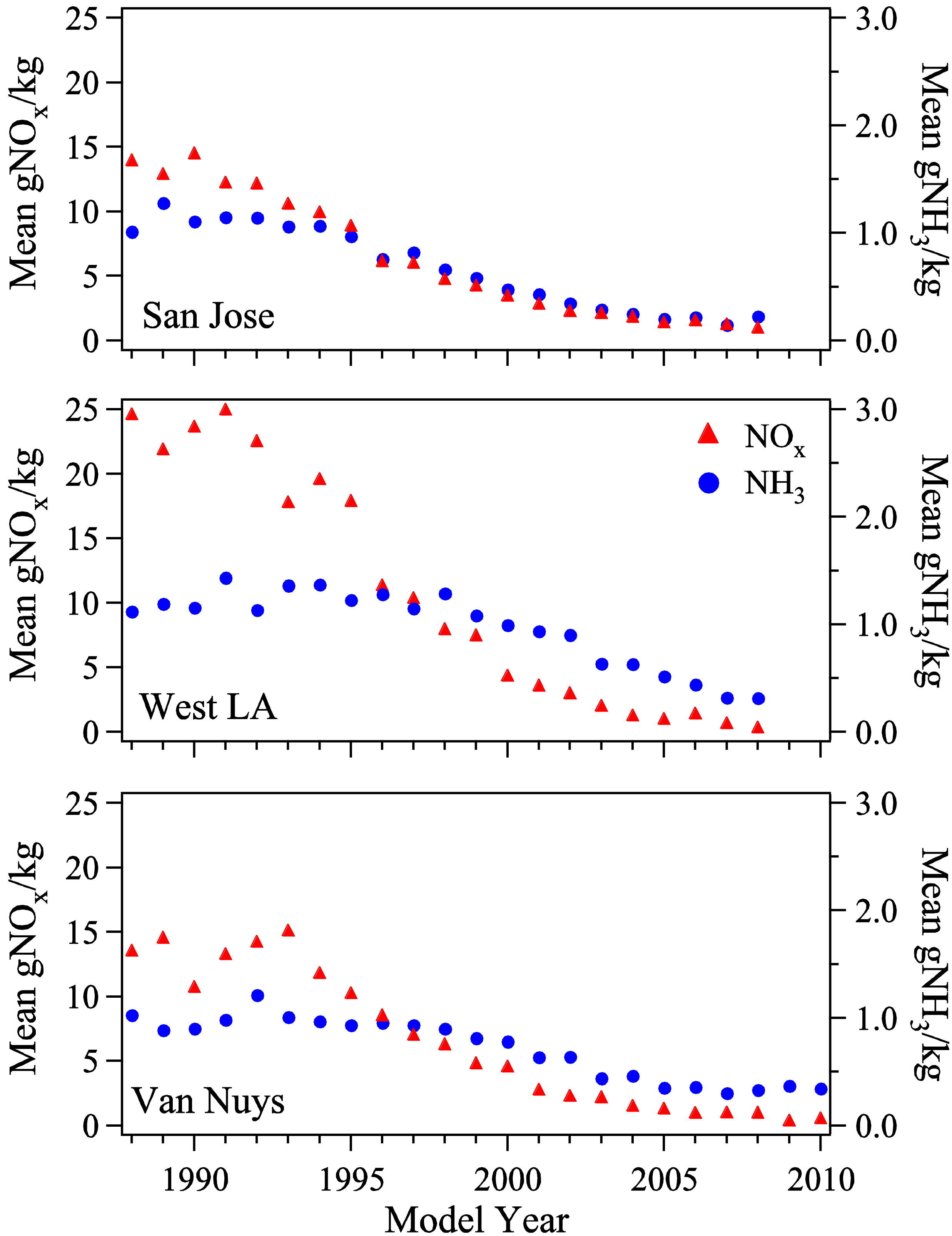


Figure 11. Mean gNO$_x$/kg (triangles, left axis) and gNH$_3$/kg (circles, right axis) emissions as a function of model year for Van Nuys and two of the 2008 California measurement sites.

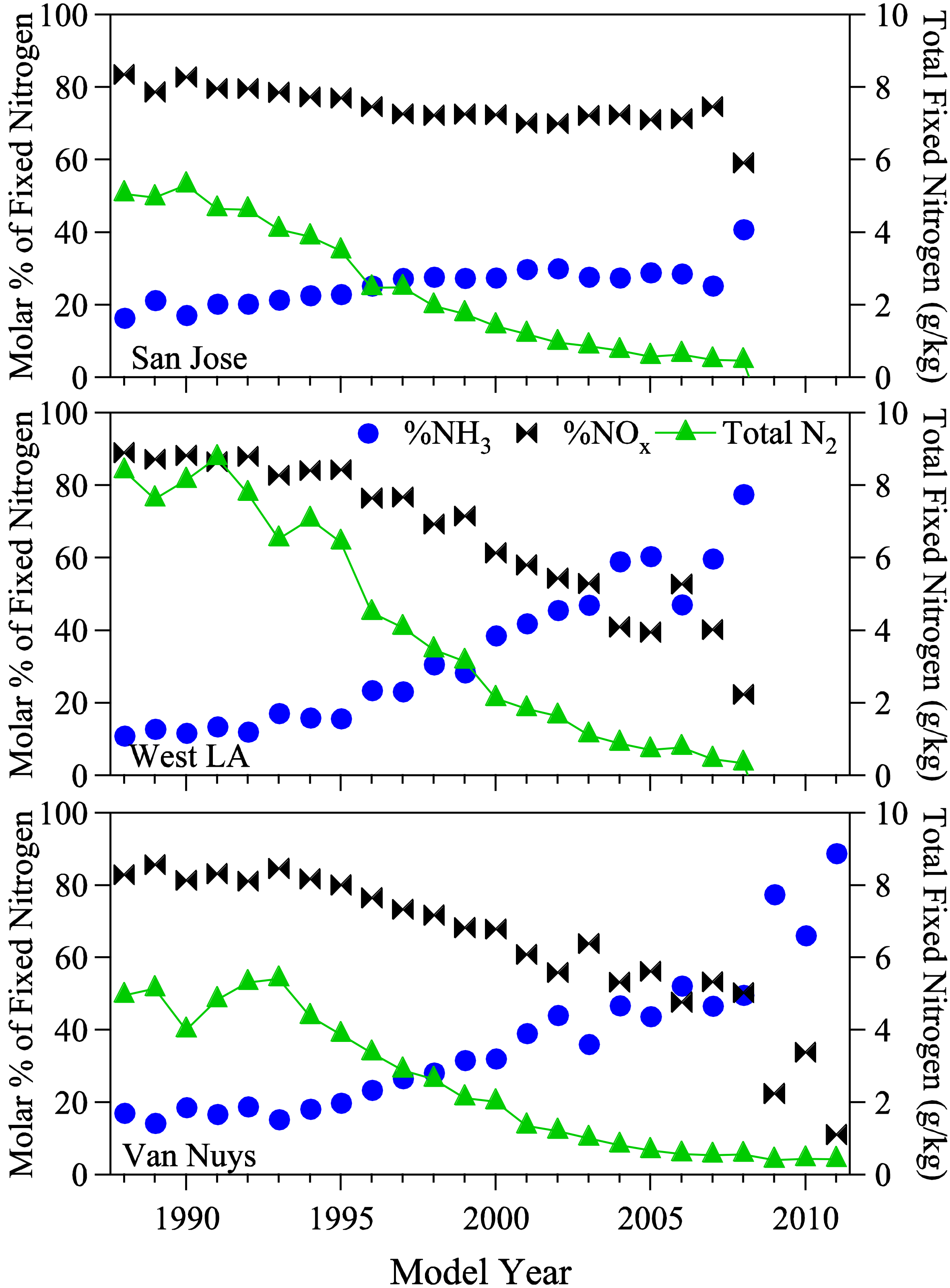


Figure 12. Total fixed nitrogen in g/kg (triangles, right axis) with the molar percent composition distributed between the NO_x (bowties, left axis) component and the NH_3 component (circles, left axis).

CONCLUSIONS

The University of Denver completed an on-road remote sensing study of motor vehicle emissions for the first time at a site on eastbound Sherman Way in Van Nuys, California, about 0.4 mile west of the Van Nuys airport tunnel. Measurements were made on five consecutive days, from Thursday, August 12, through Monday, August 16, between the hours of 9:00 and 15:30. At the measurement site, Sherman Way is a divided six-lane surface street. The middle lane of the eastbound lanes was closed for approximately 2.5 blocks before the monitoring location, forcing traffic into the inside and outside lanes. The instrument was set up just east of Whitaker Ave. across a single eastbound lane that was closest to the curb. We compiled a database that contains 12,963 records for which the State of California provided registration information. All of these records contained valid measurements for at least CO and CO_2, and most of the remaining records contained valid measurements for HC, NO, SO_2, NH_3 and NO_2. After the final report is completed for the Van Nuys Tunnel Study, which was conducted in August 2010 by the Desert Research Institute, the remote sensing database will be available from our website www.feat.biochem.du.edu.

The mean CO, HC, NO, SO_2, NH_3 and NO_2 were determined to be 0.16%, 67ppm, 186ppm, -0.7ppm, 75ppm and 4ppm (19.7 g/kg, 2.5 g/kg, 2.6 g/kg, -0.03 g/kg, 0.6 g/kg and 0.09 g/kg fuel burned) respectively. The regulated fleet emissions measured in this study exhibit a gamma distribution with the minority of the measurements responsible for the majority of the emissions. The highest emitting 10% of the measurements were responsible for 86%, 90% and 72% of the CO, HC and NO emissions respectively. One particularly egregious case is a 1995 model that alone is responsible for 5.6% of the entire fleet's measured HC emissions (three HC measurements of 1.291%, 1.367% and 2.896%; for comparison the average two-stroke snowmobile measured in Yellowstone Park in 1999 averaged 2.4%). The following table details some of the emission statistics for the six species measured and for CO, HC, NO and NH_3 highlights the skewed nature of the on-road fleet's emissions distributions.

Summary of Emission Statistics from Sherman Way in Van Nuys, August 12-16, 2010.

	%CO	HC (ppm)	NO (ppm)	SO_2 (ppm)	NH_3 (ppm)	NO_2 (ppm)
Mode	0	20	1	0	3	2
Median	0.02	30	12	-0.5	26	2
Mean	0.16	67	186	-0.7	75	4
Mean Percentile*	83	68	79	11	73	56

*Percentile in which the mean emission rate is found when the fleet emissions are rank-ordered from clean to dirty.

A historical comparison between these measurements and two past measurement campaigns in the nearby Van Nuys tunnel (in 1987 by Ingalls *et al.* and in 1993 by Fraser and Cass) show large reductions in CO and HC emissions. CO and HC gram/liter emissions of 130 and 9.1 (grams of carbon) as measured in 1993 have decreased to 15 and 1.5 grams/liter as measured in this study. CO/NO_x mass ratios have dropped from 13.3 in 1987 to 4.8 in the current work and HC/NO_x ratios have decreased from 1.7 to 0.7 for the same period. These reductions are consistent with U.S. light-duty emissions reductions reported by other researchers in the U.S.

These are the first light-duty measurements which we have collected since the large economic downturn that began in 2008. The fleet age distribution shows that relative to the 2006 and 2007 fleet fractions, the 2008 model year dropped about 10% while the 2009 model year fraction is lower by almost 40%. This undoubtedly has increased the age of the Van Nuys fleet with the average model year of 2001.5 being similar to the average model year of 2001.3 that was measured at a nearby West Los Angeles remote sensing monitoring site in March of 2008.

Unlike many of our measurements this data set includes measurements collected over a weekend. While traffic volumes were overall very similar the weekend traffic was slightly older (0.4 model years) and higher emitting for CO and HC. The NO_x emissions were not lower for the younger weekday fleet owing to the larger fraction of diesel vehicles for the week days (~1.7%) than on the weekend days (1.2% on Saturday and 0.6% on Sunday).

With this data set we report for a second time that the on-road fuel specific HC emissions of hybrid vehicles appear to be higher (almost a factor of 3 higher in this study) than similarly aged conventional vehicles. Due to the small number of hybrid vehicles (143 vehicles in this data set and 82 vehicles in the previous data set) the differences are not statistically significant, but confirmation of the previous observation (a factor of 4 higher) adds credence to there being a difference between the two fleets. Now we are not claiming that hybrid vehicles constitute a significant fraction of the fleet's HC emissions, because they do not. However, these in-use differences, if correct are important when modeling for example fleet replacement scenarios that are currently popular. In those scenarios the actual in-use HC emissions of the replacement hybrids will be understated.

Ammonia emissions are thought to be heavily influenced by driving mode, and the Sherman Way site is the first time that we have measured a cruise driving mode on a level roadway. Nearly all of our previous remote sensing measurement locations have been some type of uphill on-ramp driving. Historically the 2010 mean NH_3 emissions of 0.0075% (0.6 g/kg) are very similar to the 1993 measurements by Fraser and Cass, when scaled to account for only 76% of the 1993 fleet having catalyst. When we compare the Van Nuys measurements to recent (March of 2008) measurements at three California sites we find that the Van Nuys measurements fall between the two lowest (San Jose and Fresno of 0.49 g/kg) and the highest (West LA of 0.81 g/kg) emissions sites. The most notable differences are observed in the most recent 10 model years where the Van Nuys measurements are significantly higher than the San Jose and Fresno measurements and behave more like the ammonia emissions observed at the high load West LA site. While the cruise modes observed on Sherman Way bear no resemblance to the driving modes at the West LA site, the data bear more resemblance to the West LA data than the other two sites. A busy surface street like Sherman Way likely will result in foot on and foot off-the-throttle driving to maintain speed and spacing, and that might be a possible explanation why the NH_3 emissions are higher for the newest model years.

We also observed once again that as the reducing capacity of the catalyst starts to wane (around 15 years), driving mode becomes less important as all of the sites' ammonia emissions decrease with age at a similar rate. As NO_x emissions have decreased over the last twenty model years the amount of the total fixed nitrogen emissions have also decreased. However, the fraction of the fixed nitrogen emissions contributed by ammonia has increased.

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LITERATURE CITED

1. *National Air Quality and Emissions Trends Report, 2003 Special Studies Edition*, United States Environmental Protection Agency, Research Triangle Park, NC, 2003; EPA-454/R-03-005.

2. Spengler, J.D.; Koutrakis, P.; Dockery, D.W.; Raizenne, M.; Speizer, F.E. *Environ. Health. Perspec.* **1996,** *104,* 492-499.

3. Ghio, A.J.; Kim, C.; Delvin, R.B. *Amer. J. Resp. Crit. Care Med.* **2000,** *162,* 981-988.

4. Gauderman, W. J.; McConnell, R.; Gilliand, F.; London, S.; Thomas, D.; Avol, E.; Vora, H.; Behane, K.; Rappaport, E.B.; Lurmann, F.; Margolis, H.G.; Peters, J. *Amer. J. Resp. Crit. Care Med.* **2000,** *162,* 1383-1390.

5. Fraser, M.P.; Cass, G.R. *Environ. Sci. Technol.* **1998**, *32*, 1053-1057.

6. Battye, W.; Aneja, V.P; Roelle, P.A. *Atmos. Environ.* **2003,** *37,* 3873-3883.

7. Heywood, J.B. *Internal Combustion Engine Fundamentals.* McGraw-Hill: New York, 1988.

8. Lawson, D.R., *J. Air & Waste Manage. Assoc*. **1993**, *43*, 1567-1575.

9. Stedman, D.H.; Bishop, G.A.; Aldrete, P.; Slott, R.S. *Environ. Sci. Technol.* **1997**, *31*, 927-931.

10. Beaton, S.P.; Bishop, G.A.; Zhang, Y.; Ashbaugh, L.L.; Lawson, D.R.; Stedman, D.H. Science, 1995, *268*, 991-993.

11. Lefohn, A.S.; Shadwick, D.S.; Ziman, S.D. *Environ. Sci. Technol.* **1998**, *32*, 276A.

12. Bishop, G.A.; Stedman, D.H. *Acc. Chem. Res.* **1996**, *29*, 489.

13. Popp, P.J.; Bishop, G.A.; Stedman, D.H. *J. Air & Waste Manage. Assoc*. **1999**, *49*, 1463-1468.

14. Burgard, D.A.; Dalton, T.R; Bishop, G.A.; Starkey, J.R.; Stedman, D.H. *Rev. Sci. Inst.* **2006, 77**, 014101-1-014101-5.

15. Singer, B.C.; Harley, R.A.; Littlejohn, D.; Ho, J.; Vo, T. *Environ. Sci. Technol.* **1998**, *32*, 3241-3248.

16. Lawson, D.R.; Groblicki, P.J.; Stedman, D.H.; Bishop, G.A.; Guenther, P.L. *J. Air & Waste Manage. Assoc.* **1990**, *40*, 1096-1105.

17. Ashbaugh, L.L.; Lawson, D.R.; Bishop, G.A.; Guenther, P.L.; Stedman, D.H.; Stephens, R.D.; Groblicki, P.J.; Parikh, J.S.; Johnson, B.J.; Haung, S.C. In *PM10 Standards and Nontraditional Particulate Source Controls*; Chow, J.C., Ono, D.M., Eds.; AWMA: Pittsburgh, PA, 1992; Vol. II, pp. 720-739.

18. Bishop, G.A.; Peddle, A.M.; Stedman, D.H. *On-Road Motor Vehicle Emissions including NH_3, SO_2 and NO_2*, Final report to the California Air Resources Board, 2009.

19. Bishop, G.A.; Peddle, A.M.; Stedman, D.H.; Zhan, T. *Environ. Sci. Technol.* **2010**, *44*, 3616-3620.

20. Pokharel, S.S.; Bishop, G.A.; Stedman, D.H. *On-Road Remote Sensing of Automobile Emissions in the Chicago Area: Year 4*, Final report CRC Contract E-23-4, 2001.

21. Bishop, G. A.; Morris, J. A.; Stedman, D. H., *Environ. Sci. Technol.* **2001,** *35*, 2874-2881.

22. Jimenez, J.L.; McClintock, P.; McRae, G.J.; Nelson, D.D.; Zahniser, M.S. In *Proceedings of the 9th CRC On-Road Vehicle Emissions Workshop*, CA, 1999.

23. Pokharel, S.S.; Bishop, G.A.; Stedman, D.H. *On-Road Remote Sensing of Automobile Emissions in the Phoenix Area: Year 2*, Final report CRC Contract E-23-4, 2000.

24. Ingalls, M. N.; Smith, L. R.; Kirksey, R. E. *Measurement of on-road vehicle emission factors in the California South Coast Air Basin. Volume 1: regulated emissions*, Report to the Coordinating Research Council under Project SCAQS-1; Southwest Research Institute, San Antonio, TX, 1989.

25. Kean, A. J.; Littlejohn, D.; Ban-Weiss, G. A.; Harley, R. A.; Kirchstetter, T. W.; Lunden, M. M. *Atmos. Environ.* **2009,** *43*, 1565-1570.

26. Blanchard, C. L.; Tanenbaum, S.; Lawson, D. R. *J. Air Waste Manage. Assoc.* **2008,** *58*, 1598-1615.

27. Bishop, G.A.; Stedman, D.H. *On-Road Remote Sensing of Automobile Emissions in west Los Angeles: Year 4, October 2005*, Final report to the Coordinating Research Council, Contract E-23-4, 2006.

28. Huai, T.; Durbin, T.D.; Miller, J.W.; Pisano, J.T.; Sauer, C.G.; Rhee, S.H.; Norbeck, J.M. *Environ. Sci. Technol.* **2003,** *37*, 4841-4847.

29. Baum, M.M.; Kiyomiya, E.S.; Kumar, S.; Lappas, A.M.; Kapinus, V.A.; Lord, H.C. *Environ. Sci. Technol.* **2001,** *35*, 3735-3741.

30. Burgard, D.A.; Bishop, G.A.; Stedman, D.H. *Environ. Sci. Technol.* **2006,** *40*, 7018-7022.

31. Kirchstetter, T.W.; Singer, B.C.; Harley, R.A; Kendall, G.R.; Traverse, M. *Environ. Sci. Technol.* **1999**, *33*, 318-328.

COMMON ACRONYMS

CH_2 – Generic formula for gasoline
CO – Carbon monoxide
CO_2 – Carbon dioxide
CRC – Coordinating Research Council
EPA – Environmental Protection Agency
FEAT – Fuel Efficiency Automobile Test
FID – Flame Ionization Detector
HC – Hydrocarbons
I/M – Inspection and Maintenance
IMRC – California Inspection and Maintenance Review Committee
IR – Infrared
MY– Model Year
NDIR – Non-Dispersive Infrared
NH_3 – Ammonia
NO – Nitric Oxide
NO_2 – Nitrogen dioxide
NO_x – Nitrogen oxides
ppm – Parts per million
SO_2 – Sulfur dioxide
UV – Ultraviolet
VIN – Vehicle Identification Number
VSP – Vehicle Specific Power

APPENDIX A: FEAT criteria to render a reading "invalid" or not measured.

Not measured:

1) Beam block and unblock and then block again with less than 0.5 seconds clear to the rear. Often caused by elevated pickups and trailers causing a "restart" and renewed attempt to measure exhaust. The restart number appears in the database.

2) Vehicle which drives completely through during the 0.4 seconds "thinking" time (relatively rare).

Invalid :

1) Insufficient plume to rear of vehicle relative to cleanest air observed in front or in the rear; at least five, 10ms averages >0.25% CO_2 in 8 cm path length. Often heavy-duty diesel trucks, bicycles.

2) Excessive error on CO/CO_2 slope, equivalent to $\pm$20% for %CO. >1.0, 0.2%CO for %CO<1.0.

3) Reported %CO , <-1% or >21%. All gases invalid in these cases.

4) Excessive error on HC/CO_2 slope, equivalent to $\pm$20% for HC >2500ppm propane, 500ppm propane for HC <2500ppm.

5) Reported HC <-1000ppm propane or >40,000ppm. HC "invalid".

6) Excessive error on NO/CO_2 slope, equivalent to $\pm$20% for NO>1500ppm, 300ppm for NO<1500ppm.

7) Reported NO <-700ppm or >7000ppm. NO "invalid".

8) Excessive error on SO_2/CO_2 slope, equivalent to $\pm$40ppm.

9) Reported SO_2 < -80ppm or > 7000ppm. SO_2 "invalid".

10) Excessive error on NH_3/CO_2 slope, equivalent to $\pm$50ppm.

11) Reported NH_3 < -80ppm or > 7000ppm. NH3 "invalid".

12) Excessive error on NO_2/CO_2 slope, equivalent to $\pm$20% for NO_2 > 200ppm, 40ppm for NO_2 < 200ppm

13) Reported NO_2 < -500ppm or > 7000ppm. NO_2 “invalid”.

Speed/Acceleration valid only if at least two blocks and two unblocks in the time buffer and all blocks occur before all unblocks on each sensor and the number of blocks and unblocks is equal on each sensor and 100mph>speed>5mph and 14mph/s>accel>-13mph/s and there are no restarts, or there is one restart and exactly two blocks and unblocks in the time buffer.

APPENDIX B: Database Format.

The database Vnnuys10.dbf is a Microsoft FoxPro database file, and can be opened by any version of MS FoxPro. The files can also be read by a number of other database management programs as well, and they are available from our website at www.feat.biochem.du.edu. The following is an explanation of the data fields found in this database:

License	California license plate.
Date	Date of measurement, in standard format.
Time	Time of measurement, in standard format.
Percent_CO	Carbon monoxide concentration, in percent.
CO_err	Standard error of the carbon monoxide measurement.
Percent_HC	Hydrocarbon concentration (propane equivalents), in percent.
HC_err	Standard error of the hydrocarbon measurement.
Percent_NO	Nitric oxide concentration, in percent.
NO_err	Standard error of the nitric oxide measurement.
PercentSO2	Sulfur dioxide concentration, in percent.
SO2_err	Standard error of the sulfur dioxide measurement.
PercentNH3	Ammonia concentration, in percent.
NH3_err	Standard error of the ammonia measurement.
PercentNO2	Nitrogen dioxide concentration, in percent.
NO2_err	Standard error of the nitrogen dioxide measurement.
PercentCO2	Carbon dioxide concentration, in percent.
CO2_err	Standard error of the carbon dioxide measurement.
Opacity	Opacity measurement, in percent.
Opac_err	Standard error of the opacity measurement.
Restart	Number of times data collection is interrupted and restarted by a close-following vehicle, or the rear wheels of tractor trailer.
HC_flag	Indicates a valid hydrocarbon measurement by a “V”, invalid by an “X”.
NO_flag	Indicates a valid nitric oxide measurement by a “V”, invalid by an “X”.
SO2_flag	Indicates a valid sulfur dioxide measurement by a “V”, invalid by an “X”.
NH3_flag	Indicates a valid ammonia measurement by a “V”, invalid by an “X”.
NO2_flag	Indicates a valid nitrogen dioxide measurement by a “V”, invalid by an “X”.
Opac_flag	Indicates a valid opacity measurement by a “V”, invalid by an “X”.
Max_CO2	Reports the highest absolute concentration of carbon dioxide measured by the remote sensor over an 8 cm path; indicates plume strength.

Speed_flag Indicates a valid speed measurement by a “V”, an invalid by an “X”, and slow speed (excluded from the data analysis) by an “S”.

Speed Measured speed of the vehicle, in mph.

Accel Measured acceleration of the vehicle, in mph/s.

Tag_name File name for the digital picture of the vehicle.

Exp_date License expiration date.

Body_type California DMV body type abbreviation.

0 – Passenger vehicle
A – Ambulance
B – Bus
D – Dump
E – Panel delivery
F – Flatbed
H – Chassis
J – unknown
K – Tank
P – Pickup
R – Refrigerator
S – Station wagon
V – Van
X – Taxi or limousine
Y – Miscellaneous

Year Model year.

Vin Vehicle identification number.

Model California DMV Model abbreviation.

Make Manufacturer of the vehicle.

Fuel Fuel type G (gasoline), D (diesel), N (natural gas) and Q (hybrid).

City Registered city of legal owner.

Zipcode Zipcode of legal owner.

APPENDIX C: Temperature and Humidity Data

Data collected at the Van Nuys Airport

2010 Van Nuys Temperature and Humidity Data										
Time	8/12 °F	8/12 %RH	8/13 °F	8/13 %RH	8/14 °F	8/14 %RH	8/15 °F	8/15 %RH	8/16 °F	8/16 %RH
7:51	64	68	68	61	66	68	68	61	72	55
8:51	69	57	73	48	71	53	73	52	78	40
9:51	75	43	79	36	76	45	78	39	85	28
10:51	78	42	82	38	81	39	84	32	91	22
11:51	81	34	84	33	83	36	87	32	96	19
12:51	82	35	84	32	86	28	91	27	96	21
13:51	82	31	85	29	89	23	93	20	96	19
14:51	81	28	86	29	89	26	92	20	97	16
15:51	83	24	85	31	85	32	91	21	95	19

APPENDIX D: Field Calibration Records.

Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	SO_2 Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
8/12	9:30	0.98	0.87	0.88	0.88	0.99	0.7
8/12	12:15	0.89	0.79	0.72	0.74	1.03	0.6
8/13	9:20	1	0.88	0.91	0.71	1	0.81
8/13	12:00	0.86	0.77	0.73	0.85	0.97	0.56
8/14	8:45	1.01	0.9	0.89	0.98	1	0.72
8/14	12:00	0.89	0.8	0.75	0.89	0.96	0.57
8/15	8:55	1.04	0.91	0.93	0.94	0.98	0.67
8/15	12:26	0.89	0.78	0.72	0.94	0.98	0.56
8/16	9:15	1.02	0.91	0.82	1.07	1	0.64