2012

Multi-species Remote Sensing of Vehicle Emissions on Sherman Way in Van Nuys California

Gary A. Bishop

Brent G. Schuchmann

Donald H. Stedman

Douglas R. Lawson

MULTI-SPECIES REMOTE SENSING MEASUREMENTS OF VEHICLE EMISSIONS ON SHERMAN WAY IN VAN NUYS CALIFORNIA

Gary A. Bishop, Brent G. Schuchmann and Donald H. Stedman

Department of Chemistry and Biochemistry, University of Denver, Denver, CO

Douglas R. Lawson

National Renewable Energy Laboratory, Golden CO

ABSTRACT

As part of the 2010 Van Nuys tunnel study, researchers from the University of Denver measured on-road fuel-specific light-duty vehicle emissions from nearly 13,000 vehicles on Sherman Way (0.4 miles west of the tunnel) in Van Nuys, CA with its multi-species FEAT remote sensor a week ahead of the tunnel measurements. The remote sensing mean gram per kilogram carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x) measurements are 8.9% lower, 41%, and 24% higher than the tunnel measurements respectively. The remote sensing CO/NO_x and HC/NO_x mass ratios are 28% lower and 20% higher than the comparable tunnel ratios. Comparisons with the historical tunnel measurements show large reductions in CO, HC and NO_x over the past 23 years, but little change in the HC/NO_x mass ratio since 1995. The fleet CO and HC emissions are increasingly dominated by a few gross emitters with more than a third of the total emissions being contributed by less than 1% of the fleet. An example of this is a 1995 vehicle measured 3 times with an average HC emission of 419g/kg fuel (2-stroke snowmobiles average 475g/kg fuel) responsible for 4% of the total HC emissions. The 2008 economic downturn dramatically reduced the number of new vehicles entering the fleet, leading to an age increase (>1 model year) of the Sherman Way fleet which has increased the fleet's ammonia (NH_3) emissions. The mean NH_3 levels appear little changed from previous measurements collected in the Van Nuys tunnel in 1993. Comparisons between weekdays and weekend data show few fleet differences although the fraction of light-duty diesel vehicles decreased from the weekday (1.7%) to Saturday (1.2%) and Sunday (0.6%).

INTRODUCTION

The United States' love affair with the automobile has produced a myriad of both positive and negative consequences. As vehicle densities grew in many cities during the 20th century so did concern about vehicle emissions. That concern resulted in rules and regulations that have contributed to reducing new vehicle emissions to very low levels. This in turn has helped to measurably improve urban air quality throughout the United States (U. S. Environmental Protection Agency, 2008).

The University of Denver's introduction of an on-road vehicle emissions measurement system coincided with a vigorous debate surrounding the disagreement between the then current vehicle emission computer models and emission measurements collected in a roadway tunnel in Van Nuys, CA in 1987 (Ingalls, 1989; Ingalls et al., 1989). The disagreements between the models and the on-road tunnel measurements could only be reconciled when the skewed nature of on-road vehicle emissions, caused by a few gross emitters, was taken into account (Pierson et al., 1990; Harley et al., 1993; Knapp, 1994). The changes incorporated into the models generally improved their abilities to model on-road emissions data (Pierson et al., 1996).

It has been more than a decade since the last tunnel study and vehicle emissions model intercomparison has taken place in the United States. In that time period California has updated its vehicle emissions model several times and the U.S. Environmental Protection Agency has released a brand new vehicle emissions model (California Environmental Protection Agency; Air Resources Board, 2010; U. S. Environmental Protection Agency, 2010). As part of the latest intercomparison researchers from the University of Denver remotely measured vehicle tailpipe emissions on Sherman Way in Van Nuys, CA in advance of emission measurements in the Van Nuys tunnel (Fujita et al., 2012). This paper compares some of the statistical results from the measurement of individual vehicles, not available from the tunnel measurements that estimate the emissions of a fleet of vehicles.

EXPERIMENTAL METHODS

The Fuel Efficiency Automobile Test (FEAT) remote sensor developed at the University of Denver was used in this study and has been extensively described in the literature (Burgard et al., 2006a; Burgard et al., 2006b). The instrument consists of a non-dispersive infrared (NDIR) component for detecting carbon monoxide (CO), carbon dioxide (CO_2), and hydrocarbons (HC), and a pair of dispersive ultraviolet (UV) spectrometers for measuring oxides of nitrogen (NO and NO_2), sulfur dioxide (SO_2) and ammonia (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 front surface of the dichroic mirror and is focused onto the end of a quartz fiber bundle that is attached with an SMA fiber optic connector onto the side of the detector unit. The quartz fiber bundle is divided in two bundles carrying the UV signal to the two spectrometers. One spectrometer is aligned between 200 and 227nm and measures NO, SO_2 and NH_3. The second spectrometer measures only NO_2 via absorbtion bands around 438nm.

The remote sensor measures vehicle exhaust gases as a ratio to exhaust CO_2. The ratios are converted into fuel specific emissions of grams of pollutant per kg of fuel by carbon balance after doubling the HC/CO_2 ratio to account for tailpipe emitted carbon that has been lost due to the poor quantification of certain hydrocarbon species by NDIR absorption (Singer et al., 1998; Burgard et al., 2006a). By doubling the HC/CO_2 ratio, the fuel specific HC emissions reported by FEAT are comparable to a measurement reported with a flame ionization detector. Quality assurance calibrations were performed as dictated in the field by the atmospheric conditions and traffic volumes using three certified gas mixtures (Scott Specialty Gases, Longmont, CO) containing 6% CO, 0.6% propane, 6% CO_2, 0.3% NO and 0.04% SO_2 in nitrogen; 0.05% NO_2 and 15% CO_2 in air and 0.1% NH_3 with 0.6% propane in nitrogen. These calibrations account for day-to-day variations in instrument sensitivity and variations in ambient CO_2 levels.

A freeze-frame video image of the license plate of each vehicle is recorded along with the emission measurements. The license plate information was used to obtain non-personal vehicle information from the California registration records. In addition to emission measurements, a pair of parallel infrared beams (Banner Industries) 6 feet apart and approximately 2 feet above the roadway was used to measure the speed and acceleration of the vehicles.

RESULTS AND DISCUSSION

Vehicle emission measurements were collected for four and one-half days, from Thursday, August 12, to noon Monday, August 16, 2010, generally between the hours of 8:30 and 16:00 in the 16600 block of Sherman Way. 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. to monitor across a single eastbound lane (0º slope) that was closest to the curb. This location is approximately 0.4 miles west of the Van Nuys Airport tunnel. License plates that appeared to be in state and readable were matched against the State of California Department of Motor Vehicles records to obtain the vehicle make and model year. The remote sensor attempted 14,691 emission measurements on passing vehicles and recorded valid emission measurements that ranged between 14,008 readings for CO to 13,714 valid NO_2 measurements. The final 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 and can be found at www.feat.biochem.du.edu.

Table 1 summarizes the fuel specific median and mean emissions with standard errors of the mean, mean percentile, fractional contribution of emissions for each species top 1%, measurement success rate, fleet age and mean driving parameters for the data set. We have assumed a fuel carbon fraction of 0.85 for all of the g/kg calculations to maintain consistency with the reported tunnel measurements (Fujita et al., 2012). The standard error of the means has been calculated from the distribution of the daily means. The reported HC emissions include an adjustment to the HC distributions zero point to compensate for any site specific systematic offsets (Bishop and Stedman, 2008). The 10ppm offset for this data set was estimated from calculating the HC mode and means of the newest model year vehicles, assuming that these vehicles emit negligible levels of hydrocarbons, and using the smallest value. 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. SO_2 emissions were statistically indistinguishable from zero and are not reported. The percent emissions contribution of the top 1% have been calculated using all of the measurements but the statistic also holds if calculated using just unique vehicles. These calculations included diesel powered vehicles which accounted for approximately 1.3% of the measurements.

Table 1. Summary of emissions, measurement specifics and observed driving mode.

	g/kg emissions[a]			
	CO	HC[b]	NO^c / NO_2 / NO_x^d	NH_3
Median	2.6	0.8	0.16 / 0.05 / 0.39	0.21
Mean[e]	19.4±1.3	2.4±0.3	2.6±0.1 / 0.09±0.01 / 4.1±0.1	0.59±0.02
Mean Percentile[f]	83	68	79 / 56 / 79	73
Percent of Total Emissions from Top 1%	32%	33%	16% / 40% / 16%	12%
Attempts/Plates/Matched	14691 / 13009 / 12963			
Mean Model Year	2001.5			
Speed/Acceleration/VSP	51.7 kph / 0.5 kph/sec / 6.2 kw/tonne			

[a]Assumes a fuel carbon fraction of 0.85. [b]grams of HC using the FID correction noted in the text. [c]grams of NO. [d]grams of NO_2. [e]Standard errors of the means calculated from the daily measurement means. [f]Percentile in which the mean emission rate is found when the emissions data are rank-ordered.

Figure 1 displays the Sherman Way fleet distributed by model year for 1989 and newer vehicles. The 1988 and older models not graphed account for an additional 3.5% of the fleet. The 2001 recession is not detectable in this data set unlike previous measurements in San Jose and Fresno, CA where new car sales were noticeably reduced (Bishop et al., 2010). However, the 2008 economic downturn is striking in the lack of 2009 models found in-use with a more than 40% drop from pre-recession levels. The 2010 models will also end up with a large reduction although at the time of these measurements we doubt that they are fully accounted for. Measurements in March of 2008 in nearby West Los Angeles (S. La Brea Ave. and I-10) found a fleet average age of 7.5 years (that has changed little since our first measurements in 1999 when the fleet was 7.8 years old) to compare with the average age of 9.4 years for the Sherman Way fleet (Bishop and Stedman, 2008; Bishop et al., 2010). Measurements collected on Sherman Way at the Van Nuys

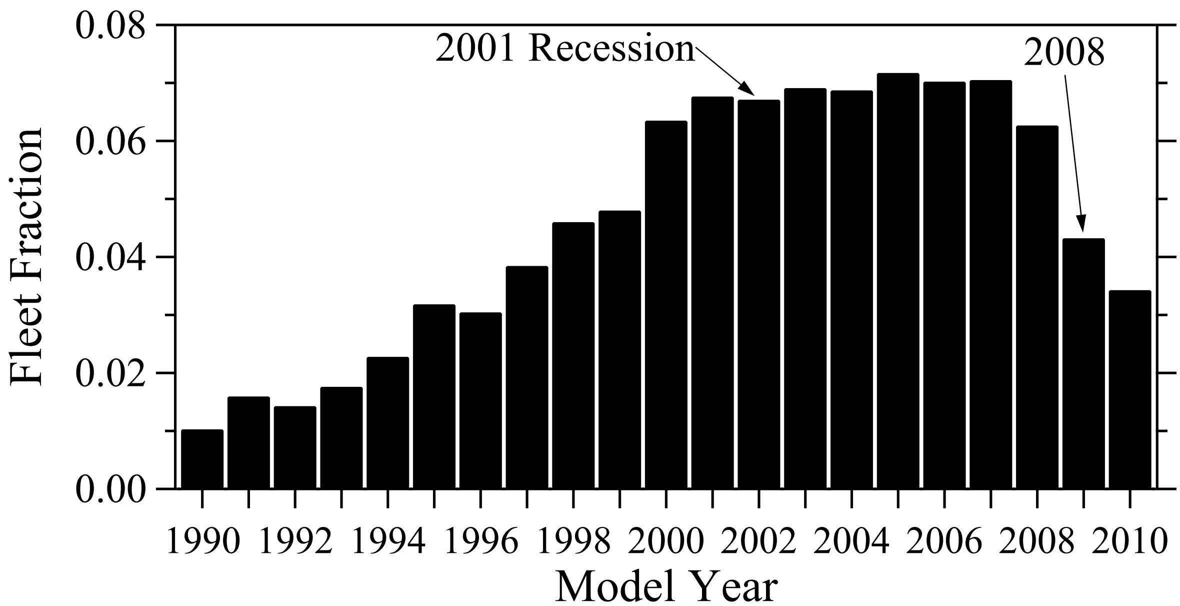

Figure 1. The measured Sherman Way fleet fraction versus model year for 1990 and newer models. The 1989 and older vehicles make up 3.5% of the total fleet. The 2001 recession is not detectable in this data set, while the 2008 downturn is quite striking in its magnitude and has rapidly aged the vehicle fleet.

Airport tunnel in 1993 and 1995 studies reported estimated average fleet ages of 7.6 and 11.5 years (Gertler et al., 1997; Fraser and Cass, 1998). On the other side of the Los Angeles Basin near Riverside average fleet ages of 7.4, 7.5 and 7.3 years were observed in data collected in 1999, 2000 and 2001 respectively (Bishop and Stedman, 2008). While it is difficult to accurately gauge the total extent of the age increase of the on-road fleet caused by the 2008 recession, it appears to be at least one model year older. Since all tailpipe emissions generally increase with age this will have a negative effect on fleet emissions, likely interrupting the downward trend in measured fleet emissions.

Figure 2 is a Venn diagram depicting the relationships among the highest-emitting CO, HC, and NO vehicles in the measured fleet during the experiment. In the Venn diagram, all areas including the rectangle are drawn to scale, according to the total number of remote sensing readings. During the four and one-half days of remote sensing measurements, there were 12,929 valid measurements for which CO, HC, and NO were measured and are represented by the area of the large rectangle. The area within each of the three circles represents the number of readings

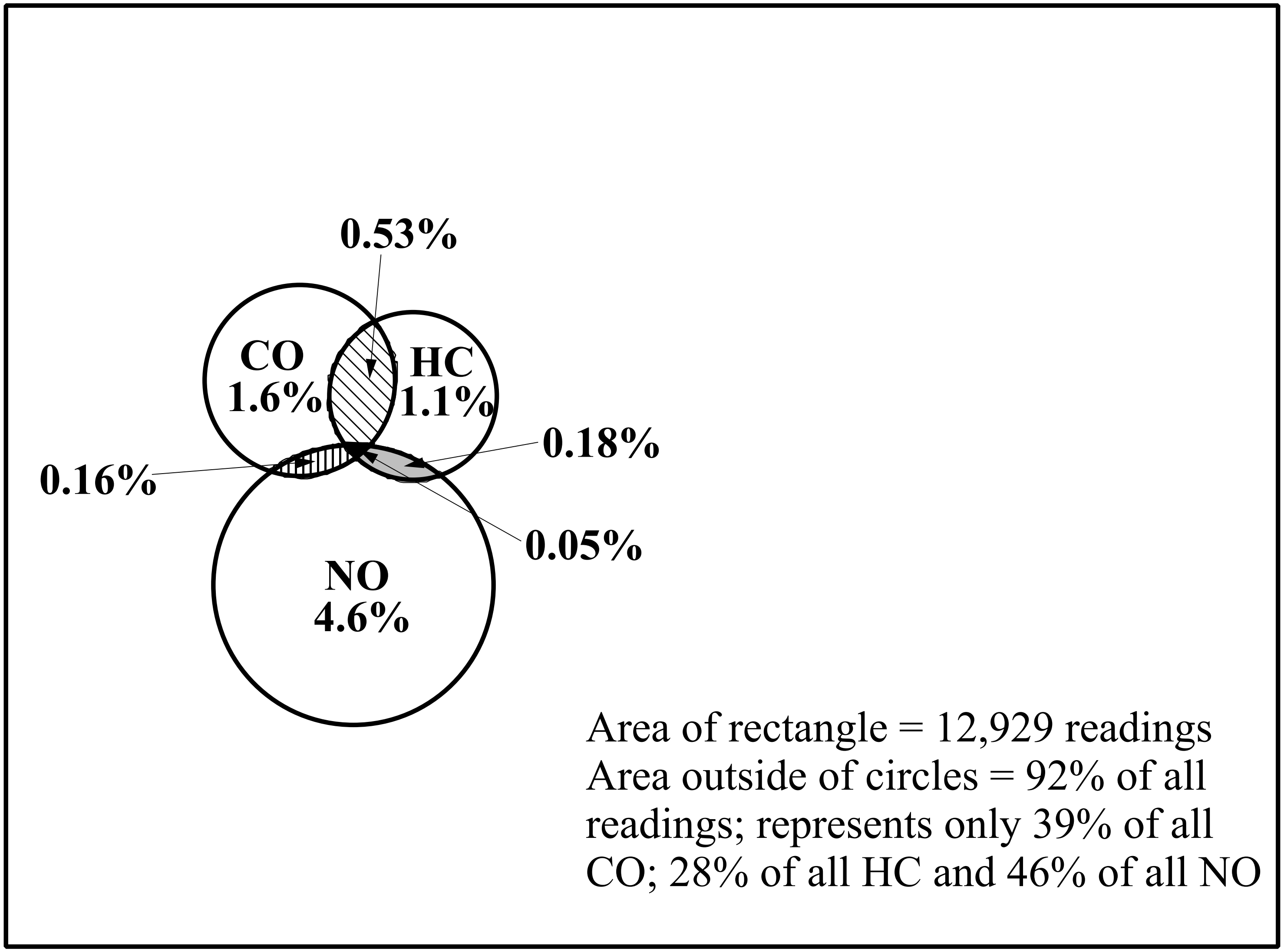

Figure 2. Amount of overlap among remote sensing measurements responsible for highest 50% of observed CO, HC, and NO. Values shown are the percentage of measurements found within each segment of the 12,929 total measurements comprising the Figure. Total area outside of circles, but contained within the drawn rectangle, is 92% of all measurements. All areas within the rectangle shown in this Figure are drawn to scale.

that were responsible for producing 50% of each of the three pollutants' total g/kg emissions. Half of the total measured CO, HC, and NO were produced by only 2.3, 1.8, and 5.0%, respectively, of the total 12,929 measurements. As reported previously, some of these measurements were produced by the same vehicle that passed by the remote sensor on different occasions. The total area within all three circles, which is only 8% of all measurements, is responsible for 61, 72, and 54% of the measured CO, HC, and NO, respectively.

The size of the circles also shows that the degree of pollution skewness is greatest for HC and CO. The largest amount of overlap among highest polluters is between CO and HC, where 76 measurements of the 536 total are among the highest half of measured CO and HC. Only 7 observations were found within the highest half of all three measured pollutants. The average model years of the highest CO, HC, and NO vehicles' measurements are 1990.9, 1994.2, and 1995.0, respectively.

The emissions distributions for CO and HC are extremely skewed as evidenced by the emission contribution of the top 1% of the measurements and the large differences between the median and mean emission values (see Table 1). This has been driven by the continued emissions reductions of newer models, but more importantly by their low malfunction rates enabling these low initial emissions to persist for many more years than previous models (Bishop and Stedman, 2008). The emission levels for gross emitters has also declined over time but their contribution to the total keeps growing with the percent of total emissions from the top 1% of measurements tripling from less than 10% in the late eighties to the low 30% for this data set.

Contrary to some reports, gross emitters are not difficult to find through the use of remote sensing, although they comprise only a small percent of the fleet (MacArthur et al., 2009). Two examples of these vehicles are a 1995 Buick and a 1986 Toyota pickup. The Buick was measured three times during the campaign and averaged 242 gCO/kg and 419 gHC/kg which is not dissimilar from mean emissions measured from 2-stroke snowmobiles in Yellowstone Park in 1999 (Bishop et al., 2001). The three measurements from this vehicle constitute only 0.02% of the total measurements but account for 0.29% of the total CO and an astounding 4% of the HC. The Toyota pickup is an interesting gross emitter for entirely different reasons. While its single measurement of 880 gCO/kg easily puts it in the top 1% for CO emissions what really distinguishes this vehicle is that it had been 2.5 years (Nov. 2007) since it last passed a

California Smog Check emissions test. State records show a failed test in 2009, though the vehicle had a valid registration according to California Department of Motor Vehicle records, a practice that has finally caught the attention of State regulators (Austin et al., 2009; Department of Consumer Affairs and Bureau of Automotive Repair, 2011). This vehicle received a passing Smog Check certificate at a test only station just 5 hours after our measurement was made. We can only hope that the owner made good use of those 5 hours and properly repaired the vehicle.

While fleet turnover has helped to eliminate the majority of the CO nonattainment areas in the US, the current 8 hour ambient ozone standard continues to pressure states like California to reduce fleet HC and NO_x emissions beyond the current levels. With on-road gross emitters accounting for an ever growing percentage of the total HC emissions they continue to be the 800lb gorilla in the room that regulators continue to ignore. This data set shows that by finding, repairing and/or scrapping only the highest emitting 2% of the fleet, half of the tailpipe HC emissions would be eliminated.

Just to the east of our measuring location on Sherman Way is a tunnel that goes under the runway at the Van Nuys Airport. Ingalls *et al.* (1989) measured gram/mile emission factors for CO, HC and NO_x in the fall of 1987 (but did not measure CO_2), Fraser and Cass measured gram/liter emission factors for CO, HC and NH_3 in the fall of 1993 and the Desert Research Institute conducted a more detailed emissions study in 1995 (Pierson et al., 1990; Gertler et al., 1997; Fraser and Cass, 1998). Table 2 compares the reported emission rates from these previous studies along with the newest tunnel measurements collected in 2010 with the on-road remote sensing results of this study (Fujita et al., 2012). Mass ratios of CO/NO_x and HC/NO_x are reported instead of molar ratios to maintain consistency with the Ingalls *et al.* data (Pierson et al., 1990). Total HC emissions are reported for all of the studies except the newest tunnel data where only Non-methane HC (NMHC) data are available.

The remote sensing mean gram per kilogram CO, HC, and NO_x measurements are 8.9% lower, 41%, and 24% higher than the tunnel measurements respectively. The remote sensing CO/NO_x and HC/NO_x mass ratios are 28% lower and 20% higher than the comparable tunnel ratios. The comparisons between the remote sensing HC (exhaust only) and tunnel NMHC measurements are made more complex as the tunnel measurements include evaporative emissions but leave out methane emissions that the remote sensor includes. The remote sensing NO_x emissions are

Table 2. On-road remote sensing emissions compared to reported historical values collected at the Van Nuys Airport tunnel.

Study Year	Mass CO/NO_x[a]	Mass HC/NO_x[a]	gCO/kg[b]	gHC/kg[b]	gNO_x/kg[b]	gNH_3/kg[b]	Model Year (Age)
1987	13.3	1.7	NA	NA	NA	NA	NA
1993	NA	NA	170[c]	14[c]	NA	0.5[c,d]	1986.4 (7.6)
1995	11.2	0.8	120	9	11	NA	1983.9 (11.5)
2010[e]	6.5 ± 0.4	0.5 ± 0.04	21.3 ± 2.5	1.7 ± 0.2	3.3 ± 0.4	NA	NA
This Study[f]	4.7 ± 0.3	0.6 ± 0.1	19.4 ± 1.3	2.4 ± 0.3	4.1 ± 0.1	0.59 ± 0.02	2001.5 (9.4)

[a]Assumes all NO_x is NO_2. [b]Assumes a fuel carbon fraction of 0.85. [c]Literature g/L values assumed a gasoline density of 0.75 kg/L. [d]Only 76% of fleet estimated to have catalyst. [e]Means of all measurement results and only non-methane HC values are reported. The errors are the propagated one-sigma errors reported for the tunnel measurements. [f]Standard errors of the means calculated from the daily means.

higher than the overall tunnel measurements despite the fact that they do not include emissions from the few percent of heavy-duty diesel trucks with elevated exhausts. The use of a sampling site 0.4 miles west of the tunnel and sampling a week prior to the tunnel measurements combined with any driving mode differences caused by the lane restrictions likely contributes to some of these differences. The historical comparisons with the remote sensing data show large reductions in CO (88% from 1993), HC (82% from 1993) and NO_x (63% from 1995) emissions along with reductions in the CO and HC to NO_x mass ratios (65% for CO/NO_x and HC/NO_x from 1987). These reductions are not necessarily linear as all species have been decreasing though not necessarily at the same rate yet it should be noted that the HC/NO_x ratio appears to have changed little since 1995.

The 2010 remote sensing ammonia mean of 0.59 ± 0.02 g/kg is a statistically significant increase of 17% since 1993; however, the fleet measured in 1993 was estimated to only have 76% of the fuel burned in the tunnel by vehicles equipped with three-way catalysts (a necessity for NH_3 production). If we assume that the ammonia emissions would linearly scale to a fleet fully equipped with three-way catalytic convertors, adding the additional 24% to the 1993 study results in a new total of 0.62 g/kg, very similar to the 2010 measurements. Recently Kean *et al.* documented NH_3 emissions decreasing at the Caldecott tunnel by 38 ± 6% since 1999 (Kean et al., 2009). The history of NH_3 emissions in the Van Nuys area is insufficient to speculate whether the reductions observed at the Caldecott tunnel should be uniformly expected or are specific to that location. In addition the lack of multiple measurements in 1993 makes any assessment of that measurement's uncertainty impossible. However, the increased age of the Sherman Way fleet as previously discussed likely has at least slowed any decrease.

Previous freeway on-ramp measurements of NH_3 in San Jose, Fresno and West Los Angeles, CA in March of 2008 resulted in NH_3 means of 0.49 ± 0.02, 0.49 ± 0.01 and 0.79 ± 0.02 g/kg respectively compared to this study's mean of 0.59 ± 0.02 g/kg (Bishop et al., 2010). The higher mean observed at the West Los Angeles site was attributed to the more aggressive driving mode at the West Los Angeles site (mean vehicle specific power (VSP) of 12.2) which is a traffic light controlled entrance to I-10. Figure 3 compares the mean NH_3 emissions by vehicle age (the same model years are ~2.5 years older at Sherman Way) for this study and the three 2008 California measurement sites. Vehicle age has been defined as the fractional measurement year minus the vehicle model year. The error bars plotted are standard errors of the mean calculated using the daily means for each model year. The age comparison assumes that there are few if any differences between the technologies and emission standards of the similarly aged vehicles, however the Sherman Way data does contain more scatter due to fewer measurements. Figure 3 shows that for the sites with the most similar driving modes (San Jose mean VSP of 14.7, Fresno mean VSP of 6.4 and Sherman Way mean VSP of 6.2) the data look similar within the measurement noise with the exception of the three newest model years from Sherman Way. They remain at higher NH_3 values and those differences account for about half of the differences in the means between Sherman Way, San Jose and Fresno. While NH_3 emissions are known to be driving mode dependent there is not an obvious explanation for the elevated emissions of the newest model year vehicles on Sherman Way (Huai et al., 2003). The other half of the difference

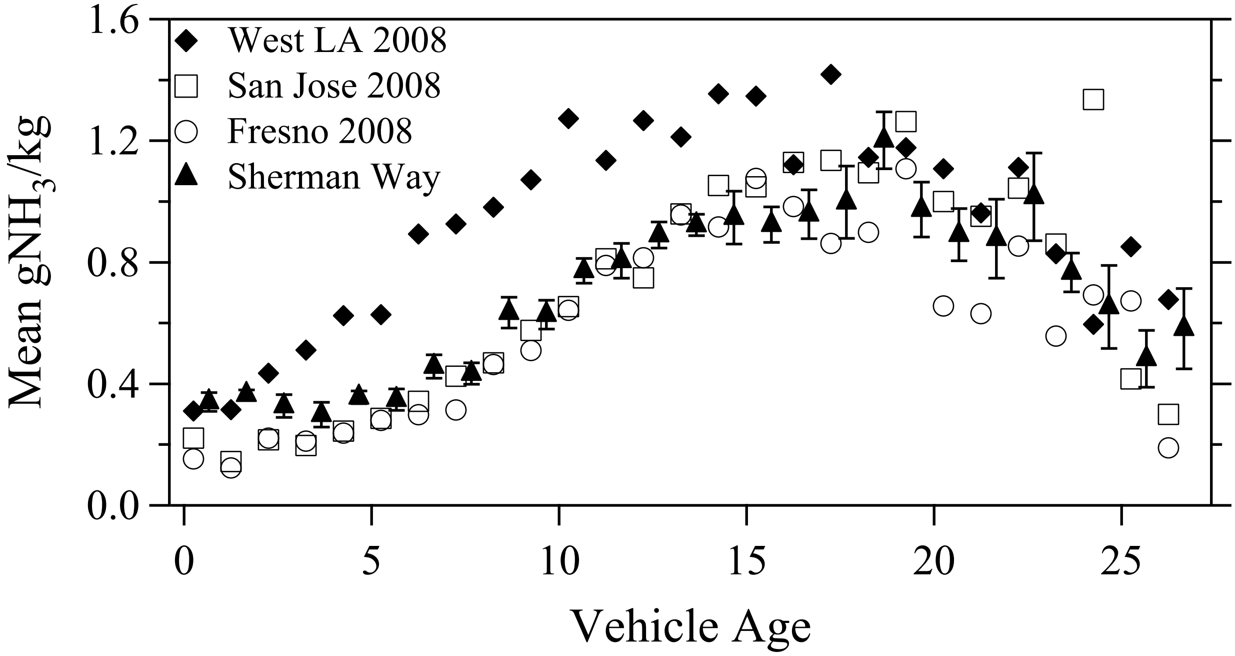

Figure 3. Mean gNH_3/kg emission versus vehicle age for the Sherman Way data (filled triangles) compared to three California sites measured in March of 2008. Vehicle age has been defined as the difference between the fractional measurement year and the vehicle model year. The error bars plotted are standard errors of the mean calculated using the daily model year means and all of the emission values have been calculated assuming a fuel carbon fraction of 0.85.

with San Jose and Fresno means is caused by the increased age of the Sherman Way fleet which has shifted the vehicle distribution to higher NH_3 emissions.

We believe that the reason the observed NH_3 emissions first increase and then decrease as a function of vehicle age is the product of two counteracting factors, catalyst reducing efficiency and overall NO_x emissions. For the newest vehicles, the catalyst is very efficient at reducing a large fraction of the small engine-out NO_x emissions into NH_3. As the vehicle ages, engine-out NO_x increases, but reducing efficiency remains high enough to allow NH_3 to also continue to increase. However, after about twenty years, catalyst reducing efficiency begins to wane, and a decreasing fraction of the elevated engine-out NO_x is converted to NH_3 leading to its decreasing levels.

Differences in the fleet composition of weekday and weekend traffic have been implicated in many metropolitan areas as being a driver for differences in ozone precursor levels (Blanchard et al., 2008). Table 3 compares the mean emission values between the weekday (Thursday, Friday and Monday morning) and weekend (Saturday and Sunday) measurements. Standard errors of the mean can only be calculated for the weekday data and have been calculated from the daily means. The weekend traffic is slightly older (0.4 model years) and slightly higher emitting for CO and HC, though not statistically significant with this small sampling. Traffic volume on Sherman Way was essentially identical on a per hour basis for each grouping. The fraction of diesel vehicles was higher on weekdays (~1.7%) than on the weekend days (1.2% on Saturday and 0.6% on Sunday). Sunday had the lowest mean NO_x emissions for the five measurement days of 3.6 gNO_x/kg.

Table 3. Emissions comparison for the weekday and weekend data.

	Vehicles (hours)	Mean Model Year	Mean g/kg emissions[a]			
			CO	HC[b]	NO[c] / NO_2 / NO_x[d]	NH_3
Weekday[e]	6757 (15)	2001.7	18.0±1.4	2.4±0.5	2.60±0.08 / 0.12±0.02 / 4.1±0.1	0.58±0.03
Weekend[f]	6206 (13.8)	2001.3	21.0	2.5	2.6 / 0.06 / 4.0	0.61

[a]Assumes a fuel carbon fraction of 0.85. [b]Grams of HC using the FID correction noted in the text. [c]Grams of NO. [d]Grams of NO_2. [e]Standard error of the means calculated using the daily means. [f]Insufficient number of days to calculate standard errors of the mean.

CONCLUSIONS

As part of the 2010 Van Nuys tunnel study, researchers from the University of Denver acquired on-road fuel-specific emissions data from nearly 13,000 light-duty vehicles on Sherman Way in Van Nuys CA with its multi-species FEAT remote sensor. The remote sensing mean gram per kilogram CO, HC, and NO_x measurements are 8.9% lower, 41%, and 24% higher than the tunnel measurements respectively. The remote sensing CO/NO_x and HC/NO_x mass ratios are 28% lower and 20% higher than the comparable tunnel ratios. HC comparisons are complicated as the remote sensor reports only exhaust HC while the tunnel measurements include evaporative emissions but do not include methane emissions. The remote sensing NO_x emissions are higher than the overall tunnel measurements despite the fact that they do not include emissions from the few percent of heavy-duty diesel trucks with elevated exhausts. The use of a sampling site 0.4 miles west of the tunnel and sampling a week prior to the tunnel measurements combined with any driving mode differences caused by the lane restrictions likely contribute to some of these differences. Comparisons with historical data sets also collected in the Van Nuys tunnel since 1987 show large reductions in CO, HC and NO_x, but little change in the HC/NO_x ratio since 1995. The fleet CO and HC emissions were shown to be increasingly dominated by a few gross emitters with more than a third of the current Sherman Way total emissions being contributed by less than 1% of the fleet. An extreme example of this is a 1995 vehicle measured three times during the four and one-half days of sampling with average HC emissions of 419g/kg (2-stroke snowmobiles typically average 475g/kg) responsible for an astonishing 4% of the total HC emissions. The 2008 economic downturn has dramatically reduced the number of new vehicles that entered the fleet during the last two model years. This has led to a significant increase in the age (>1 model year) of the Sherman Way fleet relative to previous trends. This age increase has most noticeably led to an increase in the light-duty fleet's NH_3 emissions, when compared with other California data collected in 2008. In addition, the mean NH_3 levels appear little changed from previous NH_3 measurements collected in the Van Nuys tunnel in 1993. Comparisons between weekday and weekend data sets show few fleet differences although the fraction of light-duty diesel vehicles decreased from the weekday (1.7%) to Saturday (1.2%) and Sunday (0.6%).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the funding and support received from the National Renewable Energy Laboratory under Subcontract AEV-8-88609-01. This program has been supported by the U.S. Department of Energy Office of Vehicle Technologies, Dr. James Eberhardt, Chief Scientist.

REFERENCES

Austin, T.C., McClement, D., Roeschen, J.D., 2009. *Evaluation of the California Smog Check program using random roadside data*. SR09-03-01: Sacramento, CA.

Bishop, G.A., Morris, J.A., Stedman, D.H., 2001. Snowmobile contributions to mobile source emissions in Yellowstone National Park. Environ. Sci. Technol. 35, 2874-2881.

Bishop, G.A., Peddle, A.M., Stedman, D.H., Zhan, T., 2010. On-road emission measurements of reactive nitrogen compounds from three California cities. Environ. Sci. Technol. 44, 3616-3620.

Bishop, G.A., Stedman, D.H., 2008. A decade of on-road emissions measurements. Environ. Sci. Technol. 42, 1651-1656.

Blanchard, C.L., Tanenbaum, S., Lawson, D.R., 2008. Differences between weekday and weekend air pollutant levels in Atlanta; Baltimore; Chicago; Dallas-Fort Worth; Denver; Houston; New York; Phoenix; Washington, DC; and surrounding areas. J. Air Waste Manage. Assoc. 58, 1598-1615.

Burgard, D.A., Bishop, G.A., Stadtmuller, R.S., Dalton, T.R., Stedman, D.H., 2006a. Spectroscopy applied to on-road mobile source emissions. Appl. Spectrosc. 60, 135A-148A.

Burgard, D.A., Dalton, T.R., Bishop, G.A., Starkey, J.R., Stedman, D.H., 2006b. Nitrogen dioxide, sulfur dioxide, and ammonia detector for remote sensing of vehicle emissions. Rev. Sci. Instrum. 77, 1-4.

California Environmental Protection Agency; Air Resources Board, 2010. EMFAC2007 Release. http://www.arb.ca.gov/msei/onroad/latest_version.htm (accessed May 10, 2012).

Department of Consumer Affairs, Bureau of Automotive Repair, 2011. Vehicle Test History. http://www.bar.ca.gov/pubwebquery/Vehicle/PubTstQry.aspx (accessed May 10, 2012).

Fraser, M.P., Cass, G.R., 1998. Detection of excess ammonia emissions from in-use vehicles and the implications for fine particle control. Environ. Sci. Technol. 32, 1053-1057.

Fujita, E.M., Campbell, D., Zielinska, B., Chow, J.C., Lindhjem, C., DenBleyker, A., Bishop, G.A., Schuchmann, B.G., Stedman, D.H., Lawson, D.R., 2012. Comparison of the MOVES2010a, MOBILE6.2 and EMFAC2007 mobile source emissions models with on-road traffic tunnel and remote sensing measurements. J. Air Waste Manage. Assoc. **##, ##-##**.

Gertler, A.W., Sagebiel, J.C., Wittorff, D.N., Pierson, W.R., Dippel, W.A., Freeman, D., Sheetz, L., 1997. *Vehicle emissions in five urban tunnels*. Final Report No. E-5: Atlanta, GA.

Harley, R.A., Russell, A.G., McRae, G.J., Cass, G.R., Seinfeld, J.H., 1993. Photochemical modeling of the Southern California air quality study. Environ. Sci. Technol. 27, 378-388.

Huai, T., Durbin, T.D., Miller, J.W., Pisano, J.T., Sauer, C.G., Rhee, S.H., Norbeck, J.M., 2003. Investigation of NH_3 emissions from new technology vehicles as a function of vehicle operating conditions. Environ. Sci. Technol. 37, 4841-4847.

Ingalls, M.N., 1989. In *On-road vehicle emission factors from measurements in a Los Angeles area tunnel*, Air and Waste Management Association 82nd National Meeting, Anaheim, CA, Paper No. 89-137.3.

Ingalls, M.N., Smith, L.R., Kirksey, R.E., 1989. *Measurements of on-road vehicle emission factors in the California South Coast air basin - Volume I: Regulated emissions*. SwRI-1604: Atlanta, GA.

Kean, A.J., Littlejohn, D., Ban-Weiss, G.A., Harley, R.A., Kirchstetter, T.W., Lunden, M.M., 2009. Trends in on-road vehicle emissions of ammonia. Atmos. Environ. 43, 1565-1570.

Knapp, K.T., 1994. On-road vehicle emissions: U.S. studies. Sci. Total Environ. 146-147, 209-215.

MacArthur, R., Mobley, D., Levin, L., Pierce, T., Feldman, H., Moore, T., Koupal, J., Janssen, M., 2009. Emission characterization and emission inventories for the 21st century. EM (October), 36-41.

Pierson, W.R., Gertler, A.W., Bradow, R.L., 1990. Comparison of the SCAQS tunnel study with other on-road vehicle emission data. J. Air Waste Manage. Assoc. 40, 1495-1504.

Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B., Ray, W.D., 1996. Real-world automotive emissions - Summary of studies in the Fort McHenry and Tuscarora Mountain tunnels. Atmos. Environ. 30, 2233-2256.

Singer, B.C., Harley, R.A., Littlejohn, D., Ho, J., Vo, T., 1998. Scaling of infrared remote sensor hydrocarbon measurements for motor vehicle emission inventory calculations. Environ. Sci. Technol. 32, 3241-3248.

U. S. Environmental Protection Agency, 2008. *Latest findings on national air quality; Status and trends through 2006*. EPA-454/R-07-007: Research Triangle Park.

U. S. Environmental Protection Agency, 2010. Modeling and Inventories; MOVES (Motor Vehicle Emission Simulator). http://www.epa.gov/otaq/models/moves/index.htm (accessed May 10, 2012).

ABOUT THE AUTHORS

Gary A. Bishop is a research chemist, Brent G. Schuchmann is a research assistant, and Donald H Stedman is the John Evans Professor of chemistry at the University of Denver. Douglas R. Lawson (now retired) is a principal scientist at the National Renewable Energy Laboratory. Please address correspondence to: Gary A. Bishop, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208: +1-303-871-2584; e-mail: gbishop@du.edu