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On-road Emission Measurements of Reactive Nitrogen Compounds from Three California Cities

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The three California cities of San Jose, Fresno and West Los Angeles (wLA) were visited during March 2008 to collect on-road emission measurements of reactive nitrogen compounds from light-duty vehicles. At the San Jose and wLA sites comparison with historical measurements showed that emissions of carbon monoxide (CO), hydrocarbons (HC) and nitric oxide (NO) continue to decrease in the on-road fleet yet the ratio of

nitrogen dioxide (NO_2) to NO in new diesel vehicles appears to be under going large increases. A small fleet of 2007 diesel ambulances measured in Fresno was found to have more than 60% of their emitted oxides of nitrogen as NO_2. Ammonia (NH_3) emissions are shown to have a strong dependence on model year and vehicle specific power. NH_3 means of 0.49 ± 0.02, 0.49 ± 0.01 and 0.79 ± 0.02 g/kg of fuel for San Jose, Fresno and wLA, respectively, with the larger emissions at the wLA site likely due to driving mode. NH_3 at these locations was found to account for 25%, 22% and 27% of the molar fixed nitrogen emissions. Using these mean values to construct a National fuel based NH_3 inventory results in a range of 210,000 to 330,000 short tons of NH_3 annually from light-duty vehicles.

Introduction

With larger concentrations of people living within urban areas, the issue of maintaining and even improving the quality of the air is a major challenge. Ozone and particulate matter smaller than 2.5 μm in diameter ($PM_{2.5}$) have been particularly persistent problems for the South Coast and San Joaquin Valley air basins of California. Reactive nitrogen compounds, nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), and nitrous acid (HONO) produced by internal combustion engines in combination with catalytic converters are important precursors contributing to ozone and $PM_{2.5}$ formation in these areas.

Direct emissions of HONO from modern catalyst equipped vehicles are not believed to be significant (*1*). Oxides of nitrogen (NO_x) emission rates from light-duty gasoline vehicles have been shown to be rapidly decreasing across the US but total NO_x emissions are decreasing at a slower rate due to the growth in heavy-duty diesel traffic (*2-5*). Since

NO and NO_2 are quickly interconverted only NO_2 is identified under the Clean Air Act as a criteria pollutant yet NO is the species largely emitted from light-duty vehicles. The differences in the reactivity of NO (titrates local ozone) and NO_2 (immediately available for ozone production) have important implications for ozone photochemistry. Historically, NO_2 emissions have been less than 10% of the total NO_x emitted by diesel engines (*6*). This thermodynamic and kinetic limit has been compromised with the introduction of diesel particulate filters (DPF). DPFs are often accompanied with an oxidation catalyst that converts NO into NO_2 to oxidize the trapped soot particles thus keeping the filters from clogging. In Europe, where oxidation catalyst are common on light-duty diesels and DPF equipped heavy-duty diesel have already been introduced, a number of urban areas have experienced increases in NO_2 emissions (*7*). This trend has caught the attention of regulators. For example, in its diesel retrofit program, California only allows modest increases of NO_2 due to the implementation of diesel retrofit technology, so that the adverse environmental impacts can be offset by the benefits offered in the reduction of other pollutants (*8*).

NH_3 is a rather recent motor vehicle emitted species and is an unregulated by-product of 3-way catalytic convertors over reducing NO when reducing agents are present (*9*). The importance of $PM_{2.5}$ emissions has focused new attention on understanding NH_3 emissions from light-duty vehicles. Recent inventory calculations for Fresno, CA have estimated that vehicles are a more important contributor than previously thought (*10*). With reductions in light-duty NO_x it has been assumed that NH_3 is also declining and recent tunnel measurements in California have now shown decreases among a light-duty

vehicle fleet (*11*). But the amount of nitrogen being fixed by light-duty vehicles and in what proportions as NO_x and NH_3 is not fully known.

To date, much of the command and control strategy applied to mobile source emissions has relied on the concept that we will try to reduce everything. While it has been extremely successful in reducing direct emissions of criteria pollutants, it has not been as successful in reducing ozone and $PM_{2.5}$ levels (*2, 12*). The complicated and non-linear nature of ozone and $PM_{2.5}$ chemistry make it difficult to predict how changes in the amounts of emitted nitrogen compounds affect these two secondary pollutants (*13*). However, historical knowledge of the on-road emission levels of the precursor pollutant can provide a foundation to study these air quality changes. This paper details an effort to address this issue through on-road emission measurements of NO, NO_2 and NH_3 from large light-duty vehicle fleets in the three California cities of San Jose, Fresno and West Los Angeles (wLA).

Experimental Section

The three sites sampled in this study are listed in Table 1 along with a summary of their locations, sampling specifics and mean driving modes observed. The site in San Jose was previously used for the collection of exhaust emission measurements in the fall of 1999 and the wLA site has been used in the fall of 1999, 2001, 2003, and 2005 (*2, 14*). The sites in San Jose and Fresno are curved uphill interchange ramps while the wLA location is a traffic light controlled on-ramp to eastbound I-10. All of the data sets described in this paper along with previous data sets are available for download from our website at www.feat.biochem.du.edu.

Table 1. Summary of California 2008 Sampling Sites, Measurement Specifics, and Driving Mode

City / Dates	Location / Roadway Grade	Vehicle Records Attempts / Plates / Matched	Mean Model Year	Mean Speed (mph)	Mean Acceleration (mph/sec)
San Jose March 4 - 7	NB I-280 to NB I-880 / 1.8°	31,116 / 25,371 / 24,978	2000.6	30.6	1.0
Fresno March 8 - 14	NB US 41 to WB US 180 / 1.8°	15,656 / 13,679 / 13,365	1999.8	25.4	0
West Los Angeles March 17 - 21	SB La Brea Ave to EB I-10 / 2.0°	23,579 / 18,323 / 17,953	2001.2	17.6	1.9

A University of Denver developed remote vehicle exhaust sensor, named Fuel Efficiency Automobile Test (FEAT), was used to collect all of the data sets listed in Table 1. The instrument consists of a source and detector unit aligned across a single lane roadway and consisting of a non-dispersive infrared (NDIR) component for detecting carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HC), and twin dispersive ultraviolet spectrometers for measuring NO, sulfur dioxide (SO_2), NH_3, and NO_2 and has been fully described in the literature (*15-17*). The remote sensor measures vehicle exhaust gases as a ratio to exhaust CO_2 since the path length of the plume is unknown but the ratios are constant for a given exhaust plume. The ratios can be 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 the poor quantification of certain hydrocarbon species by NDIR absorption (*15, 18*).

The speed and acceleration and 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. Measurements were collected during daylight hours with dry roadway conditions.

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; balance nitrogen; 0.05% NO_2 and 15% CO_2; 0.1% NH_3 and 0.6% propane. These calibrations account for day-to-day variations in instrument sensitivity and variations in ambient CO_2 levels caused by atmospheric pressure and instrument path length.

Results and Discussion

Table 2 provides a summary of the mean gram per kilogram of fuel emission measurements along with standard errors of the mean (SEM) for the three California sites. 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. Emissions of CO, HC and NO have shown steady decreases at sites with historical measurements (*2*). At the San Jose site CO, HC and NO emissions have decreased by 66%, 74% and 40% respectively since the 1999 measurements despite an increase of 1.2 model years in the average age of the fleet. For this same time period the wLA site has seen similar decreases of 70%, 74% and 43% for CO, HC and NO respectively while the fleet has only increased in age 0.2 model years.

Table 2. Summary of emission measurements and standard errors of the mean.

City	Mean g/kg Emissions				
	CO	HC[a]	NO[b] / NO_2 / NO_x[c]	NH_3	SO_2
San Jose	16.6 ± 1	1.5 ± 0.4	2.6 ± 0.1 / 0.05 ± 0.01 / 4.0 ± 0.1	0.49 ± 0.02	0.06 ± 0.01
Fresno	20.0 ± 0.9	2.9 ± 0.1	2.9 ± 0.1 / 0.14 ± 0.01 / 4.6 ± 0.1	0.49 ± 0.01	0.09 ± 0.02
West Los Angeles	21.4 ± 0.5	1.8 ± 0.1	3.8 ± 0.3 / 0.08 ± 0.02 / 5.9 ± 0.4	0.79 ± 0.02	0.07 ± 0.03

[a] grams of propane

[b] grams of NO

[c] grams of NO_2

Standard errors of the means calculated from the daily measurement means.

Parrish has reported on morning rush hour ambient emission measurements of molar CO/NO_x ratios at a number of sites across the US over the last two decades (*5*). Morning rush hour was chosen with the knowledge that heavy-duty diesel emissions would be reduced (on and off-road, likely biasing the resulting ratio high). This should not affect the temporal trend which he found to be decreasing at all of the sites within a range of 5.5 ± 0.4% (LA) and 8.8 ± 1.0% (Nashville) per year. Using our historical NO emissions data (this is the first year that we have measured NO_2 emissions) from the San Jose and the wLA sites we find similar trends with the molar CO/NO ratio at the San Jose site decreasing at a rate of 7.1% per year and at the wLA site of 7.0 ± 0.2% per year. The similarity between an ambient trend and our data, which only includes light-duty diesel vehicles, suggests that decreases in the light-duty fleet emissions are driving the ambient results (*4*).

As far as economic activity correlates with new car purchases, one can use the on-road fleet fraction data to compare the economic vitality of the three sites for the past decade.

Figure 1 compares the fraction of the fleet at each of the three sites by model year recognizing that the 2007 and 2008 model years may not yet be fully populated. The data show that the recession that occurred during the 2002 – 2003 time frame in the United States depressed new car sales in San Jose and Fresno but not at the wLA site. In San Jose sales increased again with the 2004 models and sales appear to have fully recovered by the 2006 models; sales never appear to have recovered at the Fresno site and account for its older average age (see Table 1).

The wLA site has the highest NO_x emissions of the three sites due in large part we believe to the low speed and higher acceleration rate at this on-ramp. In general light-duty vehicle emissions of NO_2 are small, with most model years having mean emissions of less than 0.1 g/kg, and a slight but noisy increase for the older model years. An exception was found in Fresno for 2007 model year vehicles. Quite by happen-stance our Fresno monitoring site was on the local return route for an ambulance company servicing the downtown Health Center. The 2007 model year data set contains 30 Dodge Sprinter vans (a total of 57 measurements out of 871 total measurements), 29 of which were in service as ambulances. According to vehicle VIN information and sales literature these vans were equipped with 3.0L diesel engines and an oxidation catalyst equipped DPF. As a result of these vehicles we found a larger fraction of NO_X was direct emissions of NO_2 at the Fresno site.

Table 3 compares the Fresno NO_x measurement for the 2007 model year vehicles segregated by fuel type (fuel type was determined from hand decoding the VINs because DMV fuel type was not provided). The errors reported are SEM calculated using the daily averages for the non-diesels and the Sprinters and the individual measurements for

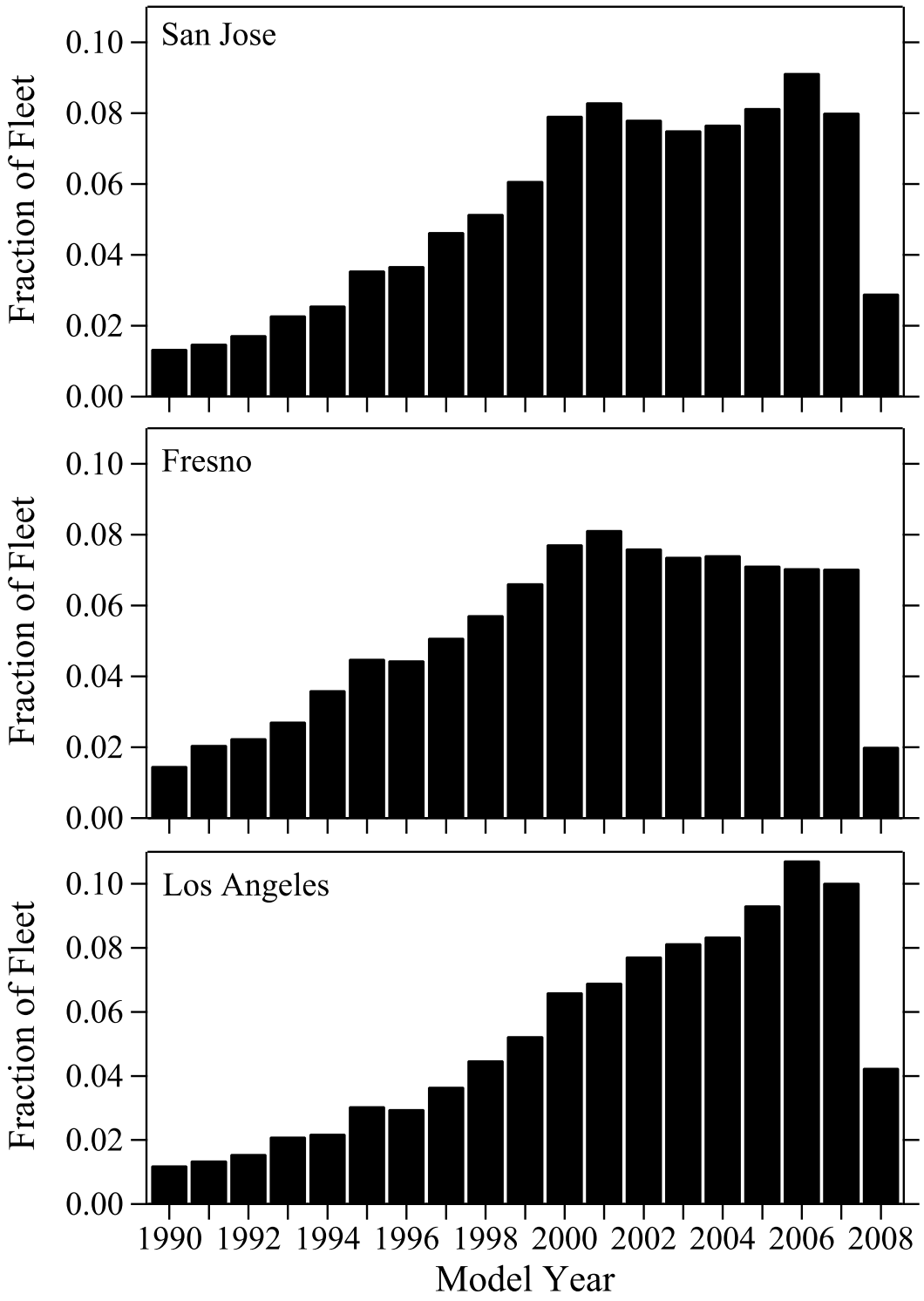

Figure 1. Fleet model year distribution for the three California cities sampled. Model years 2007 and 2008 are likely not fully populated by the time of these measurements. The US recession in 2002 – 2003 is clearly reflected in the drop in car sales beginning in 2002 in San Jose and Fresno. The Fresno sales appear never to have recovered.

Table 3. Fresno emission measurements and standard errors of the mean for 2007 model year vehicles.

Grouping	Samples	Mean %IR Opacity	Mean gNH_3/kg	Mean g/kg NO^a / NO_2 / NO_x^b	Mass Ratio NO_2 / NO_x
Sprinters[c]	57	0.6 ± 0.2	0.02 ± 0.01	2.1 ± 0.2 / 4.9 ± 0.6 / 8.0 ± 0.8	0.61
Other Diesels[d]	22	1.2 ± 0.7	0.02 ± 0.02	12.1 ± 0.9 / 1.4 ± 0.4 / 19.9 ± 1.2	0.07
Non-Diesel[c,e]	792	0.4 ± 0.04	0.14 ± 0.02	0.22 ± 0.08 / 0.08 ± 0.01 / 0.42 ± 0.12	0.19

[a] NO reported as grams of NO

[b] NO_2 and NO_x reported as grams of NO_2

[c] Standard errors of the mean calculated from the daily measurement means

[d] Standard errors of the mean calculated from the individual measurements

[e] Includes all vehicles not designated as diesel

the other diesel vehicles (since the NO_2 data are not normally distributed, the SEM for these vehicles will likely be under reported). There are large differences between the NO_x emissions of the other diesel and gasoline vehicles. While the Sprinters total NO_x emissions are between those two groups, 60% of their NO_x emissions mass is emitted as NO_2. While the NO_2 fraction of the NO_x emitted by the gasoline vehicles is larger than for the other diesel vehicles, it is a fraction of a much smaller baseline emission factor. The Sprinters only account for 0.4% of all of the Fresno measurements but 15% of the NO_2 measured at this site. In addition, we contacted the ambulance service and found out that their average yearly mileage is 50,000 miles/ambulance. If the NO_2 emissions we observed is used as a yearly average and these vehicles are estimated to have a fuel economy of 20 mpg (6.25 mpkg assuming a fuel density of 3200g/gallon) then these 29 ambulances can be expected to emit approximately 1.2 metric tonnes of NO_2 for the year. To put this into context, the whole light-duty fleet of nearly half million vehicles in

Fresno County is estimated to annually emit approximately 420 metric tonnes of NO_2, based on the California EMFAC model. Direct emissions of NO_2 can only be expected to make a poor ozone situation in the Fresno area worse and it will remain to be seen how these emissions change in the future (*19*).

The production of NH_3 emissions is contingent upon the vehicle's ability to produce NO in the presence of a catalytic convertor that has enough stored hydrogen to reduce that NO to NH_3. Dynamometer studies have shown that these conditions are met during acceleration events, particularly when the catalyst surface is slightly fuel rich from a recent deceleration (*20-22*). Figure 2 is a composite graph of NH_3 emissions versus model year for the three California sites. The SEM is plotted for the Fresno data set, calculated from the daily model year means, and provides a sense of the variability for each of the data sets. Differences in the mean emissions are apparent in the newest fifteen model years with the wLA site having higher production rates. After the peak model year, the levels begin to decline with age, and while noisy due to a shrinking number of vehicles, generally decrease at similar rates. We believe that the large differences in the newer model years at the wLA site can be attributed to the stop and then accelerate driving mode at that site. As the catalytic converters age and begin to lose their reducing capacity, driving mode becomes unimportant and NH_3 emissions decrease with increasing age.

Figure 2 also shows that while the mean NH_3 emissions are the same in Fresno and San Jose that does not mean that the emissions by model year profiles are also identical. The San Jose fleet has slightly higher emissions by model year (22 out of the 27 model years) but the differences in age between the two fleets (San Jose is 0.8 model years newer)

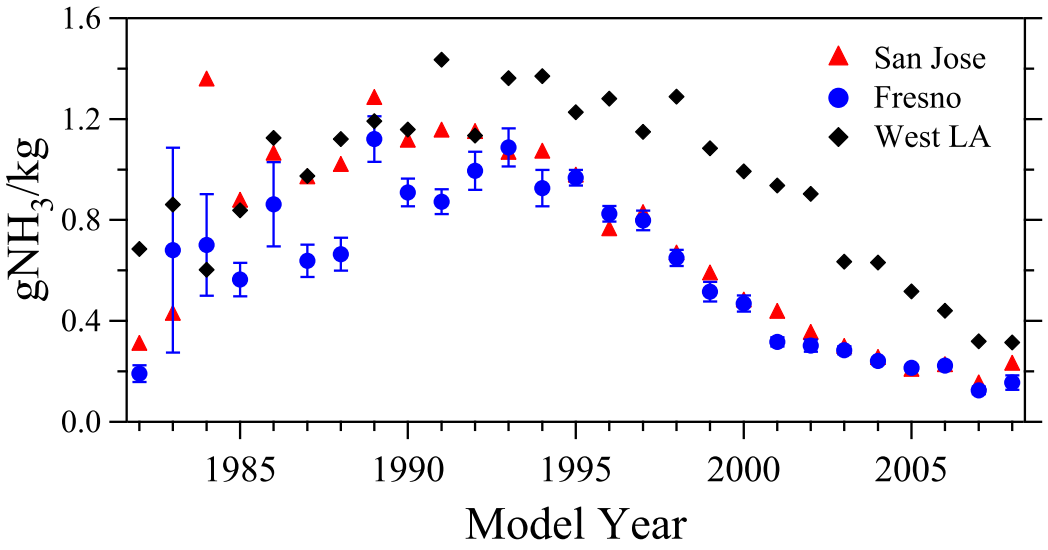

Figure 2. Mean gNH_3/kg emissions as a function of model year for the three measurement sites. Uncertainty bars for the Fresno data are standard errors of the mean determined using the seven daily means for each model year.

distributes the majority of the emissions fractions at different points along the model year axis. The Fresno fleet accumulates a large amount of its NH_3 emissions from the center of the model year peak (1994-1998 models account for 37% of the NH_3) while the San Jose emissions are contributed by newer models whose overall lower emission levels compensate for its higher average emissions by model year.

On-road NH_3 emissions in the US have been previously reported by Baum *et al.* for a LA site at 0.35 g/kg in 1999 (mean speed 50 mph, slight uphill on-ramp), by Burgard *et al.* in 2005 from gasoline-powered vehicles to be 0.47 ± 0.02 and 0.51 ± 0.01 g/kg for sites in Denver and Tulsa (mean speed 25 mph, curved uphill interchange ramps) and by Kean et al. from the Caldecott Tunnel (mean speed 36 mph, 4.1% uphill grade) in the San Francisco area in 2000 and 2006 at 0.64 ± 0.04 and 0.4 ± 0.02 g/kg (*11, 23-25*). The San

Jose and Fresno measurements (see Table 2) are similar to all of the previously reported measurements while the wLA data are the highest NH_3 emissions reported to date.

Figure 3 is a plot of the emissions of NH_3 as a function of vehicle specific power (VSP) for the 2008 measurements (*26*). The error bars included in the plot are SEM calculated from the daily averages. NH_3 shows a strong positive dependence on driving mode at all three sites. The speed and acceleration sensors measure the body of the vehicle and the increase in NH_3 at zero VSP at the wLA site may be a result of gear shifts that have lowered the VSP of the vehicle body without effecting engine loads.

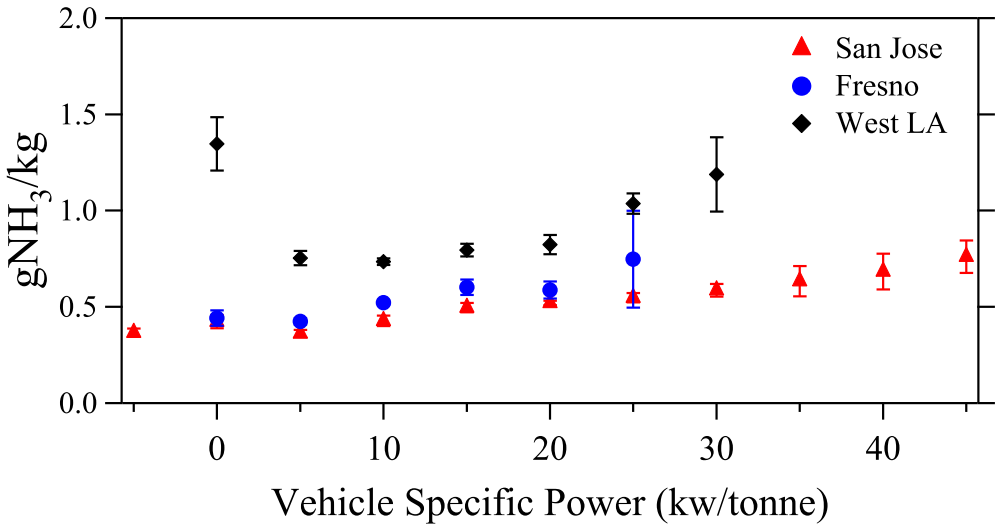

Figure 3. Mean gNH_3/kg emissions as a function of vehicle specific power for the three sites. The error bars are standard errors of the mean determined from the daily means for each vehicle specific power bin.

Figure 4 plots the mass in g/kg of NO_x and NH_3 emissions against model year for the newest 20 model years. The NO_x emissions have been plotted on a scale that generally allows them to overlap with the NH_3 emissions to highlight the similar emissions trends.

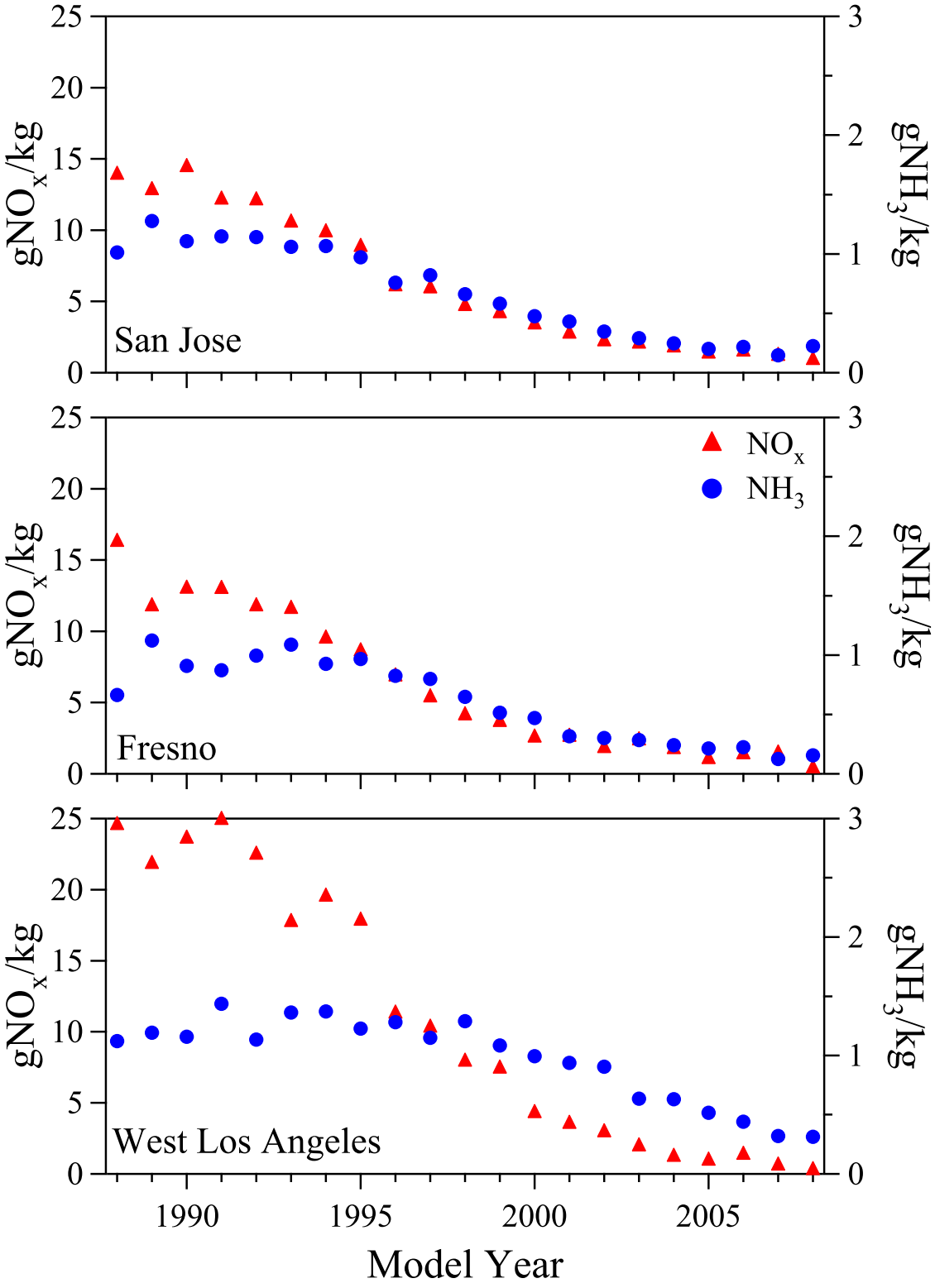

Figure 4. Mean gNO_x/kg (line and triangles, left axis) and gNH_3/kg (circles, right axis) emissions as a function of model year for the three measurement sites.

In San Jose and Fresno the NH_3 and NO_x emissions are decreasing at a similar rate over the newest 10 model years. NO_x emissions from the newest vehicles (2004 and newer) are 30% lower at the wLA site than the other two sites, then increase rapidly with the older model years. The wLA site fixes the largest amount of nitrogen and in these newer model year vehicles a larger fraction of that is being fixed as NH_3.

The mole percent ammonia of the total fixed nitrogen (moles/kg $N_{from\ NH_3}$ + moles/kg $N_{from\ NO_x}$, neglecting any unmeasured N_2O and HONO which may account for a few percent) was calculated to compare with published results (*1, 27, 28*). At the San Jose, Fresno and wLA sites NH_3 accounted for 25%, 22% and 27% of the fixed molar nitrogen emissions. This compares with 24.7% reported by Burgard *et al.* and 27% reported by Kean *et al.* (*11, 24*). Figure 5 shows the individual results for each site. The molar $\%NO_x$ and $\%NH_3$ add to 100% and are percentages of the fixed nitrogen (g/kg) values plotted by model year. The noise increases for the molar percentages in the newest model years because of the rapidly diminishing emissions. The total fixed nitrogen has decreased over the last 20 model years; however, the percent contributed by NH_3 has increased. For the newest model years, NH_3 contributes strikingly large fractions of the fixed nitrogen emissions at all sites.

Using the mean NH_3 measurements reported in this paper, national gasoline sales of 378 million gallons per day and assuming that NH_3 emissions from cold start gasoline vehicles and diesel vehicles are negligible, we can calculate a fuel-based inventory for our three sites (*29, 30*). The San Jose and Fresno fleet gNH_3/kg mean emission levels results in a National emission inventory of 210,000 short tons per year while the data from the wLA site results in a total of 330,000 short tons per year. The U.S. EPA has

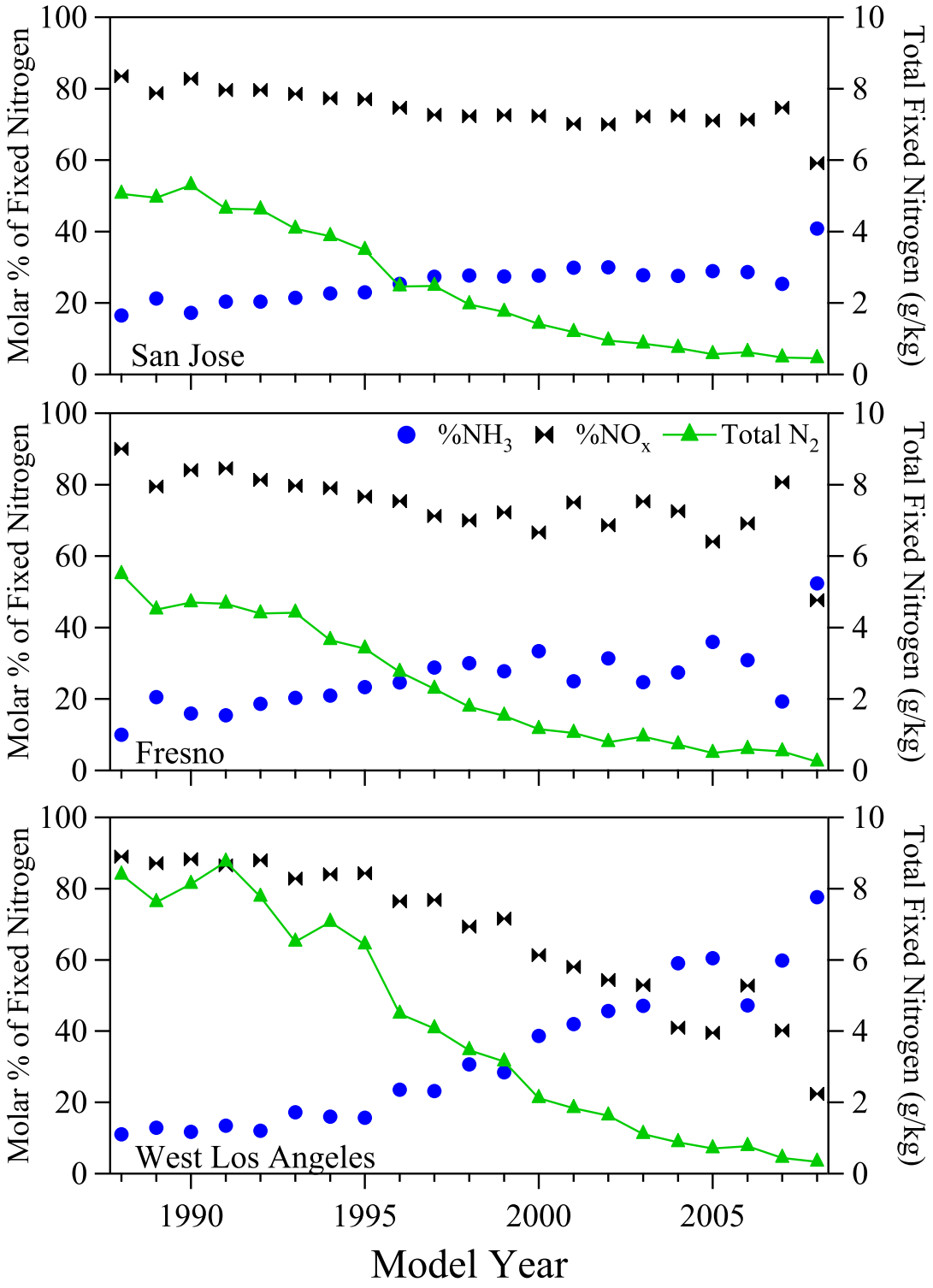

Figure 5. Total fixed nitrogen in g/kg (triangles, right axis) with the molar percent composition distributed between the NO_x (bowties, left axis) component and the NH_3 component (circles, left axis).

estimated that the 2007 national NH_3 inventory contribution from all highway vehicles amounts to 307,000 short tons per year (*31*). The EPA estimate lies closest to the high load West LA site. We would expect the majority of the gasoline consumed in the US to be consumed during cruise like driving modes which are more typical of the driving modes observed at the San Jose, Fresno and the Caldecott Tunnel sites. This would argue that the U.S. EPA national NH_3 inventory from mobile sources may be somewhat overestimated.

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