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Reactive Nitrogen Species Emission Trends in Three Light/Medium Duty U. S. Fleets

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Abstract

Repeated, fuel specific, emission measurements in Denver (2005/2013), Los Angeles (2008/2013) and Tulsa (2005/2013) provide long-term trends in on-road reactive nitrogen emissions from three light/medium duty U.S. fleets. Reductions in oxides of nitrogen (NO_x) emissions ranged from 21% in Denver (5.6 ± 1.3 to 4.4 ± 0.2 gNO_x/kg of fuel) to 43% in Tulsa (4.4 ± 0.3 to 2.5 ± 0.1 gNOx/kg of fuel) since 2005 while decreases in fleet ammonia (NH_3) emissions ranged from no change in Denver (0.45 ± 0.09 to 0.44 ± 0.02 gNH_3/kg of fuel) since 2005 to a 28% decrease in LA (0.80 ± 0.02 to 0.58 ± 0.02 gNH_3/kg of fuel) since 2008. The majority of the reduction in gasoline vehicle NO_x emissions occurred prior to the full implementation of the Tier II emission standards in 2009. High in-use NO_x emissions from small engine diesel passenger vehicles produced a significant contribution to the fleet means despite their small numbers. NH_3 emissions decreased at a slower rate than NO_x emissions due to modest NH_3 emissions reduction among the newest vehicles and increased emissions from a growing

number of older vehicles with active catalytic converters. In addition, the reactive nitrogen emissions from many new model year vehicles are now dominated by NH_3.

Introduction

Despite nearly a half century of air quality regulations, concerns remain that concentrations of ground-level ozone and fine particulate matter ($PM_{2.5}$) in the United States (US) still exceed healthy levels.[1-3] This has recently led the U. S. Environmental Protection Agency (EPA) to propose additional reductions in the National Ambient Air Quality Standards for ozone.[4] While ozone and $PM_{2.5}$ levels have been generally decreasing across the US, many urban areas still exceed the current national standards.[5-8] Emissions of reactive nitrogen species from gasoline and diesel vehicles are important constituents involved in ozone and $PM_{2.5}$ formation, making them important species to monitor.[1]The major species include nitric oxide (NO), nitrogen dioxide (NO_2) and ammonia (NH_3) with minor contributions from nitrous oxide (N_2O) and nitrous acid (HONO).

Vehicular emissions of oxides of nitrogen (NO_x) have steadily declined in the US over the last decade[5, 9, 10]. Declines of NO_x emissions from light-duty gasoline vehicles have outpaced declines from the diesel segment of the fleet which have now become the dominant source for NO_x in many areas despite their much smaller fleet size.[10, 11] Within the past decade, both the state of California and the EPA have instituted additional emission reduction requirements on both the gasoline (Tier II / LEV II required for vehicles manufactured after 2008) and diesel-fueled fleets emphasizing NO_x emission reductions.[12-14] To meet these low NO_x certification levels in diesel vehicles new NO_x after-treatment technologies such as lean NO_x traps (LNT) and selective catalytic reduction systems (SCR) have been introduced with the latter providing a potential new mobile source for NH_3 emissions.[15] Vehicles produced to comply with these regulations are now an important fraction of the on-road fleet and their in-use emission performance and durability is uncertain but an important research question for the future of NO_x emission trends.

NH_3 is not directly produced by an internal combustion engine; rather it is the result of the reduction of engine-out NO through a reduction reaction on a three-way catalytic converter which has access to several reducing agents in the exhaust including carbon monoxide (CO), hydrogen, unburned and partially burned fuel.[16] In the US, the most important source of atmospheric ammonia is associated with livestock operations, but in urban areas gasoline and natural gas vehicles with three-way catalytic converters can be an important source and it is not a currently regulated species.[17] In the South Coast Air Basin NH_3 has long been recognized as an important contributor to the formation of secondary aerosol nitrates, which are a significant component of the basin's $PM_{2.5}$.[18-20] The most recent estimates found that the automobile contribution to the NH_3 emissions inventory ranged from one third to twice that of the livestock sector, due to large uncertainties in the east basin livestock estimate.[21] A recent apportionment study in the Houston area also found that vehicles were a major contributor of ammonia[22] Future urban reductions in $PM_{2.5}$ will likely be linked with the trends in vehicle NH_3 emissions. To date, the only estimate of trends for in-use vehicle NH_3 emissions came from repeat measurements performed by Kean et al. in the Caldecott tunnel near San Francisco in 1999 and 2006. Their study found that vehicle NH_3 emissions decreased by 38 ± 6% during that time span.[23]

Through the use of three long-term sampling sites in Denver Colorado, Los Angeles, California (LA) and Tulsa, Oklahoma, the University of Denver has collected a set of repeat measurements of the major reactive nitrogen species (NO, NO_2 and NH_3) from on-road light and medium-duty vehicles. The location of these sites ensures that the vehicles are monitored in a hot-stabilized operating mode which should preclude any significant emissions of N_2O and HONO.[24, 25] These three sites provide a number of interesting fleet differences to compare and contrast and have been shown to be representative of other US urban fleets.[9] In addition the NH_3/carbon dioxide (CO_2) ratios measured at the LA location have been shown to be representative of the entire basin averaged vehicle NH_3/CO_2 ratio.[21] The fleet observed at the LA location has the largest percentage of passenger vehicles, more hybrids and the smallest light and medium-duty diesel fleet. Denver and Tulsa fleets include more trucks, both gasoline and diesel, and have slightly newer fleets. The Tulsa fleet is unique among the three in that these vehicles have never been subject to any type of emissions inspection and maintenance program. The past NO_x and NH_3 emissions from each of these sites have been previously reported; they form the baseline for the comparisons that are reported in this paper.[26, 27]

Experimental Section

Data were collected at sampling sites in Denver, CO. (NB I-25 to WB 6th Ave., 4.6º grade), Los Angeles, CA. (SB La Brea Ave. to EB I-10, 2º grade) and Tulsa, OK (WB US64 to SB US169, 2.7º grade). The Denver and Tulsa locations are curved uphill interchange ramps connecting major freeways while the LA location is a traffic light-controlled freeway entrance ramp. There are differences between measurements collected at the same site as enhancements to our exhaust sensor have added species capability (NO_2 measurements did not begin until 2008) and a nonfunctional ramp metering light changed the LA site's driving mode for the 2013 measurements. In addition, the Denver data sets that contain NH_3 measurements were collected during different seasons of the year (early summer in 2005 and winter in 2013). All of these data sets have been previously discussed in the literature and are available for download from our website at www.feat.biochem.du.edu.[26-28]

A remote vehicle exhaust sensor developed at the University of Denver named Fuel Efficiency Automobile Test (FEAT), was used to collect all of the emission measurements. The instrument consists of a light source and detector unit separated by a single lane of road. The detector is composed of four non-dispersive infrared (NDIR) detectors including a reference channel (3.9µm), CO (3.6µm), CO_2 (4.3µm), hydrocarbons (HC, 3.3µm), and two dispersive ultraviolet spectrometers. The first spectrometer measures NO, sulfur dioxide (SO_2) and NH_3 between 198 to 227nm while the second records NO_2 spectra between 430 and 450nm. All of the detectors sample at 100Hz and have been fully described in the literature.[29-31] FEAT measures vehicle exhaust gases as a ratio to exhaust CO_2 since the path length of the plume is unknown and the ratios are constant for a given exhaust plume. Each species measured ratio is scaled by its certified gas cylinder ratios measured daily as needed at each location by FEAT to correct for variations in instrument sensitivity and in ambient CO_2 levels caused by atmospheric pressure, temperature and ambient pollution differences. Three calibration cylinders are used containing: a) 6% CO, 0.6% propane, 6% CO_2 and 0.3% NO, balance nitrogen; b) 0.05% NO_2 and 15% CO_2, balance air and c) 0.1% NH_3 and 0.6% propane, balance nitrogen (Air Liquide, Longmont CO). All of the calibration cylinders have been certified to a ± 2% accuracy.

Double-blind intercomparisons have demonstrated FEAT's accuracy to be within ±5% for CO and ±15% for HC as reported by an on-board gas analyzer for an individual measurement.[32, 33] Testing with the NO channel and a late model low-emitting vehicle indicate a detection limit (3σ) of 25ppm with a measurement error of ±5% for readings at higher concentrations.[30]

However, the largest source of measurement uncertainty and variability comes from the vehicles themselves.[34]

A video image of the license plate of each vehicle was recorded and the transcribed plate was used to obtain non-personal vehicle information including make, model year and vehicle identification number (VIN) from the state registration records from Colorado, California and Oklahoma. Speed and acceleration measurements for each vehicle were attempted using a pair of parallel infrared beams (Banner Industries) 1.8m apart and approximately 0.66m above the roadway. Vehicle VIN's were decoded for 1981 and newer vehicles using the Polk VIN decoder to ascribe vehicle type classification (passenger vehicle or truck classes 1-8) and for fuel type (gasoline or diesel) when not available from the state records. For this analysis, gasoline passenger vehicles and trucks include hybrid drive-trains and any alternative fueled vehicles (ethanol and natural gas). Trucks were limited to weight classes of 1 to 6 [this includes SUV's and light-duty trucks (classes 1-3 up to 14,000 lbs.) and medium-duty trucks (classes 4-6 up to 26,000 lbs.)]. Tables S1 and S2 (supporting information) provide a detailed listing of the number of vehicles by fuel, type and truck weight class. All of the measured ratios were converted into fuel specific emissions of grams of pollutant per kg of fuel by carbon balance using a carbon mass fraction for the fuel of 0.86 and doubling of the HC/CO_2 ratio to account for the poor quantification of certain hydrocarbon species by NDIR absorption.[29, 35] One can correctly argue that the carbon mass fraction for gasoline should be 0.85 and for diesel fuel 0.87. We have chosen to stay with the value previously used in all of our published results for comparison consistency and also the fact that our measurement errors will exceed the approximately 1% difference that occurs in our choice of the carbon mass fraction.

Results and Discussion

Table 1 contains a summary of the sampling dates, vehicle record information, fleet averaged model year, percent diesel, mean fuel specific emission measurements and standard errors of the mean (SEM) for all the records and for gasoline vehicles only, and speed and acceleration collected in each city. The SEM's have been calculated from the distribution of each sites daily measurement means (see supporting information). The most notable sampling condition difference between measurement years was the failure of the ramp metering light at the LA site in 2013 which increased the mean speed by 20% and changed the driving mode from an low speed acceleration to a higher speed cruise mode.

Percent decreases in fleet NO{NO_x} emissions observed over the time interval of each cities measurement sets were 25%{21%} in Denver, 43%{40%} in LA and 48%{43%} at the Tulsa location. These percentage reductions increase slightly (especially for NO_x) if the comparison is restricted to only the gasoline portion of the fleet. One contributing factor is increased NO_x emissions in the diesel portion of the fleet beginning with the 2008 models, when oxidation catalysis and catalyzed diesel particulate filters were introduced allowing diesel vehicles to be sold nationwide. As a result the percentage of light and medium-duty diesel vehicles in the fleet slightly increased in both LA (1.5% to 1.9%) and Tulsa (2.5% to 2.8%). Fleet NH_3 emissions showed no statistically significant change in Denver, a 14% reduction in Tulsa over an eight-year period and LA experienced a decrease of 28% in five years.

In the case of the LA data sets an important question is how significant the change in driving mode may have been in affecting the comparison. Because of the skewed nature of vehicle emission distributions, as a result of a few broken vehicles, fleet age is the most important factor affecting mean emissions with driving mode having been largely eliminated in modern US

Table 1. Fleet Sampling Specifics by Location with Measured Emission Means and Standard Errors of the Mean

Location Dates Sampled	Attempts/Plates/Matched Mean Model Year (%Gasoline)	Mean g/kg of Fuel Emissions and Standard Errors of the Mean[a] All Records (Gasoline Only)				Mean Speed (mph) Acceleration (mph/sec)
		CO	HC[b]	NO[c] / NO_2 / NO_x[d]	NH_3	
Denver, CO 6/1 – 6/3 2005	5,101 / 3,900 / 3,689 1998.7 (96.5%)	44.3±3.0 (44.9±3.3)	4.0±0.5 (4.0±0.5)	3.6±0.9 / NA / 5.6±1.3[e] (3.2±0.9 / NA / 5.0±1.4[e])	0.45±0.09 (0.47±0.09)	25.1 0.7
Denver, CO 12/12,13 2013, 1/4/2014	25,881 / 19,883 / 19,229 2005.2 (96.7%)	12.6±0.9 (12.7±0.9)	1.8±0.1 (1.8±0.1)	2.7±0.1 / 0.24±0.02 / 4.4±0.2 (2.3±0.1 / 0.11±0.02 / 3.6±0.2)	0.44±0.02 (0.45±0.02)	22.9 0.01
Los Angeles, CA 3/17 – 21 2008	23,579 / 18,323 / 17,903 2001.2 (98.5%)	21.4±0.5 (21.7±0.5)	1.8±0.1 (1.8±0.1)	3.7±0.3 / 0.07±0.02 / 5.7±0.4 (3.5±0.3 / 0.05±0.02 / 5.4±0.4)	0.80±0.02 (0.80±0.02)	17.6 1.9
Los Angeles, CA 4/27 – 5/4 2013	33,807 / 27,808 / 27,184 2004.7 (98.1%)	16.4±0.6 (16.6±0.7)	2.2±0.2 (2.2±0.2)	2.1±0.1 / 0.15±0.02 / 3.4±0.1 (1.9±0.1 / 0.11±0.02 / 3.1±0.1)	0.58±0.02 (0.59±0.02)	21.9 -0.2
Tulsa, OK 9/19 – 9/23 2005	26,627 / 20,353 / 18,877 1999.3 (97.5%)	33.5±0.9 (34.0±0.9)	2.2±0.2 (2.2±0.2)	2.9±0.2 / NA / 4.4±0.3[e] (2.5±0.2 / NA / 3.9±0.2[e])	0.50±0.01 (0.51±0.01)	24.5 -0.4
Tulsa, OK 9/30 – 10/4 2013	29,268 / 21,988 / 21,083 2006.3 (97.2%)	13.4±0.4 (13.6±0.4)	2.1±0.3 (2.1±0.3)	1.5±0.04 / 0.14±0.02 / 2.5±0.1 (1.3±0.03 / 0.06±0.02 / 2.0±0.1)	0.43±0.01 (0.44±0.01)	24.3 -0.01

[a] Calculated using a carbon mass fraction of 0.86 [b]HC grams expressed using an NDIR correction factor of 2 [c]Grams of NO [d]Grams of NO_2 [e]NO_2 measurements were unavailable for the Denver and Tulsa 2005 data sets. For those data sets the NO_x means have been calculated directly from the measured NO means and are likely 1 to 2% low as NO_2 emissions have not been estimated.

fleets.[9] Figure S1 (see supporting information) graphs the gNH_3/kg of fuel and gNO_x/kg of fuel for the 2008 and 2013 LA data sets as a function of vehicle specific power (VSP) showing the overlap between the two data sets driving modes and the generally flat emissions versus VSP plots.[36] If we limit each data set to VSP's between -5 and 20 kw/tonne, which coincides with the range observed on the Federal Test Procedure, we can normalize the 2013 data to the driving mode observed in 2008 eliminating the difference (see Table S3A – S3C in the supporting information). After this adjustment 2013 mean emissions for gNO_x/kg of fuel are 3.1 ± 0.1 and for gNH_3/kg of fuel are 0.61 ± 0.03 representing percent reductions of 46% for NO_x (an increase of 15%) and 24% for NH_3 (a decrease of 14%) from the previous fleet comparisons.

Figure 1 presents the 2013 LA NO_x measurements by model year: the gNO_x/kg of fuel emissions by vehicle and fuel type are in the top panel, the fleet percentages by vehicle and fuel type are in the middle panel (gasoline plotted on the left axis and diesel the right) and the fuel specific fleet gNOx/kg of fuel percent contributions by vehicle and fuel type in the bottom panel. Gasoline NO_x emissions have experienced a steady decline with passenger and truck mean fuel-specific emissions converging after the 2002 model year. Diesel truck NO_x emission declines start much later, but catch up with an order of magnitude reduction from 34.2 g NO_x/kg of fuel for 1996 - 2004 models to 3.3 g NO_x/kg of fuel for the 2011 and newer models, which is approaching the emission levels for the gasoline fleet. In addition, the 2008 recession significantly reduced the emissions of the LA truck fleet with large reductions in fleet populations for both the gasoline and diesel segment.[28] While diesel passenger cars are a tiny percentage of the LA fleet (0.3% for the entire data set and 0.6% for 2009 and newer models), their high emissions (~3 times higher for 2009 and newer models, 18.3 gNO_x/kg of fuel versus 6.3 gNO_x/kg of fuel for similar model year diesel trucks) combines to create a significant percent

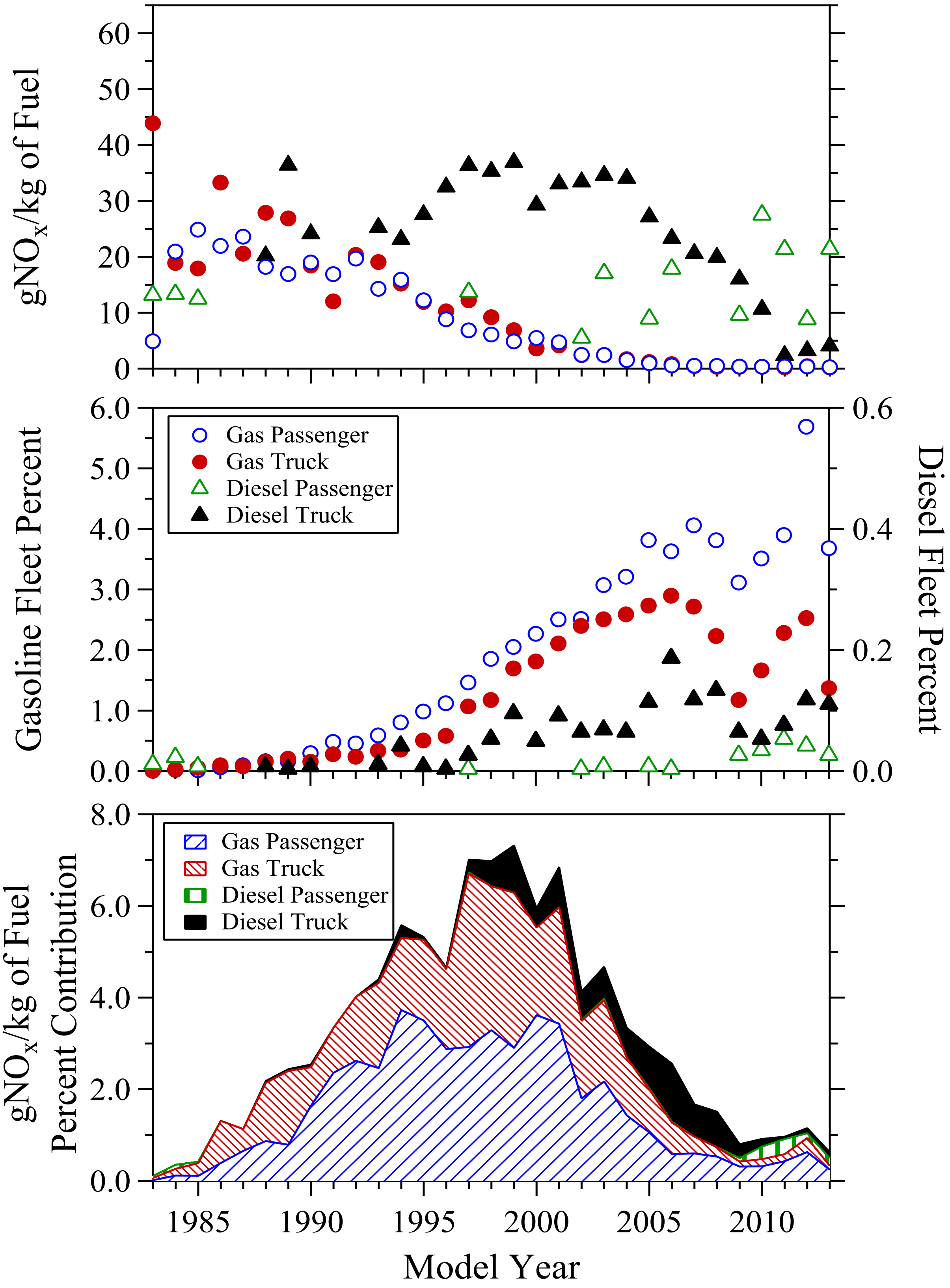

Figure 1. 2013 Los Angeles gNO$_x$/kg of fuel emissions (top panel), fleet percent's (middle panel) and gNO$_x$/kg of fuel percent contributions (bottom panel) versus model year for gasoline and diesel passenger vehicles and trucks. Gasoline includes all hybrids, flex-fuel and natural gas vehicles. Trucks have been restricted to weight classes of 1 to 6, which includes SUV's through medium-duty trucks.

contribution for the newest models. Figures S2 and S3 (see supporting information) are the companion plots for the Denver and Tulsa data sets showing a similar NO_x emissions pattern as LA for their gasoline and diesel vehicles.

Through the combination of the three cities 2013 data sets (refer to Table S2), Figure 2 can be used to further examine the diesel passenger vehicle emissions. In Figure 2a the mean gNO_x/kg of fuel emissions are plotted against model year for diesel passenger vehicles with 2-liter engines (circles) and diesel trucks (squares). Not plotted are six measurements of 2011 and newer diesel passenger vehicles with engines larger than 2-liters which have NO_x emissions similar to the diesel trucks. We have chosen these groupings because it generally coincides with after-treatment technologies with the smaller engine diesel vehicles utilizing LNT systems and the diesel trucks and larger engine passenger vehicles using SCR for NO_x control. The bottom panel is a stacked bar chart for these two groups showing the contribution of NO (converted to NO_2 equivalents) and NO_2 to the total NO_x. The uncertainties displayed are standard errors of the mean calculated from the daily means (see supporting information). Figure 2a shows that 2011 and newer diesel truck NO_x emissions have decreased significantly from older model years coinciding with the introduction of selective catalytic reduction systems. The 2009 and newer model 2-liter diesel passenger vehicles show a different pattern with on-road NO_x emissions levels (18.2 ± 2.3 gNO_x/kg of fuel, right horizontal line) that are statistically unchanged when compared with the 2006 and older 2-liter passenger models (20.6 ± 3.7 gNO_x/kg of fuel, left horizontal line). Figure 2b, however, shows that there are major differences between the two groups of diesel passenger vehicles which accompanied the introduction of Tier-II emission standards. The 2009 and newer 2-liter diesel passenger vehicles show a significant shift in the ratio of NO and NO_2 towards the more toxic NO_2 emissions making it the now their major NO_x

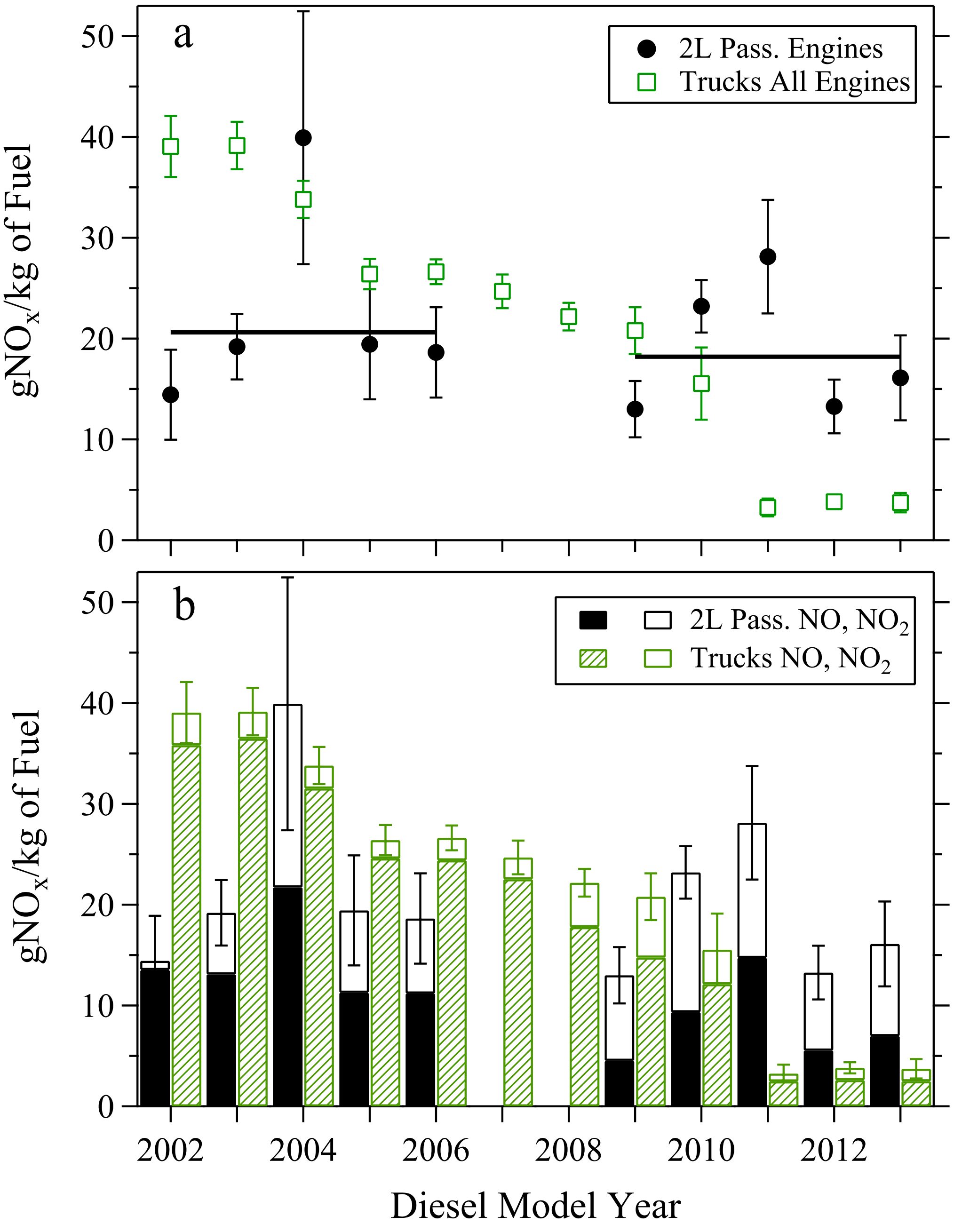

Figure 2. Diesel vehicle gNO_x/kg of fuel emissions from a combined data set for the 2013 measurements in Denver, LA and Tulsa by model year. The top panel graphs average gNO_x/kg of fuel data for 2-liter diesel passenger vehicles (circles) and diesel trucks (squares) as defined by the Polk VIN decoder. The black horizontal lines show the mean emission levels for the 2002-2006 (left) and 2009-2013 (right) 2-liter diesel passenger vehicles which are before and after TIER II/ LEV II implementation. The bottom panel graphs the contribution that NO (converted to NO_2 equivalents) and NO_2 make to the total NO_x for the same vehicle groupings. The uncertainties plotted are standard errors of the mean determined from the daily means for the 2-liter passenger vehicles and diesel trucks.

component (NO_2/NO_x ratios of 0.57 for 2009 and newer and 0.33 for all previous model years). Recent in-use measurements in Europe, where small engine diesels dominate the on-road fleet, have reported large increases in NO_x emissions for diesel passenger cars and light commercial vehicles despite large reductions in the certification standards.[37-40] Extensive portable emission measurements in the US from two 2-liter light-duty diesel passenger vehicles equipped with LNTs showed similar high in-use NO_x and NO_2 emissions; this is in sharp contrast to these vehicle's low NO_x emissions on laboratory certification tests.[41]

Figures 3a and 3b compare the Tulsa 2005 (open symbols) and 2013 (filled symbols) measurement year data sets gNO_x/kg of fuel (circles, bottom panel) and gNH_3/kg of fuel (triangles, top panel) emissions as a function of vehicle age for the gasoline fleet. Standard errors of the mean that are plotted were calculated from the daily model year means (see supporting information). Zero age vehicles are model years 2006 and 2014 for the 2005 and 2013 data sets respectively. Since the 2005 Tulsa data set is lacking measurements for NO_2, mean gNO/kg of fuel has been converted directly into gNO_x/kg of fuel for this comparison. Since the NO_2 component for the gasoline fleet is small (~1 to 2%), this underestimates the total NO_x only slightly without affecting the trends. The comparison highlights the fact that large reductions in light-duty NO_x emissions have occurred for 4 to 19 year old vehicles. This age group has 60% less gNO_x/kg of fuel emissions in 2013 than they did in the 2005 measurements. In the 2013 measurements this age group is composed of all on-board diagnostic II (OBDII) compliant 1996 to 2010 model year vehicles. Also note that, despite age, the fleet Tier-II emission reductions of gNO_x/kg of fuel emissions appear to have been fully instituted several years prior to the 2009 models (when Tier-II emission standards were required for all vehicles) as the mean model year emissions are statistically identical for the first 7 model years of the 2013 data set.[12]

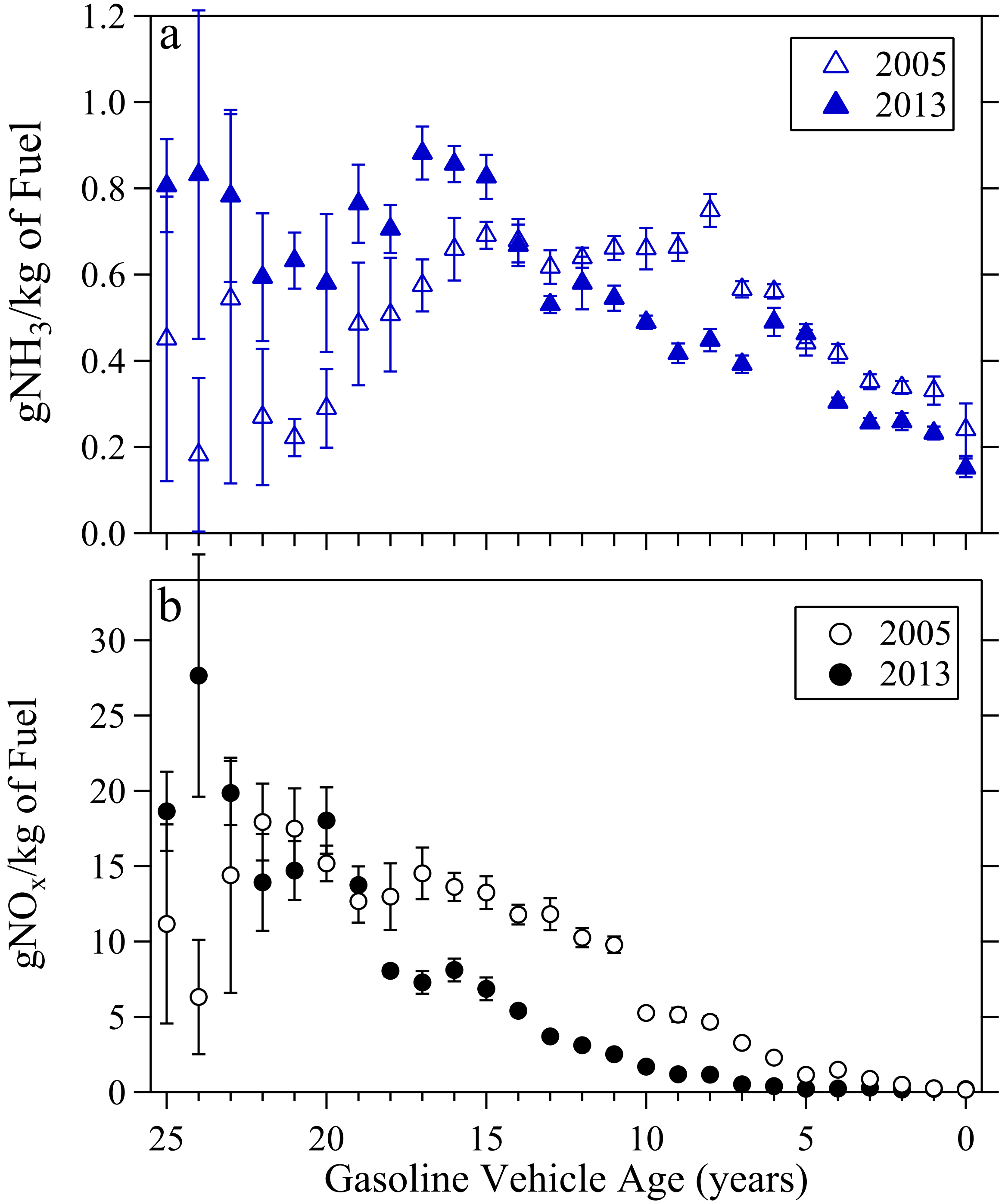

Figure 3. Tulsa 2005 (open symbols) and 2013 (filled symbols) gNH_3/kg of fuel (top panel, triangles) and gNO_x/kg of fuel (bottom panel, circles) emissions versus vehicle age for only the gasoline portion of the fleet. The errors plotted for each year's data are standard errors of the mean determined from the daily means for each model year. Zero year vehicles represent 2006 and 2014 model years respectively.

The largest reduction in NO_x emissions during the previous two decades, which we have previously noted, coincided not with a change in emission limits but with the introduction of the OBDII systems beginning with the 1996 models.[9, 42] In the 2005 measurements, the observed gNO_x/kg of fuel emissions for the 1996 models, which were 10 years old, were almost a factor of two lower than those for the 1995 model year vehicles (5.3 ± 0.3 vs 9.8 ± 0.6). Eight years later the 2013 data set shows that those NO_x emissions difference contracted slightly (8.1 ± 0.4 vs 13.7 ± 1.2) but remained the largest single year gNO_x/kg of fuel emissions change in the 2013 measurements. While these large reduction coincided with OBD-II's introduction the diagnostic system does not appear to have as significantly altered fleet NO_x emission deterioration rates, as evidenced by the consistency in the emission difference maintained between the 1995 (increased 40%) and 1996 (increased 53%) models during the intervening eight years.

As previously discussed, fleet-wide reductions in NH_3 emissions in Tulsa have accompanied the reductions of NO_x but at a slower rate, having only decreased by 14% since 2005. Figure 3a shows that for ten year old and newer vehicles, where one might expect the largest reductions, NH_3 has only been modestly reduced by 25%. During this time, the percentage of the fleet that still has an active catalytic converter, which is required for the reduction of NO to NH_3, has increased working against the newer vehicle reductions. NH_3 emissions peaked for gasoline vehicles in the 2005 measurements somewhere between 8 to 15-year old vehicles (1998 – 1991 models) before declining. In the 2013 measurements this emissions peak has been extended out to 17-year old vehicles (1997 models) before declining at a slower rate than observed in the 2005 data set. In Denver and LA (28%) NH_3 reductions have also lagged NO_x declines with no statistical significant reduction of NH_3 between the two Denver data sets. So, while new vehicle NH_3 emissions are declining, the number of vehicles in the fleet capable of producing NH_3 has increased, which seems to have slowed the NH_3 emissions overall rate of decline since the rate reported earlier by Kean et al.[43]

The sizable difference in the rates of reduction for on-road NO_x and NH_3 emissions has resulted in a dramatic shift in the makeup of the exhaust of today's gasoline vehicles. Figure 4 is a stacked bar chart showing the 2005 and 2013 Tulsa measurements for the total moles of nitrogen per kg of fuel with the NO_x (solid portion) and NH_3 (hatched portion) nitrogen contributions indicated. The inset graph enlarges the y-axis for the first ten model years. Figure 5 is a companion graph which plots the molar percent fixed nitrogen for the NO_x (circles) and NH_3 (triangles) contributions versus model year for the 2005 (open symbols with a line) and 2013 (filled symbols) gasoline vehicles in Tulsa. Figure 4 emphasizes the large reductions in reactive nitrogen emissions achieved during the past eight years, and Figure 5 highlights the shift in the source of those remaining reactive nitrogen emissions in the newest vehicles. In the 2005 measurements only the two newest model years had reactive nitrogen emissions dominated by NH_3. That has expanded to the first eight model years in 2013. With catalytic converters continuing to retain their activity for longer periods of time, we would expect this trend to continue leading to a growing number of vehicle model years that emit NH_3 as the dominant fixed nitrogen compound. This trend was also observed in the LA (5 model years in 2008 expanding to nine in 2013) and Denver (one model year in 2005 to four in 2013) data sets which are shown in Figures S4 and S5.

Urban air chemistry in the United States was once dominated by CO emissions. Accompanying the CO emissions were significant emissions of NO_x and hydrocarbons (HC). While all three of these traditional vehicle emissions are rapidly disappearing, NH_3 is becoming a major emitted nitrogen species due to its slower decline in modern fleets. This shift in exhaust

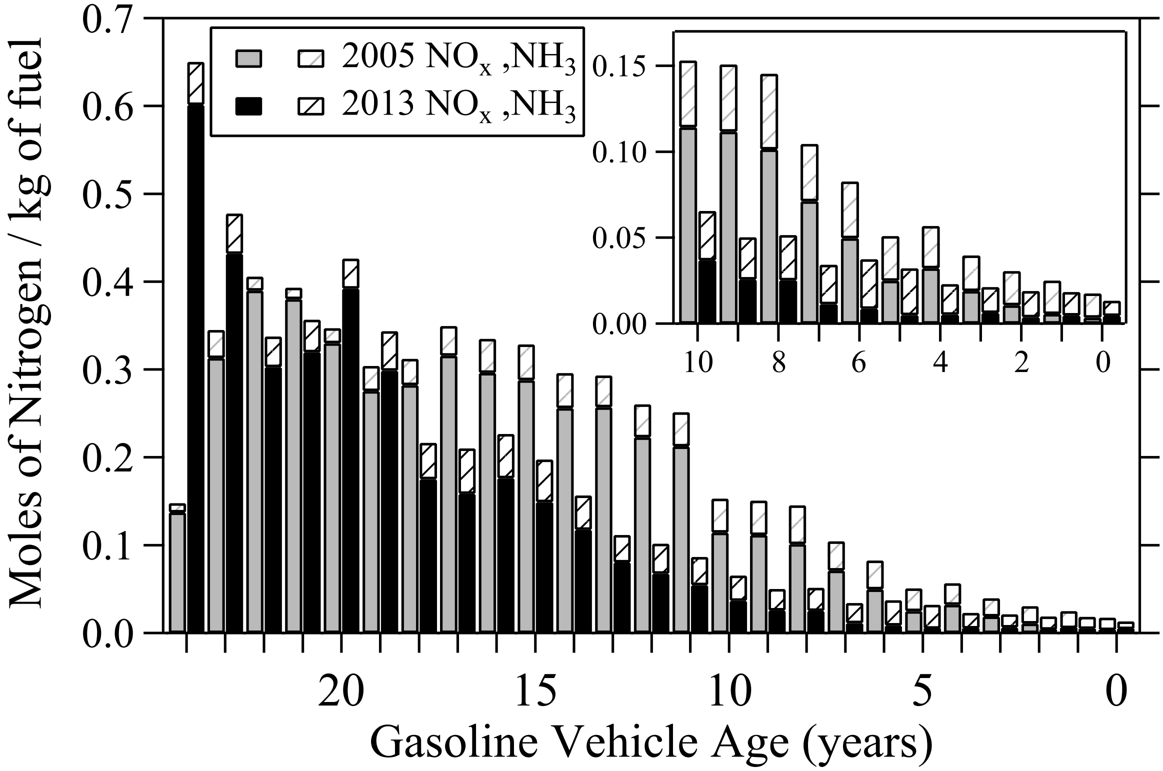

Figure 4. Stacked bar chart of moles of nitrogen per kilogram of fuel as a function of vehicle age for gasoline only vehicles in the 2005 and 2013 Tulsa data sets. Zero year vehicles represent 2006 and 2014 model years respectively. The solid bars represent the moles of nitrogen contributed by the oxides of nitrogen and the hatched bars represent the moles of nitrogen

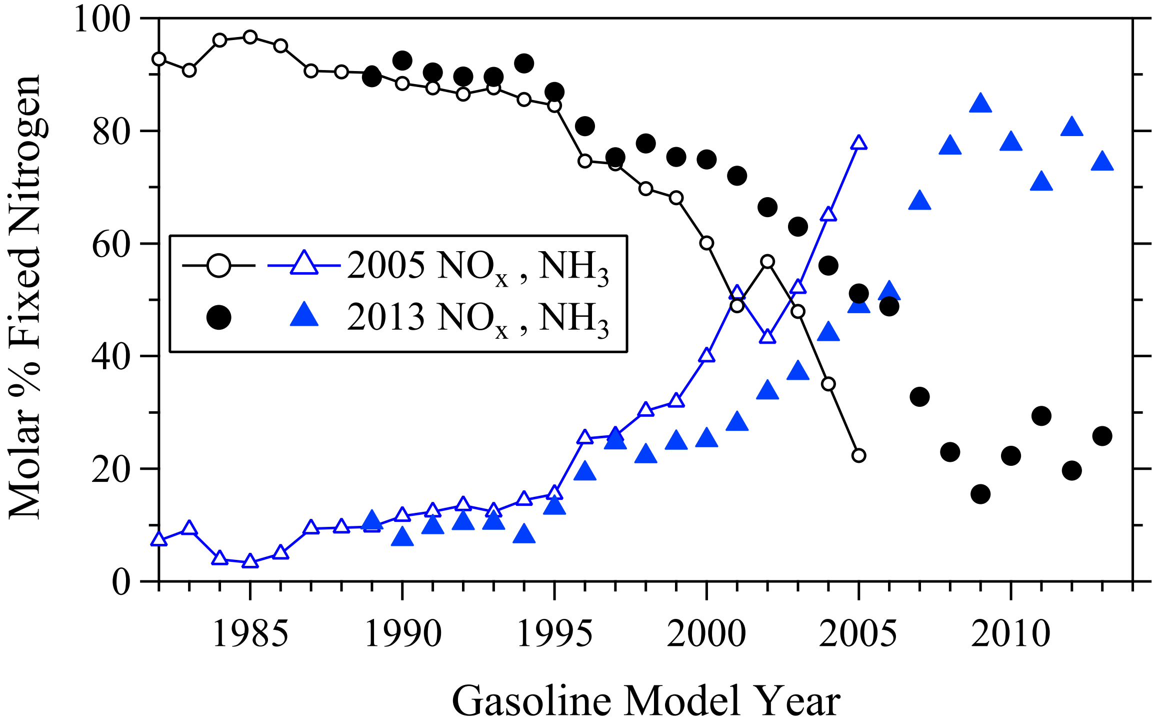

Figure 5. Molar percent fixed nitrogen contributions for NOx (circles) and NH$_3$ (triangles) versus model year for the 2005 (open symbols) and 2013 (filled symbols) gasoline only vehicles in the Tulsa data sets.

chemistry (or the exhaust constituents) will have profound effects on the chemistry of gasoline vehicle exhaust. Historically, gasoline vehicle emissions of fixed nitrogen have been dominated by the oxides of nitrogen which become acidic and are involved in local ozone destruction (NO) at the emissions point and, later in downwind regions, ozone production (NO_2), secondary particulate formation (NH_4NO_3) and acid deposition (HNO_3).[44] NH_3 is a weak base that readily reacts in the atmosphere to form secondary aerosols (NH_4NO_3 and $(NH_4)_2SO_4$), whose formation rates may be the most affected by these changes.

ASSOCIATED CONTENT

Supporting Information. Supplementary tables (S1 – S3C) and figures (S1 – S5) referenced in the text. This material is available free of charge via the Internet at http://pubs.acs.org."

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Notes

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Supporting Information For:

Reactive Nitrogen Species Emission Trends in Three Light-/Medium-Duty United States Fleets

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Summary of Supporting Information:

10 Pages (excluding cover): Tables S1 – S3C and Figures S-1 – S-5

Tables

Figures

markers in the bottom panel are the number of vehicles in each bin for each data set. Note that the data plotted have not been adjusted for any age differences.

S2. 2013 Tulsa gNO_x/kg of fuel emissions (top panel), fleet percents (middle panel) and gNO_x/kg of fuel percent contributions (bottom panel) versus model year for gasoline and diesel passenger vehicles and trucks. Gasoline includes all hybrids, flex-fuel and natural gas vehicles. Trucks have been restricted to weight classes of 1 to 6, which includes SUV's through medium-duty trucks.

S3. 2013 Denver gNO_x/kg of fuel emissions (top panel), fleet percents (middle panel) and gNOx/kg of fuel percent contributions (bottom panel) versus model year for gasoline and diesel passenger vehicles and trucks. Gasoline includes all hybrids, flex-fuel and natural gas vehicles. Trucks have been restricted to weight classes of 1 to 6, which includes SUV's through medium-duty trucks.

S4. Molar percent fixed nitrogen contributions for NO_x (circles) and NH_3 (triangles) versus model year for the 2008 (open symbols) and 2013 (filled symbols) gasoline vehicles in the Los Angeles data sets.

S5. Molar percent fixed nitrogen contributions for NO_x (circles) and NH_3 (triangles) versus model year for the 2005 (open symbols) and 2013 (filled symbols) gasoline vehicles in the Denver data sets.

How we calculate standard errors of the mean

Because vehicle emissions from US vehicle fleets are not normally distributed the assigning of uncertainties on fleet emission means involves a process that many readers may not be familiar with. Standard statistical methods that were developed for normally distributed populations when used on a skewed distribution results in uncertainties that are unrealistically too small due to the large number of samples. The Central Limit Theorem in general says that the means of multiple samples, randomly collected, from a larger parent population will be normally distributed. Since we almost always collect multiple days of emission measurements from each site, we use these daily measurements as our randomly collected multiple samples from the larger population and report uncertainties based on their distribution. We calculate means, standard deviations and finally standard errors of the mean for this group of daily measurements. We report the means for all of the emission measurements and then calculate a standard error of the mean for the entire sample by applying the same error percentage obtained from the ratio of the standard error of the mean for the daily measurements divided by the daily measurement mean. An example of this process is provided below for the 2013 Tulsa gNO_x/kg of fuel and gNH_3/kg of fuel measurements. For NO_x measurements we require both the NO/CO_2 and NO_2/CO_2 measurements to be valid as defined by FEAT slope error validity requirements, while for NH_3 these requirements are only for the NH_3/CO_2 measurements.[1] While this example is for a fleet mean we also use this technique when we report standard errors of the mean for individual model years or specific fuel or technology types.

Tulsa 2013

Date	Mean gNO_x/kg of fuel	Counts	Mean gNH_3/kg of fuel	Counts
9/30/13	2.1649	2664	0.44193	3092
10/1/13	1.8639	3692	0.45655	4208
10/2/13	2.0012	4001	0.42519	4362
10/3/13	2.0219	3790	0.44275	4462
10/4/13	1.9048	3768	0.4416	4381
Daily Mean	1.99		0.44	
Standard Error for the daily means	0.05		0.01	
Fleet Mean	1.98		0.44	
Standard Error for the fleet mean	0.05		0.01	
As reported in Table 1	2.0 ± 0.1		0.44 ± 0.01	

Table S1. Summary of Gasoline Passenger and Truck Records by City and Measurement Year.

City Year	Gasoline Records (pre-1981)	Percent Passenger (Trucks)	Gasoline Truck Records					
			Class 1	Class 2	Class 3	Class 4	Class 5	Class 6
Denver 2005	3562 (24)	46% (54%)	1158	714	14	5	2	1
Denver 2013	18601 (32)	42% (58%)	6701	3899	72	39	1	1
Los Angeles 2008	17634 (59)	57% (43%)	4789	2614	75	33	3	2
Los Angeles 2013	26680 (57)	60% (40%)	6659	3716	90	39	6	3
Tulsa 2005	18406 (71)	45% (55%)	5485	4472	61	5	0	4
Tulsa 2013	20516 (18)	40% (60%)	5980	6146	37	16	0	3

Table S2. Summary of Diesel Passenger and Truck Records by City and Measurement Year.

City Year	Diesel Records	Percent Passenger (Trucks)	Diesel Truck Records					
			Class 1	Class 2	Class 3	Class 4	Class 5	Class 6
Denver 2005	128	4% (96%)	0	70	21	11	6	15
Denver 2013	628	16% (84%)	10	328	106	26	26	33
Los Angeles 2008	269	6% (94%)	0	100	23	54	24	44
Los Angeles 2013	510	14% (86%)	4	149	44	90	73	77
Tulsa 2005	471	3% (97%)	3	249	125	31	20	27
Tulsa 2013	587	8% (92%)	7	329	129	14	28	32

Table S3A. Los Angeles 2008 Measurements.

VSP Bin	Mean gNO_x/kg of Fuel	Counts	Total NO_x Emissions	Mean gNH_3/kg of Fuel	Counts	Total NH_3 Emissions
-5	0.151	5	0.76	0.967	6	5.80
0	10.421	109	1135.84	1.346	112	150.78
5	5.717	903	5162.30	0.753	910	685.43
10	6.444	4299	27703.57	0.735	4306	3163.19
15	5.557	6692	37186.71	0.795	6673	5305.44
20	4.612	3182	14676.40	0.823	3168	2607.26
Totals		15190	85865.58		15175	11917.89
Means			5.65			0.79

Table S3B. Los Angeles 2013 Measurements.

VSP Bin	Mean gNO_x/kg of Fuel	Counts	Total NO_x Emissions	Mean gNH_3/kg of Fuel	Counts	Total NH_3 Emissions
-5	3.252	381	1239.14	0.703	427	300.02
0	2.427	2750	6675.53	0.603	2956	1782.79
5	3.201	8846	28316.50	0.571	9120	5211.33
10	3.364	9166	30838.92	0.576	9334	5376.57
15	2.839	2072	5882.68	0.574	2102	1206.23
20	3.034	237	719.09	0.767	236	181.07
Totals		23452	73671.86		24175	14058.01
Means			3.14			0.58

Table S3C. Los Angeles 2013 Measurements Normalized to the 2008 Driving Mode.

VSP Bin	2013 Mean gNO_x/kg of Fuel	2008 Counts	Total NO_x Emissions	2013 Mean gNH_3/kg of Fuel	2008 Counts	Total NH_3 Emissions
-5	3.252	5	16.26167	0.703	6	4.215719
0	2.427	109	264.5939	0.603	112	67.54819
5	3.201	903	2890.549	0.571	910	519.99
10	3.364	4299	14463.94	0.576	4306	2480.342
15	2.839	6692	18999.46	0.574	6673	3829.301
20	3.034	3182	9654.665	0.767	3168	2430.616
Totals		15190	46289.47		15175	9332.01
Means			3.05			0.61

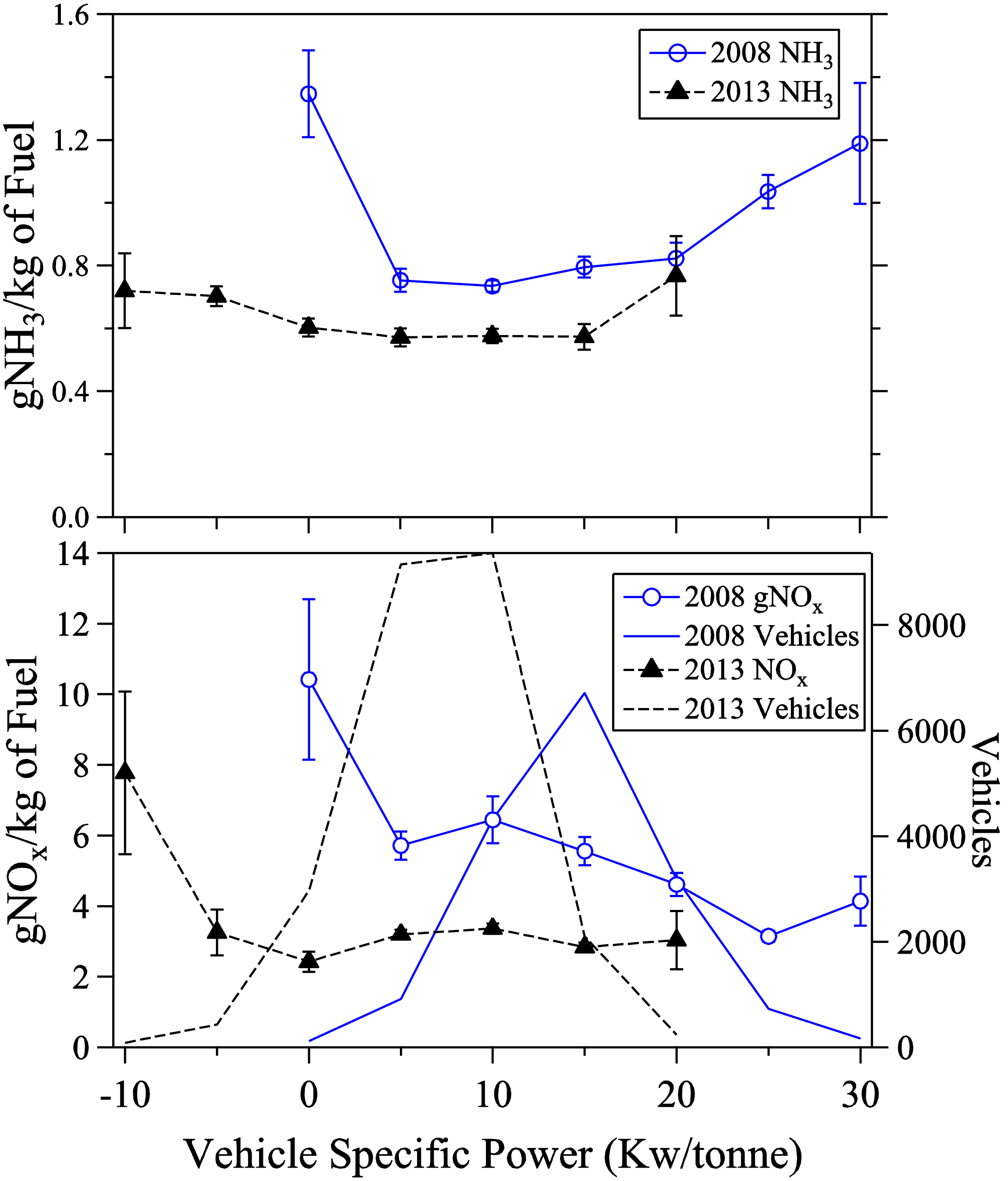

Figure S1. Vehicle gNH_3/kg of fuel (top panel) and gNO_x/kg of fuel (bottom panel) emissions as a function of vehicle specific power for the 2008 and 2013 Los Angeles measurements. Error bars are standard errors of the mean calculated from daily samples and the lines without markers in the bottom panel are the number of vehicles in each bin for each data set. Note that the data plotted have not been adjusted for any age differences.

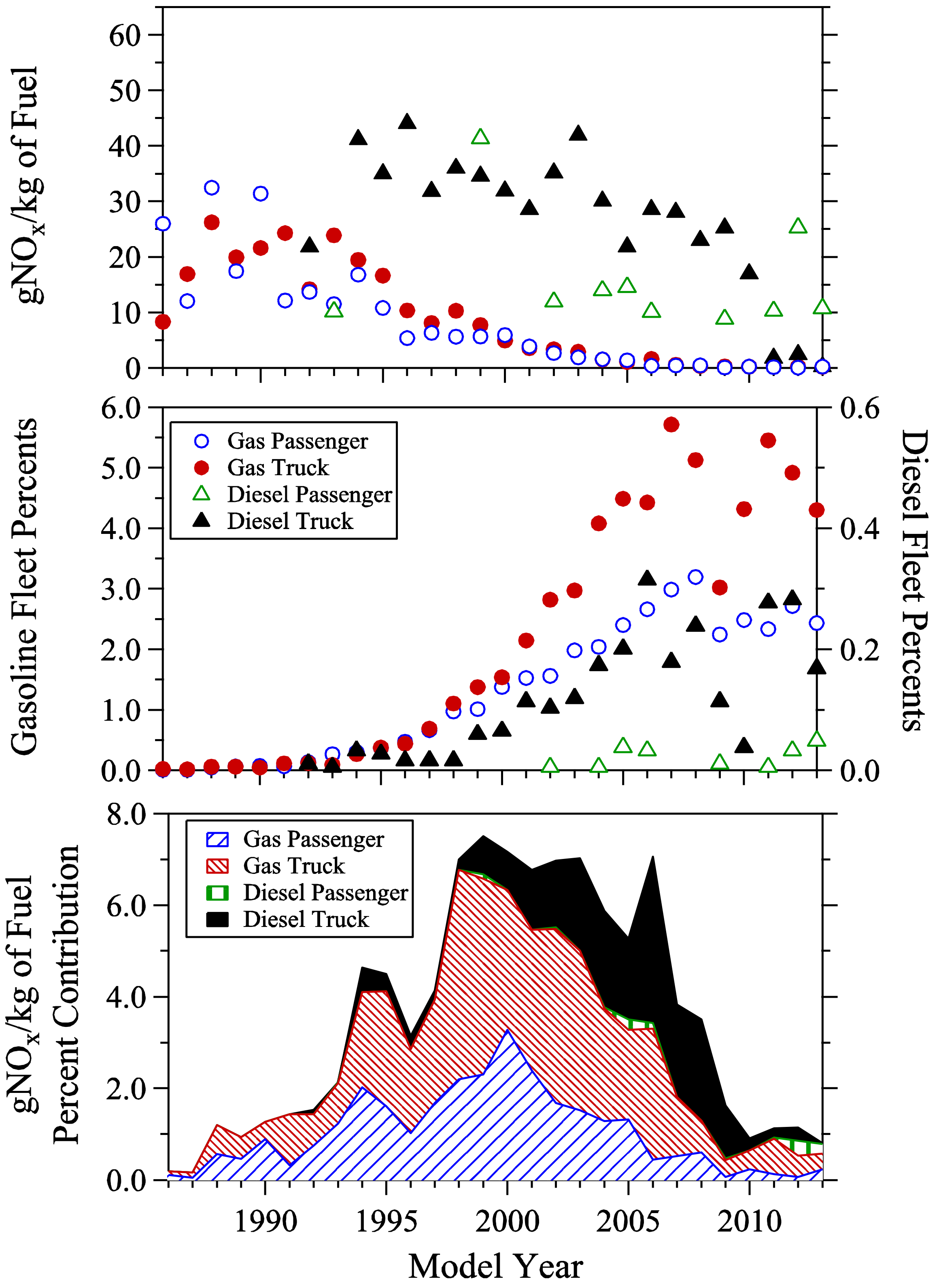

Figure S2. 2013 Tulsa gNOx/kg of fuel emissions (top panel), fleet percents (middle panel) and gNOx/kg of fuel percent contributions (bottom panel) versus model year for gasoline and diesel passenger vehicles and trucks. Gasoline includes all hybrids, flex-fuel and natural gas vehicles. Trucks have been restricted to weight classes of 1 to 6, which includes SUV's through medium-duty trucks.

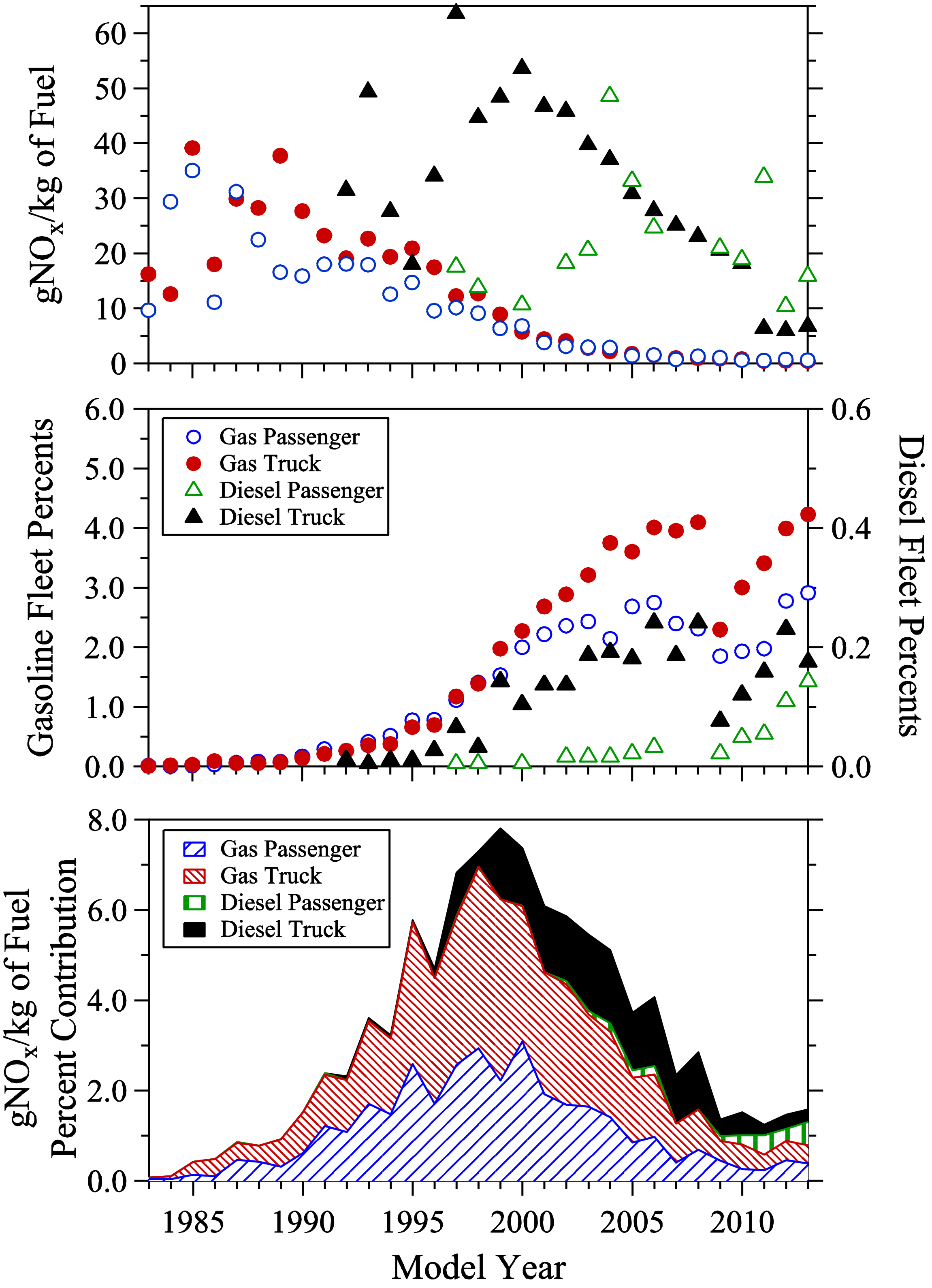

Figure S3. 2013 Denver gNOx/kg of fuel emissions (top panel), fleet percents (middle panel) and gNOx/kg of fuel percent contributions (bottom panel) versus model year for gasoline and diesel passenger vehicles and trucks. Gasoline includes all hybrids, flex-fuel and natural gas vehicles. Trucks have been restricted to weight classes of 1 to 6, which includes SUV’s through medium-duty trucks.

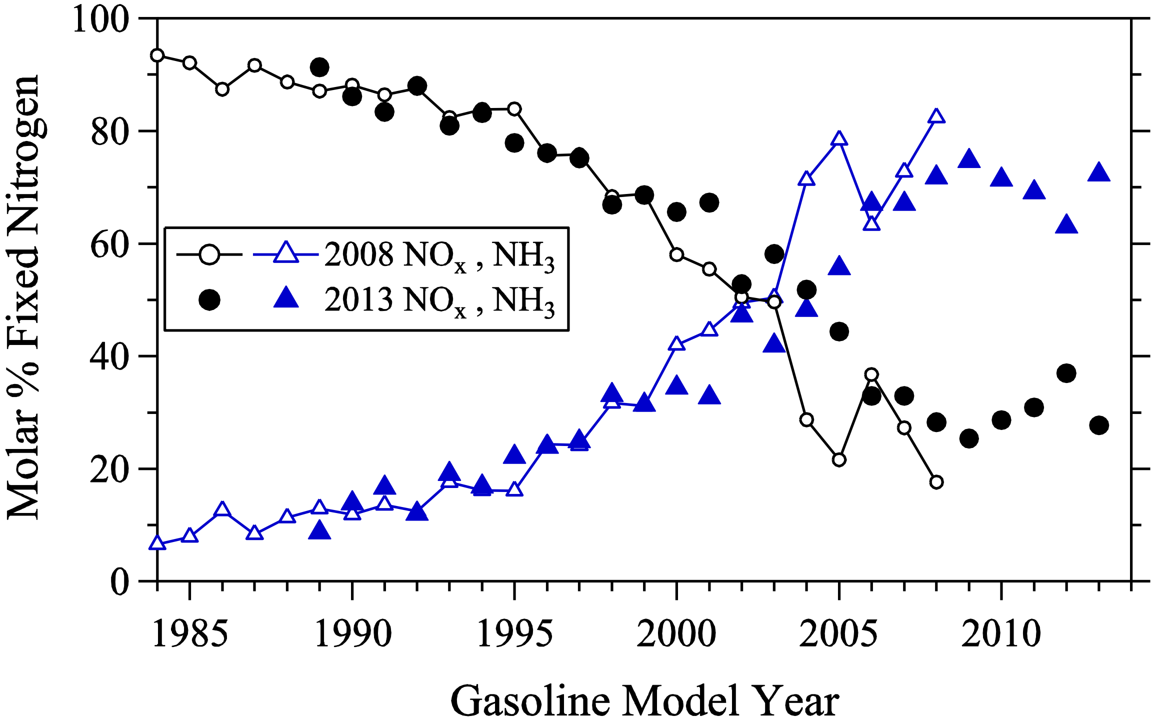

Figure S4. Molar percent fixed nitrogen contributions for NO_x (circles) and NH_3 (triangles) versus model year for the 2008 (open symbols) and 2013 (filled symbols) gasoline vehicles in the Los Angeles data sets.

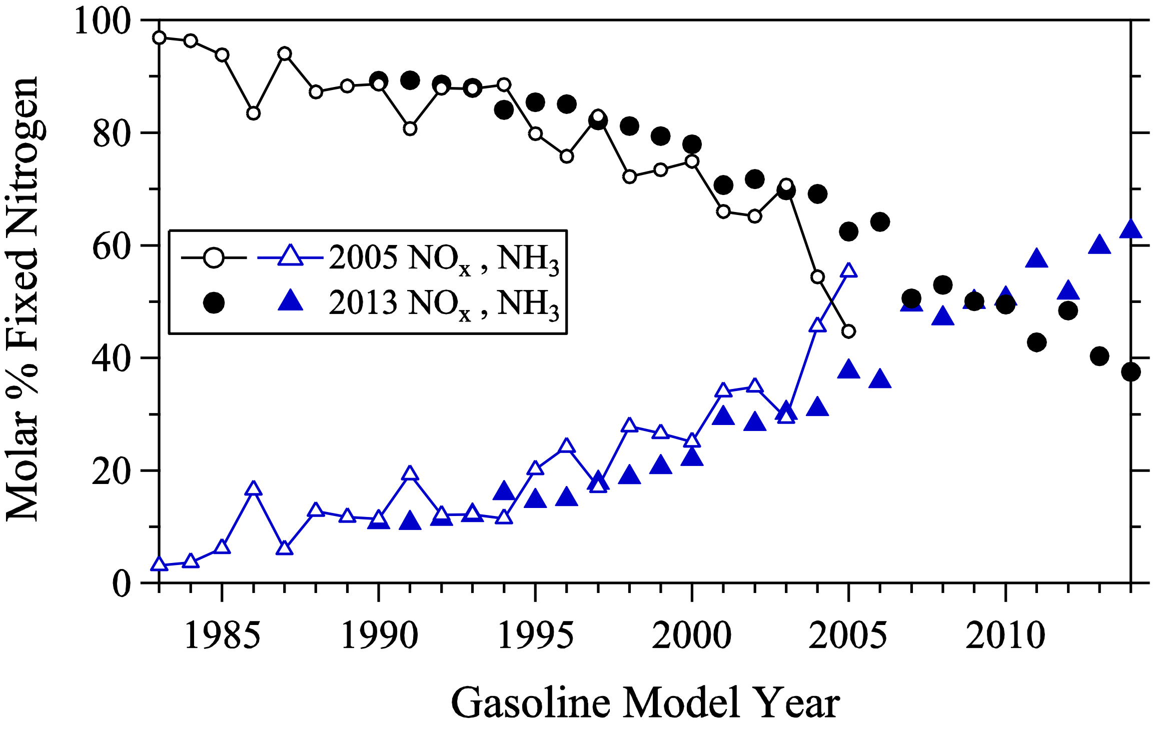

Figure S5. Molar percent fixed nitrogen contributions for NO$_x$ (circles) and NH$_3$ (triangles) versus model year for the 2005 (open symbols) and 2013 (filled symbols) gasoline vehicles in the Denver data sets.

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