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 (NO2) to NO in new diesel vehicles appears to be undergoing 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 NO2. Ammonia (NH3) emissions are shown to have a strong dependence on model year and vehicle specific power. NH3 means are 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. NH3 at these locations was found to account for 25%, 22%, and 27% of the molar fixed nitrogen emissions, respectively. Using these mean values to construct a national fuel-based NH3 inventory results in a range of 210000 to 330000 short tons of NH3 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 (PM2.5) 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 (NO2), ammonia (NH3), and nitrous acid (HONO) produced by internal combustion engines in combination with catalytic converters are important precursors contributing to ozone and PM2.5 formation in these areas.

Direct emissions of HONO from modern catalyst-equipped vehicles are not believed to be significant (1). OXides of nitrogen (NOx) emission rates from light-duty gasoline vehicles have been shown to be rapidly decreasing across the United States, but total NOx emissions are decreasing at a slower rate due to the growth in heavy-duty diesel traffic (2–5). Because NO and NOx are quickly interconverted, only NO 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 NO2 (immediately available for ozone production) have important implications for ozone photochemistry. Historically, NO2 emissions have been less than 10% of the total NO 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 NO2 to oxidize the trapped soot particles thus keeping the filters from clogging. In Europe, where oxidation catalysts are common on light-duty diesels and DPF-equipped heavy-duty diesels have already been introduced, a number of urban areas have experienced increases in NO2 emissions (7). This trend has caught the attention of regulators. For example, in its diesel retrofit program, California only allows modest increases of NOx because of 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).

NH3 is a rather recent motor vehicle emitted species and is an unregulated byproduct of three-way catalytic converters over reducing NO when reducing agents are present (9). The importance of PM2.5 emissions has focused new attention on understanding NH3 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 NOx, it has been assumed that NH3 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 compared to NOx and NH3 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 PM2.5 levels (2, 12). The complicated and nonlinear nature of ozone and PM2.5 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, NO2, and NH3 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 Web site at www.feat.biochem.du.edu.

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 nondispersive infrared (NDIR) component for detecting carbon monoxide (CO), carbon dioxide (CO2), hydrocarbons (HC), and twin dispersive ultraviolet spectrometers for measuring NO, sulfur dioxide (SO2), NH3, and NO2, and has been fully described in the literature (15–17). The remote sensor measures vehicle exhaust gases as a ratio to exhaust CO2 because 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 kilogram of fuel by carbon balance after doubling the HC/CO2 ratio to account for the poor quantification of certain hydrocarbon species by NDIR absorption (15, 18).

The speed and acceleration and freeze-frame video image of the license plate of each vehicle was recorded along with a measurement for the day-to-day variations in instrument sensitivity and variations in ambient CO2 levels caused by atmospheric 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. NO2 emissions have been calculated by converting the measured gNO/kg into gNO2/kg and summing with the measured gNO2/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.

Parrish has reported on morning rush hour ambient emission measurements of molar CO/NO2 ratios at a number of sites across the United States 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 NO2 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 at 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 model year data set is the first year that we have measured NO2 emissions. 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 model year data set is the first year that we have measured NO2 emissions.
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 the other diesel vehicles (because the NO₂ data are not normally distributed, the SEM for these vehicles will likely be underestimated). There are large differences between the NO₃ emissions of the other diesel and gasoline vehicles. While the NO₂ fraction of the NO emissions is larger than that for the other diesel vehicles, it is a fraction of a much smaller baseline emission factor. The Sprinters total NO₂ emissions of the groupings samples mean %IR opacity mean gNH₃/kg mean g/kg NO₂/NO/NO₃, mass ratio NO₂/NO₃

<table>
<thead>
<tr>
<th>grouping</th>
<th>samples</th>
<th>mean %IR opacity</th>
<th>mean gNH₃/kg</th>
<th>mean g/kg NO₂/NO/NO₃</th>
<th>mass ratio NO₂/NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sprinters</td>
<td>57</td>
<td>0.6 ± 0.2</td>
<td>0.02 ± 0.01</td>
<td>2.1 ± 0.2/4.9 ± 0.6/8.0 ± 0.8</td>
<td>0.61</td>
</tr>
<tr>
<td>other diesels</td>
<td>22</td>
<td>1.2 ± 0.7</td>
<td>0.02 ± 0.02</td>
<td>12.1 ± 0.9/1.4 ± 0.4/19.9 ± 1.2</td>
<td>0.07</td>
</tr>
<tr>
<td>non-diesel</td>
<td>792</td>
<td>0.4 ± 0.04</td>
<td>0.14 ± 0.02</td>
<td>0.22 ± 0.08/0.08 ± 0.01/0.42 ± 0.12</td>
<td>0.19</td>
</tr>
</tbody>
</table>

a NO reported as grams of NO. b NO₂ and NO₃ reported as grams of NO. 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.

Fresno County is estimated to annually emit approximately 420 metric tons of NO₂ based on the California EMFAC model. Direct emissions of NO 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 NH₃ 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 the NO to NH₃. 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 NH₃ 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 15 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 because of 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 NH₃ emissions decrease with increasing age.

FIGURE 2. Mean gNH₃/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 seven daily means for each model year.
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 (Table 2) are similar to all of the previously reported measurements, while the wLA data are the highest NH3 emissions reported to date.

Figure 3 is a plot of the emissions of NH3 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. NH3 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 NH3 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 4 plots the mass in g/kg of NOx and NH3 emissions against model year for the newest 20 model years. The NOx emissions have been plotted on a scale that generally allows them to overlap with the NH3 emissions to highlight the similar emissions trends. In San Jose and Fresno, the NH3 and NOx emissions are decreasing at a similar rate over the newest 10 model years. NOx emissions from the newest vehicles (2004 and newer) are 30% lower at the wLA site than the other two sites and 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 NH3.

The mole percent ammonia of the total fixed nitrogen (mol/kg N\text{fixed} = \text{mol/kg NH}_3 + \text{mol/kg NO}_x \text{ neglecting any unmeasured N}_2\text{O and HONO that may account for a few percent}) was calculated to compare with published results (1, 27, 28). At the San Jose, Fresno, and wLA sites, NH3 accounted for 25%, 22%, and 27% of the fixed molar nitrogen emissions, respectively. 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 %NOx and %NH3 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 NH3 has increased. For the newest model years, NH3 contributes strikingly large fractions of the fixed nitrogen emissions at all sites.

Using the mean NH3 measurements reported in this paper, national gasoline sales of 378 million gallons per day, and assuming that NH3 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 gNH3/kg mean emission levels results in a national emission inventory of 210000 short tons per year,
while the data from the wLA site results in a total of 330000 short tons per year. The U.S. EPA has estimated that the 2007 national NH3 inventory contribution from all highway vehicles amounts to 307000 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 United States 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 NH3 inventory from mobile sources may be somewhat overestimated.  

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**Literature Cited**

8. Verification Procedure, Warranty and In-Use Compliance Requirements for In-Use Strategies to Control Emissions from Diesel Engines. California Code of Regulations; Title 13, Division 3, Chapter 14, Section 2701–2709.