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EXECUTIVE SUMMARY

The University of Denver has completed the eighth year of a multi-year remote sensing study in the Chicago area, with measurements made in Septembers of 1997 through 2000, 2002, 2004, 2006 and 2014. The remote sensor used in the 2014 study measured the ratios of CO, HC, NO, SO_2 and NH_3 to CO_2 in motor vehicle exhaust. Mass emissions per mass or volume of fuel are determined from these ratios and are the units used for the major results in this report. From these ratios, we can also calculate the percent concentrations of CO, CO_2, HC, NO, SO_2 and NH_3 in the exhaust that would be observed by a tailpipe probe, corrected for water and any excess air. The system used in this study was configured to determine the speed and acceleration of the vehicle, and was accompanied by a video system to record the license plate of the vehicle and, from this record, the vehicle's model year. Since fuel sulfur has been nearly eliminated in US fuels, SO_2 emissions have followed suit. Vehicle SO_2 measurements were collected but not calibrated and are not included in the discussion of the results.

The eighth campaign of this study involved fieldwork on September 8 - 13, 2014, conducted at the on-ramp from Algonquin Rd. to eastbound I-290 in northwest Chicago. This year's data collection was hampered by wet and unusually cool weather that forced an extension of the week of measurements into Saturday for the first time. For the 2014 measurements, a database was compiled containing 20,395 records for which the State of Illinois provided make and model year information. All of these records contain valid measurements for at least CO and CO_2, and most records contain valid measurements for the other species. The database, as well as others compiled by the University of Denver, can be found at www.feat.biochem.du.edu.

The CO, HC, NO, NH_3 and NO_2 mean and standard errors of the mean emissions for the fleet measured in this study were 9.4 ± 0.8 gCO/kg (0.07 ± 0.01 %), 1.3 ± 0.2 gHC/kg (35 ± 5 ppm), 1.5 ± 0.1 gNO/kg (105 ± 7 ppm), 0.71 ± 0.02 gNH$_3$/kg (89 ± 3 ppm) and -0.04 ± 0.02 gNO$_2$/kg (-1.5 ± 0.8 ppm) respectively. The negative NO_2 means are likely the result of a negative measurement bias which was not adjusted for because of its small magnitude. When compared with previous measurements from 2006, mean CO (-42%) and HC (-41%) emissions have experienced significant reductions while NO (-17%) has declined at a slower rate. The emissions measurements in this study exhibit a gamma distribution, and the skewedness has continued to increase during the intervening years. The 99th percentile for the 2014 measured fleet is responsible for 34%, 43%, 25% and 10% of the CO, HC, NO and NH_3 emissions, respectively.

The effect of the 2008 economic recession is very noticeable in the loss of 2009 and 2010 models from this Chicago fleet. However, the reductions in those models are less than observed at other E-106 sites. In Chicago, 2009 model year vehicles were 26% fewer than 2008 models, and the 2010 models were 17% fewer. This compares to reductions of 37% and 19% for those models in the 2013 Tulsa OK data set. Fleet fractions for the 2013 and 2014 model year vehicles appear to have fully recovered to prerecession levels. This combination resulted in only a slight age increase of this site's fleet of 0.5 model year to 7.5 years old since 2006.

The Chicago site is only the seventh site to have NH_3 emission measurements collected since 2005. The observed mean of 0.71 ± 0.02 is the second highest mean observed, surpassed only by the 2008 measurements at the metered ramp site in west Los Angeles. The driving mode in Chicago bears some resemblance to the west LA arrangement, as the majority of the traffic at the Chicago site enters the ramp from a light-controlled double turn lane on Algonquin Rd. The Chicago 2014 trends though are very similar to the 2013 Tulsa measurements, including the vehicle age that coincides with peak NH_3 emissions. When correlating the age-aligned model year groupings, the resulting slope is 1.06 with an R^2 of 0.86. As previously seen in Denver, LA and Tulsa, NH_3 dominates the total fixed nitrogen species present in the newest model year vehicles in Chicago. In the newest model years, NH_3 comprises approximately 80% of a small amount of total fixed nitrogen. The cross over point where NH_3 and NO_x emissions are equal occurs in 10 year old vehicles in Chicago.

INTRODUCTION

Since the early 1970's, many heavily populated U.S. cities have violated the National Air Quality Standards (NAAQS) established by the Environmental Protection Agency (EPA) pursuant to the requirements of the federal Clean Air Act.[1, 2] Carbon monoxide (CO) levels become elevated primarily due to direct emission of the gas, and ground-level ozone, a major component of urban smog, is produced by the photochemical reaction of nitrogen oxides (NO_x) and hydrocarbons (HC). Ambient levels of particulate emissions can result either from direct emissions of particles or semi-volatile species or from secondary reactions between gaseous species, such as ammonia and nitrogen dioxide. As of 2010, on-road vehicles continued to be estimated as one of the larger sources for major atmospheric pollutants, contributing approximately 44% of the CO, 34% of the VOC's, 8% of the NH_3 and 34% of the NO_x to the national emission inventory.[3]

The use of the internal combustion engine (and its combustion of carbon-based fuels) as a primary means of transportation, makes it a significant contributor of species covered by the NAAQS. For a description of the internal combustion engine and causes of pollutants in the exhaust, see Heywood.[4] Properly operating modern vehicles with three-way catalysts are capable of partially (or completely) converting engine-out CO, HC and nitric oxide (NO) emissions to carbon dioxide (CO_2), water, and nitrogen. Control measures to decrease mobile source emissions in non-attainment areas include inspection and maintenance (I/M) programs, reformulated and oxygenated fuel mandates, and transportation control measures, but the effectiveness of these measures is difficult to quantify. Many areas remain in ozone non-attainment. The eight-hour ozone standards introduced by the EPA in 1997, tightened in 2008, with expected further tightening, mean that many new locations are likely to have difficulty meeting the standards in the future.[5]

In 1997, the University of Denver began conducting on-road tailpipe emission surveys at a site northwest of Chicago IL, in Arlington Heights to follow long term emission trends. Since 1997, measurements have also been collected in Los Angeles CA, Denver CO, Omaha NE, Phoenix AZ, Riverside CA, and Tulsa OK.[6] Following a protocol established by the Coordinating Research Council (CRC) as part of the E-23 program, the data collected have provided valuable information about the changes in fleet average on-road emission levels. The data have been used by many researchers to study fleet emission trends.

Reflecting a desire to continue evaluation of historical and recent emissions trends, several of the E-23 sites have been chosen for additional data collection. This report describes the on-road emission measurements taken in the Chicago IL area in the fall of 2014, under CRC Contract No. E-106. Measurements were made on parts of six consecutive days, from Monday, September 8, to Saturday, September 13, between the hours of 9:00 and 18:30 on the on-ramp from Algonquin Rd. to southbound I-290/SH53. Measurements have previously been collected seven times at this same location in 1997, 1998, 1999, 2000, 2002, 2004 and 2006.

MATERIALS AND METHODS

The FEAT remote sensor used in this study was developed at the University of Denver for measuring the pollutants in motor vehicle exhaust; it has been extensively discussed in the literature.[7-9] The instrument consists of a non-dispersive infrared (NDIR) component for detecting CO, CO_2, and HC and twin dispersive ultraviolet (UV) spectrometers (0.26 nm/diode resolution) for measuring oxides of nitrogen (NO and NO_2), SO_2 and NH_3. The source and detector units are positioned on opposite sides of a single lane road in a bi-static arrangement. Collinear beams of infrared (IR) and UV light are passed across the roadway into the IR detection unit then focused through a dichroic beam splitter, which separates 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 from the surface of the dichroic beam splitter and focused onto the end of a quartz fiber bundle mounted to a coaxial connector on the side of the detector unit. The quartz fibers in the bundle are divided in half to carry the UV signal to two separate spectrometers. The first spectrometer's wavelength ranges from 227nm down to 198nm to measure the species of NO, SO_2 and NH_3. The absorbance from each respective UV spectrum of SO_2, NH_3, and NO is compared to a calibration spectrum using a classical least squares fitting routine in the same region to obtain the vehicle emissions. The second spectrometer measures only NO_2 by measuring an absorbance band at 438nm in the UV spectrum and comparing it to a calibration spectrum in the same region.[10] All species are sampled at 100Hz. Since the removal of sulfur from US gasoline and diesel fuel, SO_2 emissions have become negligibly small. While SO_2 measurements were collected as a part of this study, they will not be reported or discussed because the sensor was not calibrated for SO_2 emissions.

The exhaust plume path length and density of the observed plume are highly variable from vehicle to vehicle, and depend on, among other things, the height of the vehicle's exhaust pipe, engine size, wind, and turbulence behind the vehicle. For these reasons, the remote sensor measures directly only ratios of CO, HC, NO, NH_3 or NO_2 to CO_2. The molar ratios of CO, HC, NO, NH_3 or NO_2 to CO_2, termed Q^{CO}, Q^{HC}, Q^{NO}, Q^{NH3} and Q^{NO2} respectively, are constant for a given exhaust plume; they are useful parameters for describing a hydrocarbon combustion system. This study reports measured emissions as grams/kilogram of fuel (g/kg of fuel) or as molar %CO, %HC, %NO, %NH_3 and %NO_2 in the exhaust gas, corrected for water and excess air not used in combustion. The HC measurement is calibrated with propane, a C_3 hydrocarbon. Based on measurements using flame ionization detection (FID) of gasoline vehicle exhaust, the remote sensor is only half as sensitive to exhaust hydrocarbons on a per carbon atom basis as it is to propane on a per carbon atom basis as demonstrated by Singer et al.[11] To calculate mass emissions as described below, the %HC values reported are first multiplied by 2.0 as shown below to account for these "unseen" hydrocarbons, assuming that the fuel used is regular gasoline. These percent emissions can be directly converted into mass emissions by the following equations.

$$\text{gm CO/gallon} = 5506 \cdot \%CO \,/\, (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \quad (1a)$$
$$\text{gm HC/gallon} = 2(8644 \cdot \%HC) \,/\, (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \quad (1b)$$
$$\text{gm NO/gallon} = 5900 \cdot \%NO \,/\, (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \quad (1c)$$
$$\text{gm NH}_3\text{/gallon} = 3343 \cdot \%NH_3 \,/\, (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \quad (1d)$$
$$\text{gm NO}_2\text{/gallon} = 9045 \cdot \%NO_2 \,/\, (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \quad (1e)$$

These equations show that the relationships between emission concentrations and mass emissions are: (a) linear for NO_2 and NH_3, (b) nearly linear for CO and NO and (c) linear at low concentrations for HC. Thus, the percent difference in emissions calculated from the concentrations of pollutants reported here is equivalent to a difference calculated from masses. Note that NO is reported as grams of NO, while vehicle emission factors for NO_x are normally reported as grams of NO_2, even when the actual compound emitted is nearly 100% NO in the case of gasoline-fueled vehicles.

The major relationship reported here is the direct conversion from the measured pollutant ratios to g/kg of fuel. This is achieved by first converting the pollutant ratio readings to moles of pollutant per mole of carbon in the exhaust using the following equation:

$$\frac{\text{moles pollutant}}{\text{moles C}} = \frac{\text{pollutant}}{CO + CO_2 + 6HC} = \frac{(\text{pollutant}/CO_2)}{(CO/CO_2) + 1 + 6(HC/CO_2)} = \frac{(Q^{CO}, 2Q^{HC}, Q^{NO}...)}{Q^{CO} + 1 + 6Q^{HC}} \quad (2)$$

Next, moles of pollutant are converted to grams by multiplying by molecular weight (e.g., 44 g/mole for HC since propane is measured), and the moles of carbon in the exhaust are converted to kilograms by multiplying (the denominator) by 0.014 kg of fuel per mole of carbon in fuel, assuming gasoline is stoichiometrically CH_2. Again, the HC/CO_2 ratio must use two times the reported HC (see above) because the equation depends upon carbon mass balance and the NDIR HC reading is about half a total carbon FID reading.[11]

$$\text{gm CO/kg} = (28Q^{CO} \,/\, (1 + Q^{CO} + 6Q^{HC})) \,/\, 0.014 \quad (3a)$$
$$\text{gm HC/kg} = (2(44Q^{HC}) \,/\, (1 + Q^{CO} + 6Q^{HC})) \,/\, 0.014 \quad (3b)$$
$$\text{gm NO/kg} = (30Q^{NO} \,/\, (1 + Q^{CO} + 6Q^{HC})) \,/\, 0.014 \quad (3c)$$
$$\text{gm NH}_3\text{/kg} = (17Q^{NH3} \,/\, (1 + Q^{CO} + 6Q^{HC})) \,/\, 0.014 \quad (3d)$$
$$\text{gm NO}_2\text{/kg} = (46Q^{NO2} \,/\, (1 + Q^{CO} + 6Q^{HC})) \,/\, 0.014 \quad (3e)$$

Quality assurance calibrations are performed twice daily in the field unless observed voltage readings or meteorological changes are judged to warrant additional calibrations. The multi-species instrument used in this study requires three calibration cylinders. The first contains 6% CO, 6% CO_2, 0.6% propane and 0.3% NO; the second contains 0.1% NH_3 and 0.6% propane and the final cylinder contains 0.05% NO_2 and 15% CO_2. A puff of gas is released into the instrument's path, and the measured ratios from the instrument are compared to those certified by the cylinder manufacturer (Air Liquide). These calibrations account for day-to-day variations in instrument sensitivity and variations in ambient CO_2 levels caused by local sources, atmospheric pressure and instrument path length. Since propane is used to calibrate the

instrument, all hydrocarbon measurements reported by the remote sensor are reported as propane equivalents.

Studies sponsored by the California Air Resources Board and General Motors Research Laboratories have shown that the remote sensor is capable of CO measurements that are correct to within ±5% of the values reported by an on-board gas analyzer, and within ±15% for HC.[12, 13] The NO channel used in this study has been extensively tested by the University of Denver, but we are still awaiting the opportunity to have it independently validated in an extensive blind study and instrument intercomparison. Tests involving a late-model low-emitting vehicle indicate a detection limit (3σ) of 25 ppm for NO, with an error measurement of ±5% of the reading at higher concentrations.[8] A list of criteria for determining data validity is shown in Appendix A.

The remote sensor is accompanied by a video system to record a freeze-frame image of the license plate of each vehicle measured. The emissions information for the vehicle and a time and date stamp are also recorded on the video image. The images are stored digitally, so that license plate information may be incorporated into the emissions database during post-processing. A device to measure the speed and acceleration of vehicles driving past the remote sensor was also used in this study. The system consists of a pair of infrared emitters and detectors (Banner Industries) which generate two parallel infrared beams passing across the road, six feet apart and approximately two feet above the surface. Vehicle speed is calculated (reported to 0.1 mph) from the time that passes between the front of the vehicle blocking the first and the second beam. To measure vehicle acceleration, a second speed is determined from the time that passes between the rear of the vehicle unblocking the first and the second beam. Acceleration is calculated (reported to 0.001 mph/sec) from these two speeds and the time difference between the two speed measurements. Appendix B defines the database format used for the data set.

RESULTS AND DISCUSSION

Following the six days of data collection in September of 2014, the digital images were transcribed for license plate identification. Plates that appeared to be in state and readable were sent to the State of Illinois to be matched against the state non-personal vehicle registration information. The resulting database contained 20,395 records with make and model year information and valid measurements for at least CO and CO_2. The database and all previous databases compiled for CRC E-106 and CRC E-23-4 campaigns can be found at www.feat.biochem.du.edu. Most of these records also contain valid measurements for HC, NO, NH_3 and NO_2.

The data reduction process of the measurements is summarized in Table 1. The table details the steps beginning with the number of attempted measurements and ending with the number of records containing both valid emissions measurements and vehicle registration information. An attempted measurement is defined as a beam block followed by a half second of data collection. If the data collection period is interrupted by another beam block from a close following vehicle, the measurement attempt is aborted and a new attempt is made to measure the second vehicle.
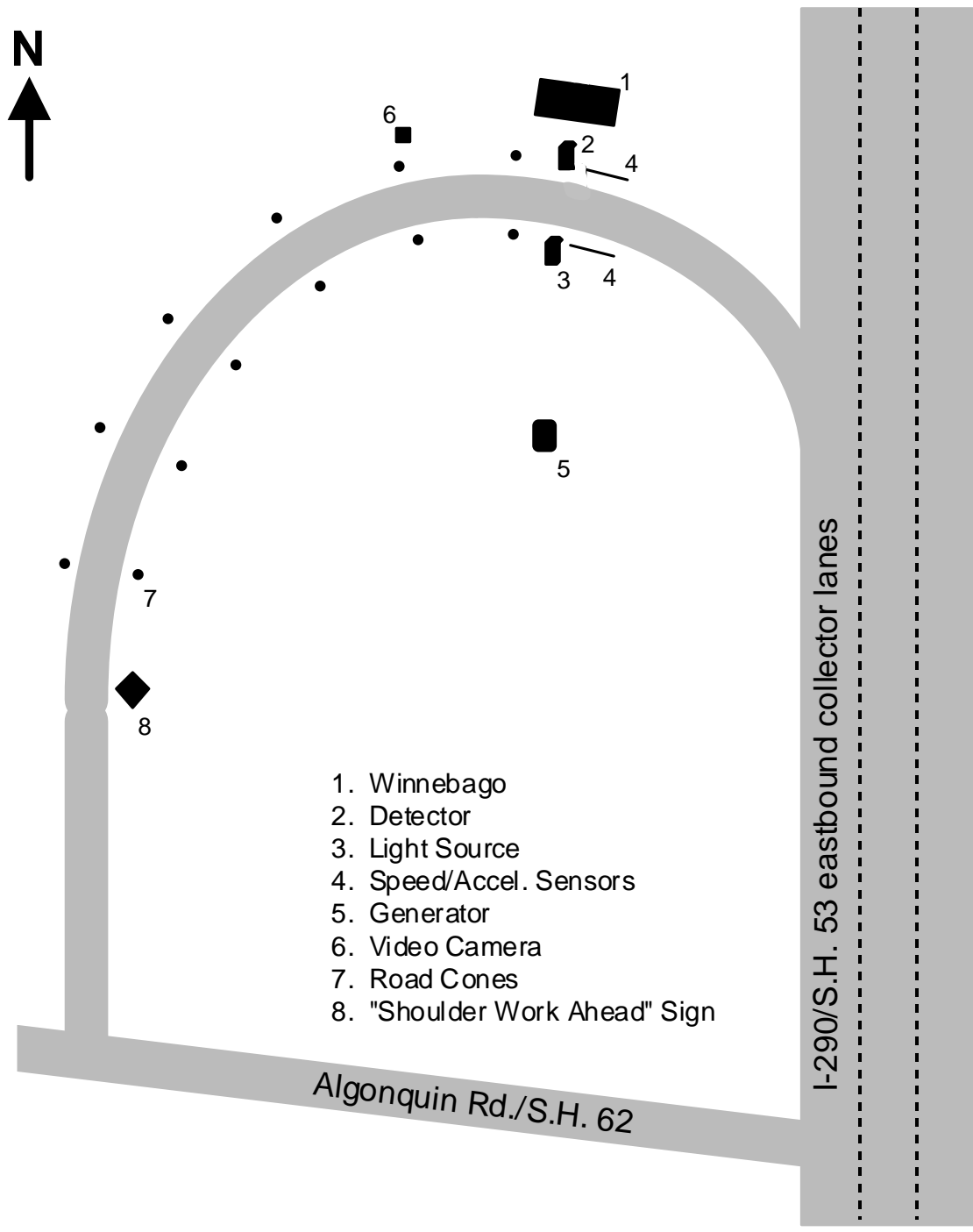
Figure 1. Area map of the on-ramp from Algonquin Road to eastbound I-290 in northwest Chicago, showing remote sensor configuration and safety equipment.

Figure 2. A photograph looking east at the Algonquin Rd. monitoring site and 2014 remote sensing setup.

Table 1. Validity Summary.

	CO	HC	NO	NH_3	NO_2
Attempted Measurements	26,824				
Valid Measurements	23,913	23,856	23,912	23,891	21,466
Percent of Attempts	89.1%	88.9%	89.1%	89.1%	80.0%
Submitted Plates	20,638	20,590	20,637	20,617	18,556
Percent of Attempts	76.9%	76.8%	76.9%	76.9%	69.2%
Percent of Valid Measurements	86.3%	86.3%	86.3%	86.3%	86.4%
Matched Plates	20,395	20,282	20,394	20,375	18,332
Percent of Attempts	76.0%	75.6%	76.0%	76.0%	68.3%
Percent of Valid Measurements	85.3%	85.0%	85.3%	85.3%	85.4%
Percent of Submitted Plates	98.8%	98.5%	98.8%	98.8%	98.8%

In this case, the beam block from the first vehicle is not recorded as an attempted measurement. Invalid measurement attempts arise when the vehicle plume is highly diluted, or the reported error in the ratio of the pollutant to CO_2 exceeds a preset limit (See Appendix A). The significant loss of data in this process occurs during the plate reading process, when out-of-state vehicles and vehicles with unreadable plates (obscured, missing, dealer, out of camera field of view) are omitted from the database.

Table 2 provides an analysis of the number of vehicles that were measured repeatedly and the number of times they were measured. Of the 20,395 records used in this analysis, 10,755 (53%) were contributed by vehicles measured once, and the remaining 9,640 (47%) records were from vehicles measured at least twice. A more detailed look at emissions from vehicles measured repeatedly in Chicago will follow.

Table 2. Number of measurements of repeat vehicles.

Number of Times Measured	Number of Vehicles
1	10,755
2	2,023
3	994
4	494
5	87
6	23
7	4
>7	3

Table 3 is the data summary; included are summaries of all previous remote sensing databases collected by the University of Denver at the I-290 and Algonquin Rd. site. These other measurements were conducted in September of 1997, 1998, 1999, 2000, 2002, 2004 and 2006. Mean fleet emissions have continued to decrease at the Algonquin Rd. site, with large reductions in previously measured species over the eight year period. Fleet age has also increased, although not as much as might have been expected from the fleet age changes observed at the other E-106 sites.[14] As noted in previous years, the percentage of emissions from the 99th percentile continues to increase indicating that the emission distributions are becoming more skewed. This is consistent with the observation that newer vehicles remain lower-emitting longer than previous models. Afternoon traffic levels in 2014 were similar to several of the previous year measurements, with a drop in traffic speeds and some stop-and-go driving brought about by congestion on the freeway during the afternoon. Negative NO_2 values are likely a result of a small negative measurement bias in the capacity to measure negligible levels of NO_2 from a predominantly gasoline-fueled fleet. Because of the small size of the bias we have chosen not to offset adjust the NO_2 measurements for this analysis.

The mean HC values have been adjusted to remove an artificial offset in the measurements. This offset, restricted to the HC channel, has been reported in previous CRC reports. The offset was exacerbated this year by unseasonably cold weather during the last three days of measurements.

Table 3. Historical data summary.

Study Year	1997	1998	1999	2000	2002	2004	2006	2014
Mean CO (%) (g/kg of fuel)	0.45 (55.8)	0.39 (49.0)	0.35 (44.2)	0.26 (32.8)	0.23 (28.9)	0.17 (21.5)	0.13 (16.1)	0.074 (9.4)
Median CO (%)	0.14	0.15	0.09	0.05	0.07	0.04	0.02	0.011
Percent of Total CO from the 99th Percentile	13.9%	14.6%	16.5%	19.6%	20.4%	22.3%	26.3%	34.4%
Mean HC (ppm)[a] (g/kg of fuel)[a] Offset (ppm)	130 (5.3) 80	130 (5.3) 120	109 (4.5) 70	94 (3.9) 60	80 (3.2) 10	72 (2.8) 20	58 (2.2) 10	35 (1.3) 12.5/30[b]
Median HC (ppm)[a]	50	50	50	40	40	30	30	9
Percent of Total HC from the 99th Percentile	21.0%	26.7%	22.8%	22.2%	21.9%	24.8%	33.9%	42.5%
Mean NO (ppm) (g/kg of fuel)	400 (5.5)	405 (5.7)	378 (5.3)	316 (4.5)	262 (3.7)	236 (3.3)	125 (1.8)	105 (1.5)
Median NO (ppm)	160	140	121	79	52	39	14	5
Percent of Total NO from the 99th Percentile	8.7%	8.1%	9.7%	11.2%	13.2%	13.5%	18.8%	24.9%
Mean NH_3 (ppm) (g/kg of fuel)								89 (0.71)
Median NH_3 (ppm)								43
Percent of Total NH_3 from the 99th Percentile								10.3%
Mean NO_2 (ppm) (g/kg of fuel)								-1.5 (-0.04)
Median NO_2 (ppm)								-3.6
Percent of Total NO_2 from the 99th Percentile								N.A.
Mean Model Year	1992.7	1993.6	1994.3	1994.9	1997.4	1999.2	2001.0	2007.5
Mean Fleet Age[c]	5.3	5.4	5.7	6.1	5.6	5.8	7	7.5
Mean Speed (mph)	25.1	24.7	25.8	24.5	24.2	24.3	23.9	24.0
Mean Acceleration (mph/s)	0.1	0.8	0.2	0.5	-0.4	0.4	0.4	0.2
Mean VSP (kw/tonne) Slope (degrees)[d]	5.3 1.5°	9.3 1.5°	6.0 1.5°	7.9 1.5°	-6.9 1.0°	6.0 1.0°	5.9 1.0°	4.8 1.0°

[a] Indicates values that have been HC offset adjusted as described in text.
[b] Different offset values applied to the first 3 and last 3 days due to weather change.
[c] Assumes new vehicle model year starts September 1.
[d] Roadway was repaved between 2000 and 2002, which caused a slight change in the slope of the roadway.

The Chicago area broke a 111 year record with two consecutive September days (Thursday and Friday) with high temperatures below 60°F. Low temperatures and a high dew point increased the number of vehicles observed at the site with visible water vapor exhaust plumes significantly. Liquid water can interfere with the IR wavelengths used for detecting HC emissions, which can artificially increase the measured HC values. This can be seen in the differences in the mean gHC/kg of fuel emissions calculated for Monday to Wednesday of 1.7g/kg (mean model year of 2007.5) and for Thursday to Saturday of 3.1g/kg (mean model year of 2007.4). Prior to calculating the offsets, all license plate images with HC measurements larger than 300ppm (~12.4g/kg of fuel) were re-examined for visible water vapor. This re-examination identified 66 out of approximately 1400 measurements, which were labeled in the database by changing the value of the HC_flag from 'V' (valid) to 'S' (steam). Unless otherwise stated the HC measurements labeled as having visible water vapor in the exhaust been excluded from the HC analysis.

The offset is calculated by computing the mode and means of the newest model year vehicles, and assuming that these vehicles emit negligible levels of hydrocarbons, using the lowest of either of these values as the offset. The offset adjustment subtracts this value from all of the hydrocarbon data. For the 2014 Chicago data this process was done twice, once on the first three days of measurements and then again on the last three days of measurements. Since it is assumed that the cleanest vehicles emit little hydrocarbons, this approximation will only err slightly towards clean because the true offset will be a value somewhat less than the average of the cleanest model year and make. Using this approach to correct for water vapor interference should be valid in adjusting the means for the last three days but will overcorrect vehicles that are fully warmed up and have dry exhaust systems and will undercorrect those with water vapor interferences.

Figure 3 plots the gHC/kg of fuel measurement frequency of the original (top panel) and offset adjusted data (bottom panel) distributions about zero. An offset adjustment of 12.5ppm (~0.5g.kg) was determined for the first three days, and the value was 30ppm (~1.3g/kg) for the last three days. The offsets were calculated on 2009 and newer model year vehicles; Figure 3 displays the distribution for the entire fleet. The adjustment appears to have effectively normalized the two distributions with the resulting mean for the first three days of 1.1gHC/kg of fuel and 1.6g/kg of fuel for the last three days. Unless otherwise stated, the analysis of the HC measurements in this report uses the offset adjusted data.

In the eight years since the last measurements in Chicago IL, mean CO (-42%) and HC (-41%) emissions have experienced significant reductions while NO (-17%) emissions have declined at a slower rate. The percent of emissions contributed by the highest emitting 1% of the fleet (the 99th percentile) increased for all measured species. The average age of the Chicago fleet has also increased by half a year likely due to the most recent recession.

The inverse relationship between vehicle emissions and model year is shown in Figure 4 for data collected during each of the eight campaigns. The HC data have been offset adjusted as previously described. It has been eight years since the previous measurements; there are
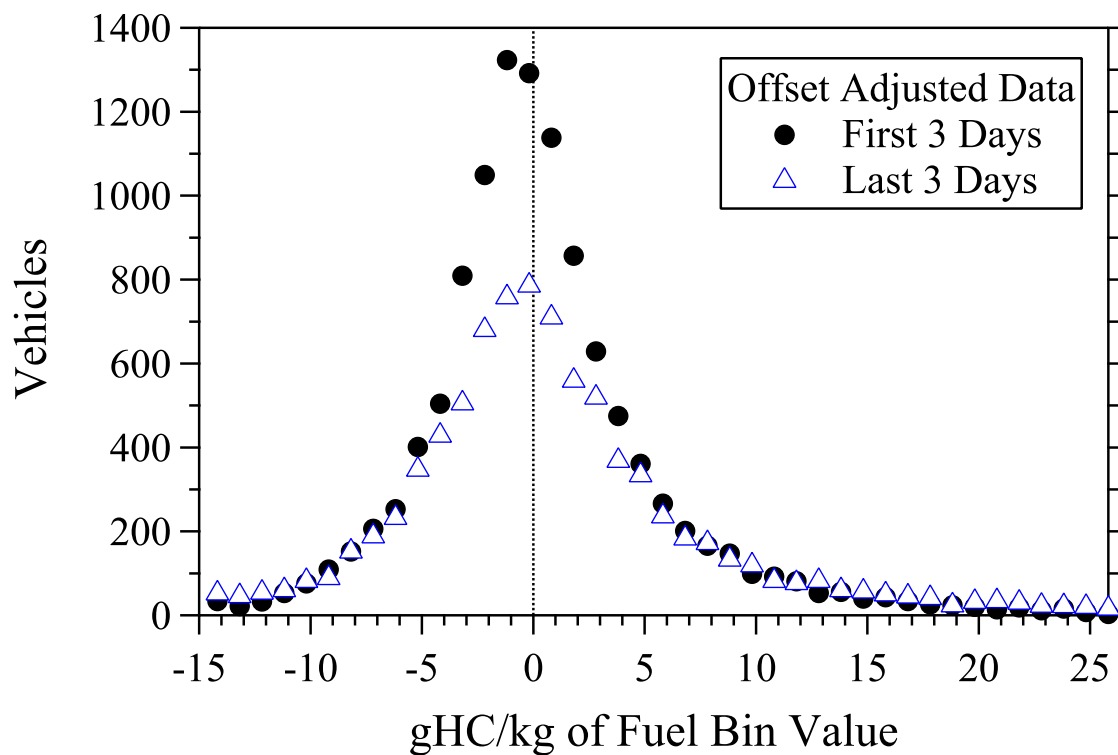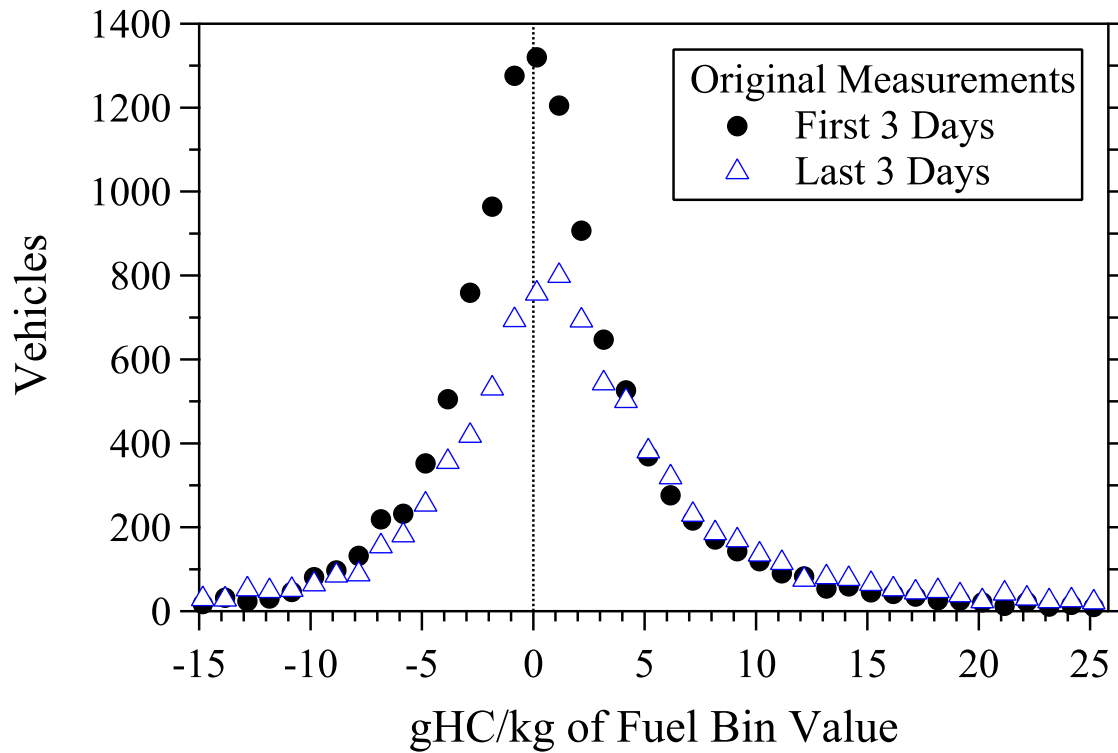
Figure 3. Chicago gHC/kg of fuel frequency distributions for measurements collected during the first three days of measurements (Sept. 8 – 10, 2014, filled circles) and the last three days of measurements (Sept. 11 – 12, 2014, open triangles). The top graph plots the original measurements and the bottom graph the offset adjusted data.
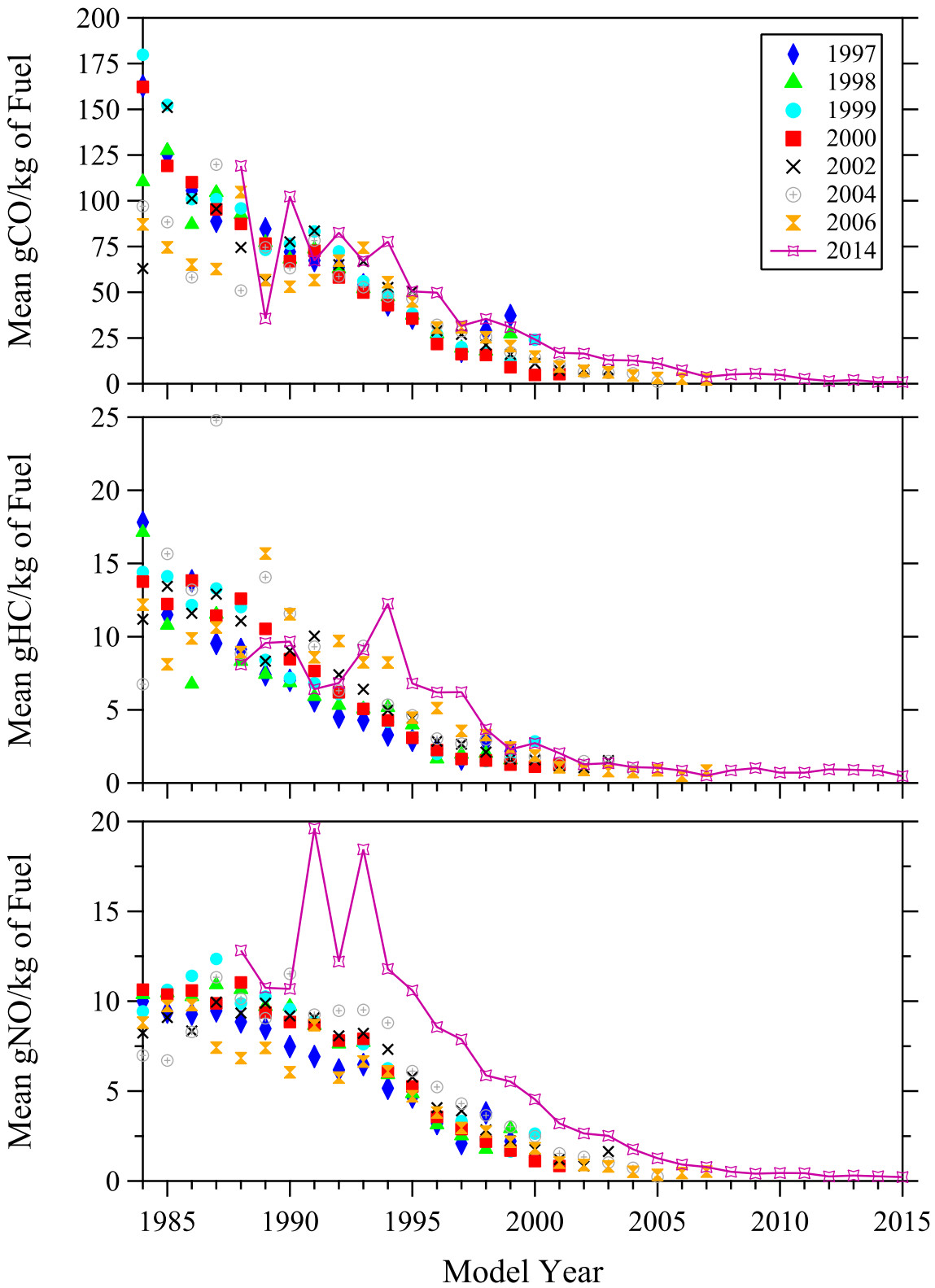
Figure 4. Chicago historical fuel specific mean vehicle emissions plotted as a function of model year. HC data have been offset adjusted as described in the text.

noticeable changes in both the emissions of the middle-aged vehicles measured in 2006 and the emission trends for the newest models. 2002 to 1995 model year vehicles show significant increases in all three exhaust species plotted in Figure 4; NO emissions show the largest jump. If we compare 1996 vehicles measured in 2014 with those measured in 2006, the CO emissions increased 62%, HC 21% and NO 125% respectively. Some of the increase in NO emissions can be attributed to the fact that the 2006 NO measurements were lower than might have been expected from previous campaigns. The emissions have trended decidedly downward. However, emission trends for the newest models have continued to decrease and more importantly remain at very low levels for more model years than observed in 2006. Mean fuel specific emissions for the newest model years are statistically indistinguishable for approximately twice as many model years as previously seen in the 2006 data. This means that if one compared emissions for similarly aged vehicles, the "middle-aged vehicles" measured in 2014 would show larger reductions in emissions than comparably aged 2006 vehicles.

As originally presented by Ashbaugh et al., vehicle emissions by model year, with each model year divided into emission quintiles, were plotted for data collected in 2014.[15] This resulted in the plots shown in Figures 5 - 7. The bars in the top graphs represent the mean emissions for each quintile. The middle graphs give the fraction of the fleet for each model year. The impact of the recent reduction in light-duty vehicle sales due to the economic recession is clearly evident in the fleet model year fraction beginning in 2009 and continuing through 2012. The bottom graphs, which are a product of the first two graphs, display the fraction of the total emissions by quintiles and model year. Model years older than 1996 and not graphed account for ~1.7% of the measurements and contribute between 14.9% (HC) and 15.5% (CO) of the emissions. The bottom graphs illustrate that at least the first three quintiles of the measurements (60%), regardless of model year; make an essentially negligible contribution to the total emissions. The large accumulations of negative emissions in the first two quintiles are the result of ever decreasing emission levels. The instrument is designed such that when measuring a zero emission plumes, half of the readings will be negative and half will be positive. As the lowest emitting segments of the fleets continue to dive toward zero emissions, the negative emission readings will continue to grow toward half of all the measurements. The newest model years are at that stage now for all species.

The economic recession's reduction of fleet fractions of the 2009 vehicles is shown in the middle plots. The 2009 models were only reduced by 26% at the Chicago site, a smaller contraction than those observed in Denver, Los Angeles or Tulsa.[14] The Denver and Tulsa fleet saw a disproportionate reduction in trucks; the authors believe that trucks are a smaller percentage of the Chicago site's fleet, which might help to explain some of the differences. However, a more detailed exploration of these differences is not possible at this time, since the authors do not have the benefit of VIN decoded data. The fleet fractions appear to have fully recovered by the time 2013 models were introduced. The recession has increased the age of the Chicago site's fleet; Table 3 shows that the fleet is ~0.5 model year older than the 2006 data set, which at the time was significantly older than the previous six data sets (they ranged from 5.3 to 6.1 years old). This smaller age increase than previously observed at the other sites may also be a product

Figure 5. 2014 CO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional CO emissions by model year and quintile (bottom).

Figure 6. 2014 HC emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional HC emissions by model year and quintile (bottom).

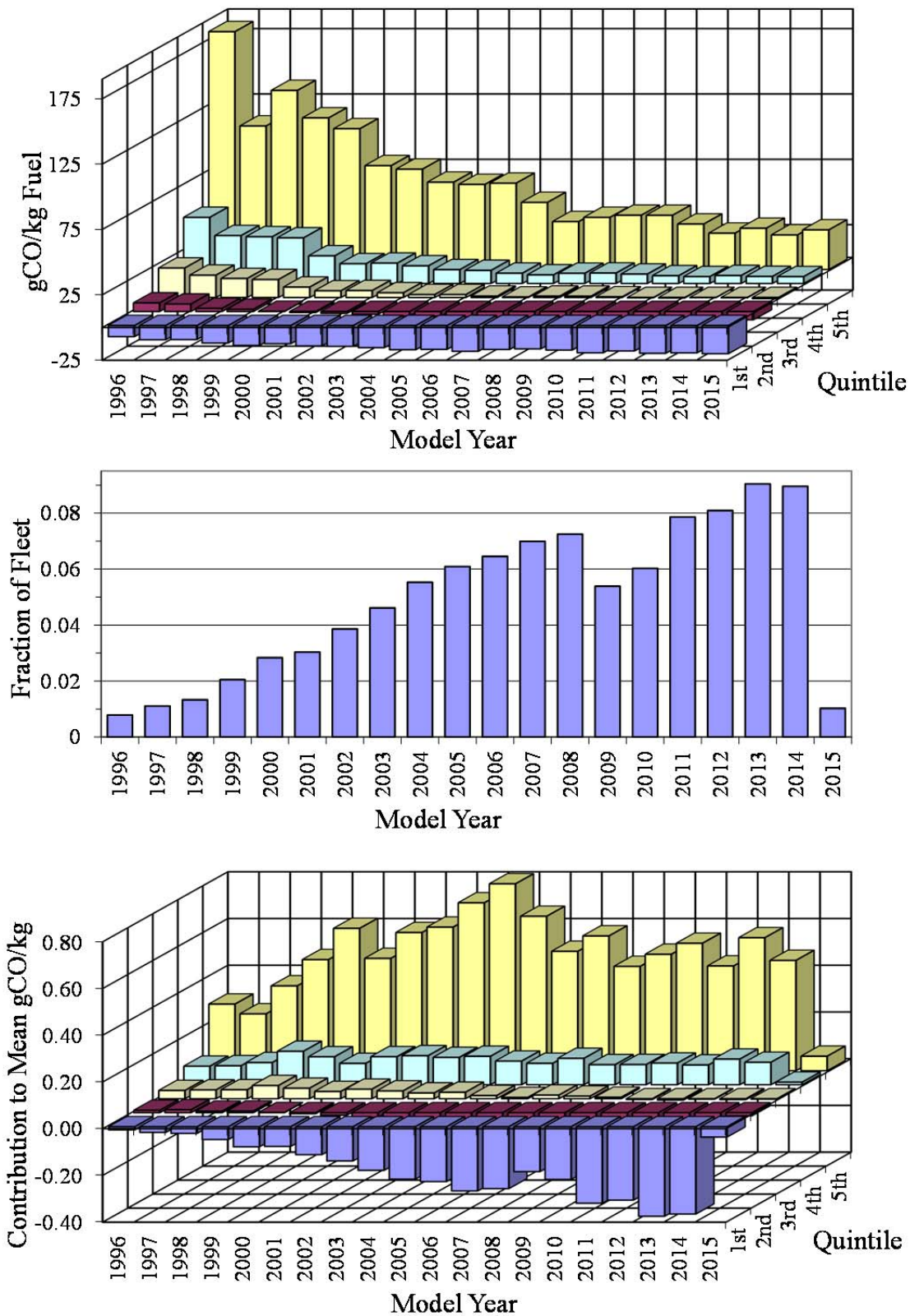**Figure 7.** 2014 NO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional NO emissions by model year and quintile (bottom).
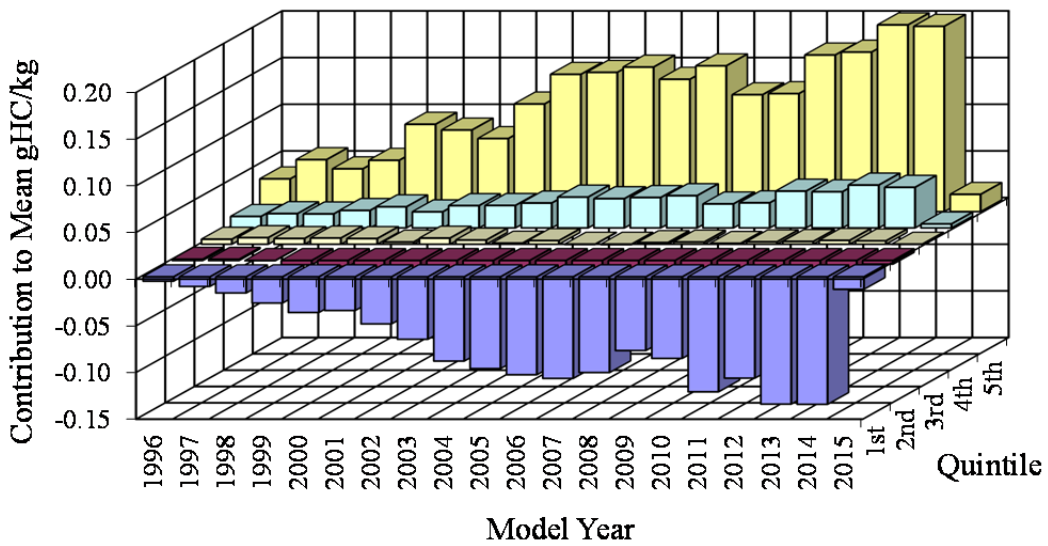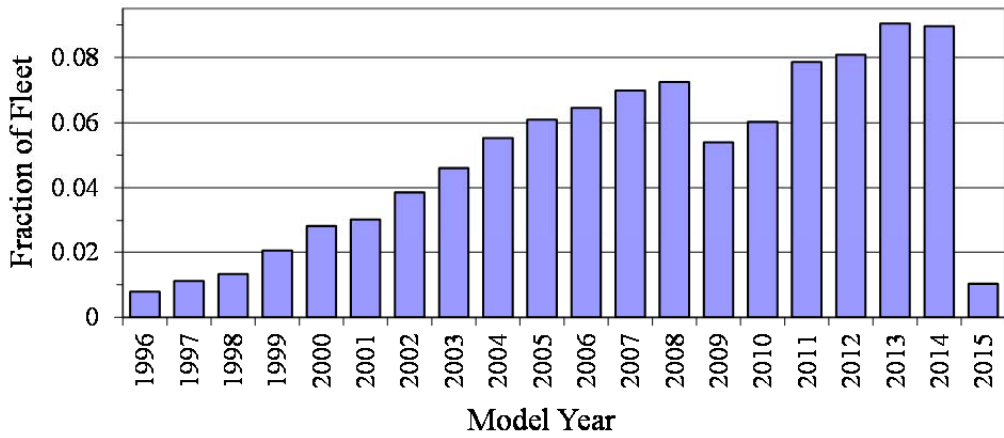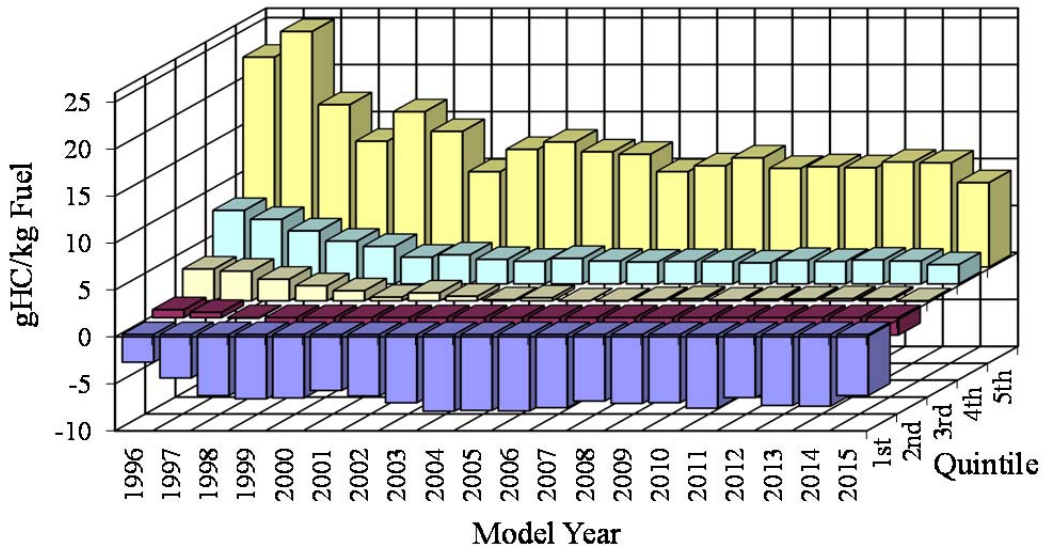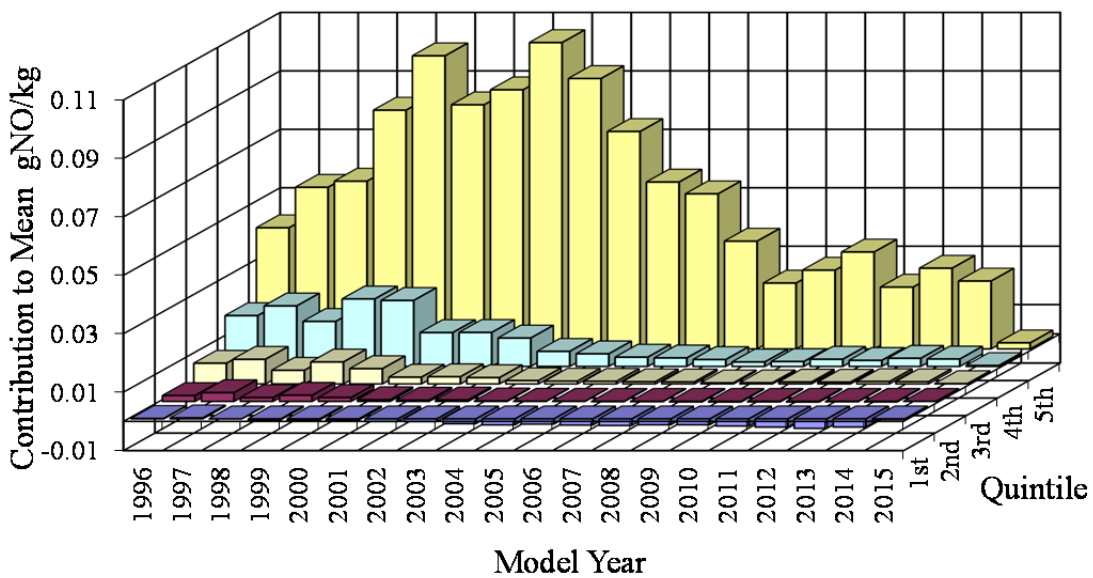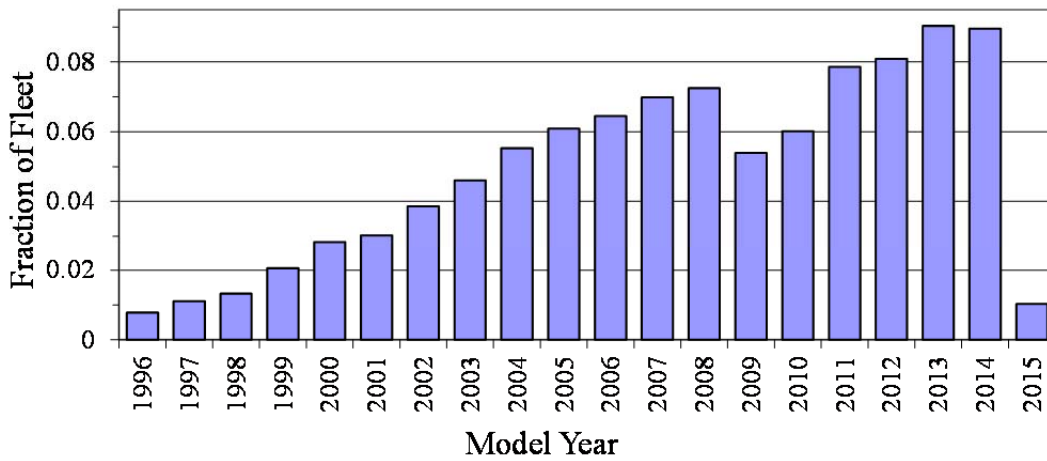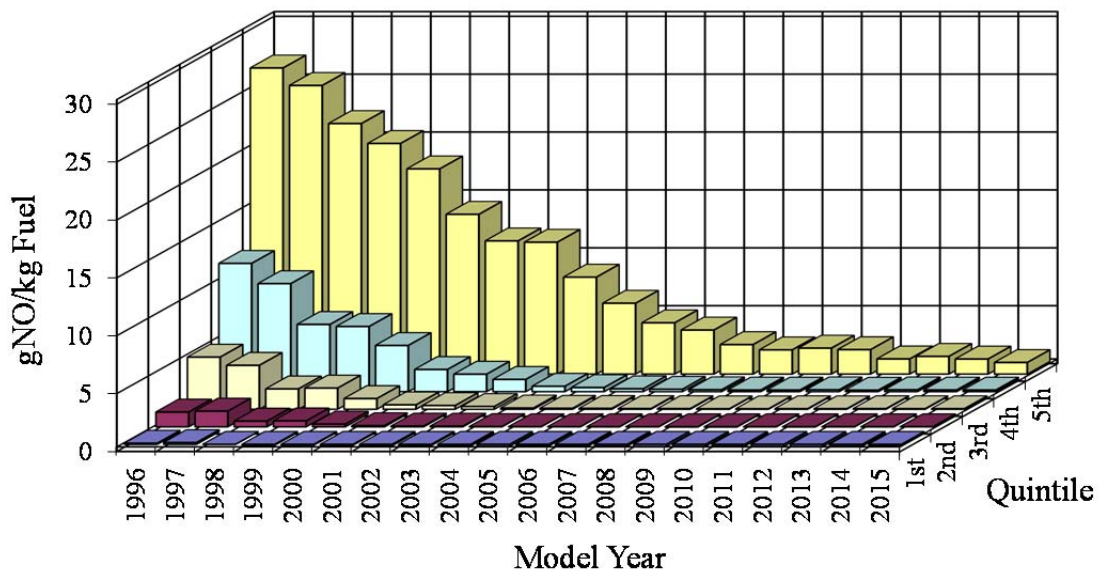
of the later sampling data which has allowed fleet turnover to catch up and reduce the age of the Chicago area fleet.

An equation for determining the instantaneous power of an on-road vehicle proposed by Jimenez[16], takes the form

$$VSP = 4.39 \cdot \sin(slope) \cdot v + 0.22 \cdot v \cdot a + 0.0954 \cdot v + 0.0000272 \cdot v^3 \quad (4)$$

where VSP is the vehicle specific power in kW/metric tonne, *slope* is the slope of the roadway (in degrees), *v* is vehicle speed in mph, and *a* is vehicle acceleration in mph/s. This equation is derived from dynamometer studies and is necessarily an approximation. The first term represents the work required to climb the gradient, the second term is the *f = ma* work to accelerate the vehicle, the third is an estimated friction term, and the fourth term represents aerodynamic resistance. This equation was used to calculate vehicle specific power for all measurements in each of the eight years' databases. This equation, like all dynamometer studies, does not include any load effects arising from road curvature. The emissions data, binned according to vehicle specific power, are graphed in Figure 8. All of the specific power bins contain at least 100 measurements and the HC data have been offset adjusted.

All of the species show reduced emissions when compared with previous data sets. All three species emissions also show less dependence on vehicle specific power than previous years' data. The error bars included in the plot are standard errors of the mean calculated from the daily averages. These uncertainties were generated for these γ-distributed data sets by applying the central limit theorem. Each day's average emission for a given VSP bin was assumed to be an independent measurement of the average emissions at that VSP. Normal statistics were then applied to these daily averages.

The use of VSP can reduce the influence of any changes in driving behavior from the mean vehicle emissions over the many data sets. Table 4 shows the mean emissions from all vehicles in the 1997, 1998, 1999, 2000, 2002, 2004, 2006 and 2014 databases with specific powers between –5 and 20 kw/tonne. Note that these emissions do not vary considerably from the mean emissions for the entire set of databases, as shown in Table 3. Table 4 shows the mean emissions for the 1998, 1999, 2000, 2002, 2004, 2006 and 2014 databases, adjusted for vehicle specific power to match the 1997 VSP distribution.

The normalization of the data to the 1997 driving mode is accomplished by applying the mean vehicle emissions for each VSP bin (between –5 and 20 kw/tonne) from a certain year's measurements to the vehicle distribution, by vehicle specific power, for each bin from 1997. A sample calculation for vehicle specific power-adjusted mean NO emissions is shown in Appendix D. Because all VSP data are adjusted to the 1997 vehicle frequency distribution by VSP bin, the 1997 adjusted values are the same as the measured values except the HC data, which include an extra calculation to adjust for the yearly HC offset. Each measurement year's adjusted values for HC in Table 4 include this additional adjustment. Over the seventeen year period, the reduction in all three species goes far beyond just driving mode dependence as discussed earlier. VSP normalized CO emissions have declined by almost a factor of 6 and HC
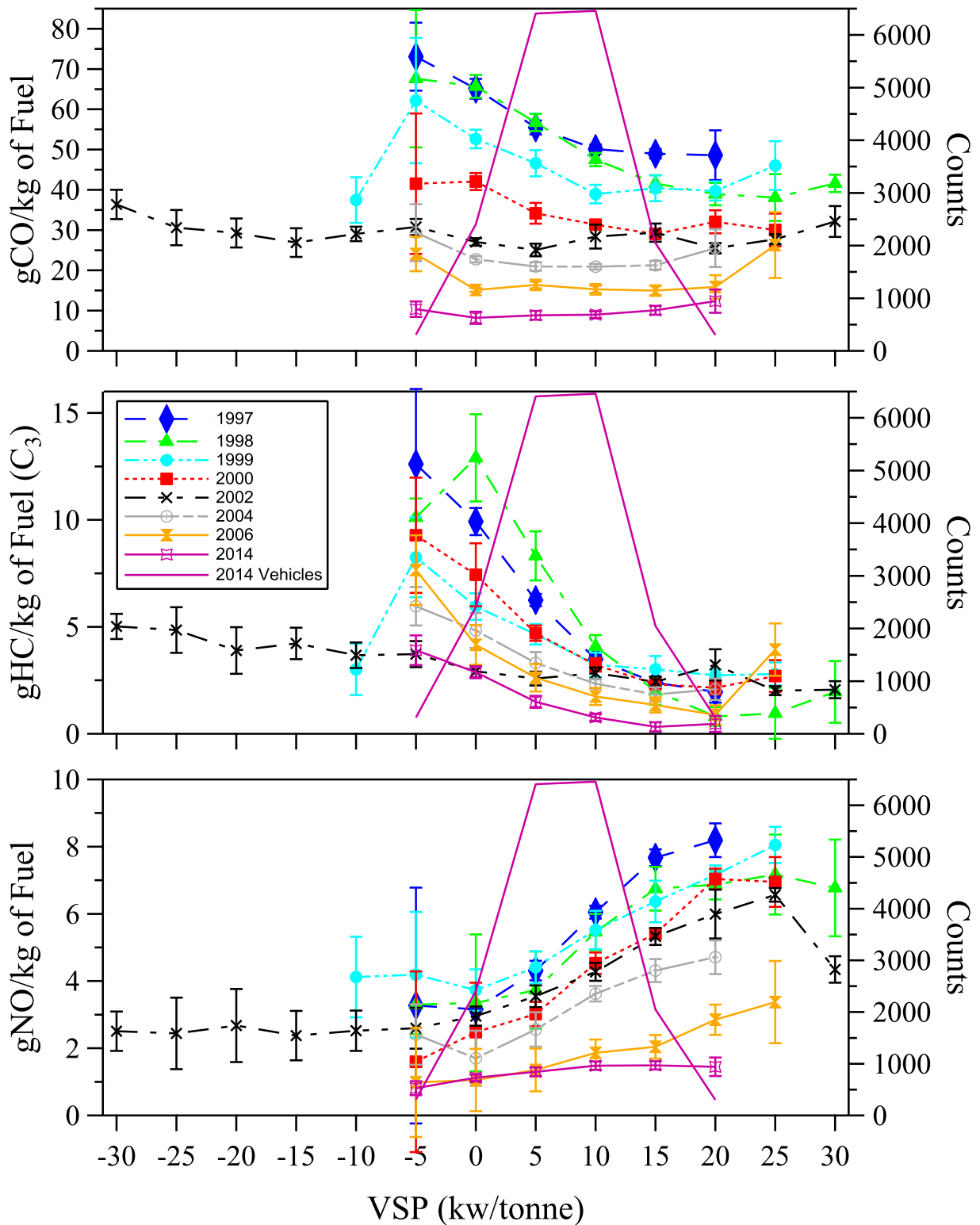
Figure 8. Vehicle emissions as a function of vehicle specific power for all of the Chicago data sets. The uncertainties are plotted as the standard errors of the mean calculated from daily samples. The solid line without markers is the vehicle count profile for the 2014 data set.

Table 4. Vehicle specific power adjusted fleet emissions (-5 to 20 kw/tonne only) with standard errors of the means calculated using daily averages.

Means	1997 measured (adjusted)	1998 measured (adjusted)	1999 measured (adjusted)	2000 measured (adjusted)	2002 measured (adjusted)	2004 measured (adjusted)	2006 measured (adjusted)	2014 Measured (adjusted)
gCO/kg	53.4±1.0 (53.4±1.0)	47.2± 1.3 (51.2±1.4)	43.7±2.3 (43.3±2.3)	32.2±0.9 (33.1±0.9)	27.7±1.2 (27.3±1.2)	21.4±0.8 (21.4±0.8)	15.7±0.9 (15.7±0.9)	9.1.±0.8 (9.2±0.8)
gHC/kg[a]	8.2 ±0.2 (4.9±0.2)	9.2±0.6 (5.9±0.4)	6.9±0.5 (4.0±0.3)	3.0±0.2 (4.0±0.3)	3.3±0.3 (2.7±0.2)	3.7±0.3 (2.9±0.3)	2.7±0.5 (2.3±0.5)	1.3±0.2 1.2±0.2)
gNO/kg	5.5±0.3 (5.5±0.3)	5.6±0.1 (4.9±0.1)	5.2±0.3 (5.2±0.3)	4.4±0.2 (4.0±0.2)	3.9±0.2 (4.1±0.2)	3.3±0.1 (3.2±0.1)	1.7±0.1 (1.7±0.1)	1.4±0.1 .4±0.1)

[a]HC emissions are offset adjusted as described in the text.

and NO emissions have been reduced by a factor of 4.

A similar normalization can be applied to a fleet of specific model year vehicles to track deterioration, provided a baseline of only the model years measured in 1997 is used. A sample calculation, for the model year adjusted mean NO emissions, is shown in Appendix E. Table 5 shows mean emissions for all vehicles from model year 1983 to 1997, as measured in each of the eight years of data. Applying the vehicle frequency distribution by model year observed in 1997 to the mean emissions by model year from the later studies yields the model year adjusted fleet emissions. The number of 1983-1997 models has shrunk by almost a factor of 25 during the 17 years that have elapsed since the first measurements. The CO and HC measured mean emissions have only increased slightly (~+7% for CO and ~+9% for HC) during this time, while the model year-adjusted emissions show much larger increases (+46% for CO and +120% for HC). NO emissions show large increases for both the measured (+86%) and the adjusted means (+109%). This is reflective of the increases in NO emissions with model year shown in Figure 4.

Table 5 shows an interesting result: during the nine years from 1997 to 2006 the 1997 fleet saw no statistically significant deterioration with increasing age for the model year adjusted average CO and NO emissions. In the subsequent eight years large increases have occurred. Since 2006 the fleet age has almost doubled (11.5 to 20.1 years) and the number of measurements has shrunk dramatically significantly increasing the standard errors of the mean for the adjusted values. It is possible that we have reached the limits of this type of analysis, at least when using the model year adjusted factors, since only 1995-1997 model years include more than 100 measurements and 1983 and 1985 models have zero measurements. Because of the skewed nature of emission distributions, the model year adjusted emissions increases seen in 2014 may now be influenced by sampling bias which is not reflected in the uncertainty estimates. If the emissions deterioration analysis is restricted to only the mean emissions of the observed 1983 -1997 fleet, where there is no bias caused by the age adjustment, only the fleet NO emissions have an increase which is statistically significant.

Table 5. Measured and model year adjusted[a] fleet emissions. Uncertainties are standard errors of the means calculated from the daily means.

Means	1997 measured (adjusted)	1998 measured (adjusted)	1999 measured (adjusted)	2000 measured (adjusted)	2002 measured (adjusted)	2004 measured (adjusted)	2006 measured (adjusted)	2014 measured (adjusted)
gCO/kg	53.0±0.9 (53.0±0.9)	52.0±0.8 (53.3±0.8)	53.8±1.9 (57.1±2.0)	46.4±1.4 (51.2±1.6)	50.6±2.0 (56.8±2.2)	46.3±1.9 (53.3±2.1)	46.2±1.9 (52.8±2.4)	56.6±3.1 (77.3±4.3)
gHC/kg[b]	8.1±0.2 (4.8±0.2)	4.9±1.2 (5.0±0.6)	5.0±0.6 (5.4±0.4)	5.1±0.3 (5.6±0.4)	5.4±0.5 (6.3±0.5)	5.7±0.4 (7.4±0.6)	6.2±0.5 (7.6±1.5)	8.8±0.9 (10.6±1.0)
gNO/kg	5.6±0.3 (5.6±0.3)	6.3±0.1 (6.4±0.1)	6.6±0.3 (6.8±0.3)	6.2±0.2 (6.6±0.2)	6.4±0.3 (7.0±0.3)	7.0±0.3 (7.7±0.3)	4.9±0.4 (5.7±0.4)	10.4±0.6 (11.7±0.6)
Number of Vehicles	18,251	19,319	16,639	13,394	9,372	6,220	4,238	733
Age (years)	5.2	6.0	6.8	7.6	9.1	9.9	11.5	20.1

[a]To match the 1983-1997 model year distribution observed during the 1997 measurements.

[b]HC emissions are offset corrected for all of the years adjusted data.

The University of Denver did not have the capability to measure light-duty vehicle NH_3 emissions until 2005, which makes Chicago the seventh site to have NH_3 measurements collected. The mean reported in Table 2 (0.71 ± 0.02) is the second highest mean observed, surpassed only by the 2008 west Los Angeles measurements. The west LA site features a traffic light-controlled on-ramp that encourages stop-and-go driving followed by generally purposeful acceleration onto the freeway. Dynamometer studies have shown that these conditions are ideal for NH_3 production.[17] The driving mode in Chicago bears some resemblance to the west LA arrangement as the majority of the Chicago traffic enters this ramp from a light-controlled double turn lane on Algonquin Rd. which merges to a single lane before our measurement site and the freeway entrance. The loss of a traffic lane forces many of the vehicles to slow considerably before entering the ramp's 180° curve after which they need to accelerate back to highway speeds while passing the measurement site to enter the freeway.

Figure 9 shows a graph of gNH_3/kg of fuel emissions by model year for the 2014 Chicago data and compares them against similar data collected in Tulsa OK in Fall 2013. The uncertainties are standard errors of the means calculated from the daily means. It is important to recognize that the same model year vehicles in Tulsa are a year older in Chicago. The trends are remarkably similar between the two sites. The Chicago data have a noticeably higher trend line, and therefore the higher mean (0.71 vs 0.43). Average speed is similar between the two locations (Chicago 24 mph and Tulsa 24.3 mph) but the Chicago site has a positive acceleration (0.2 versus -0.01) due to the congestion produced just prior to the turn where the double turn lanes merge into a single lane. Tulsa has a higher VSP due to a steeper roadway grade.

Figure 10 compares the Chicago and Tulsa gNH_3/kg of fuel data grouped by model year and plotted against each other for vehicles of the same age. The uncertainties plotted are standard errors of the means calculated from the daily means. The slope of the line is 1.07 ± 0.09 with a
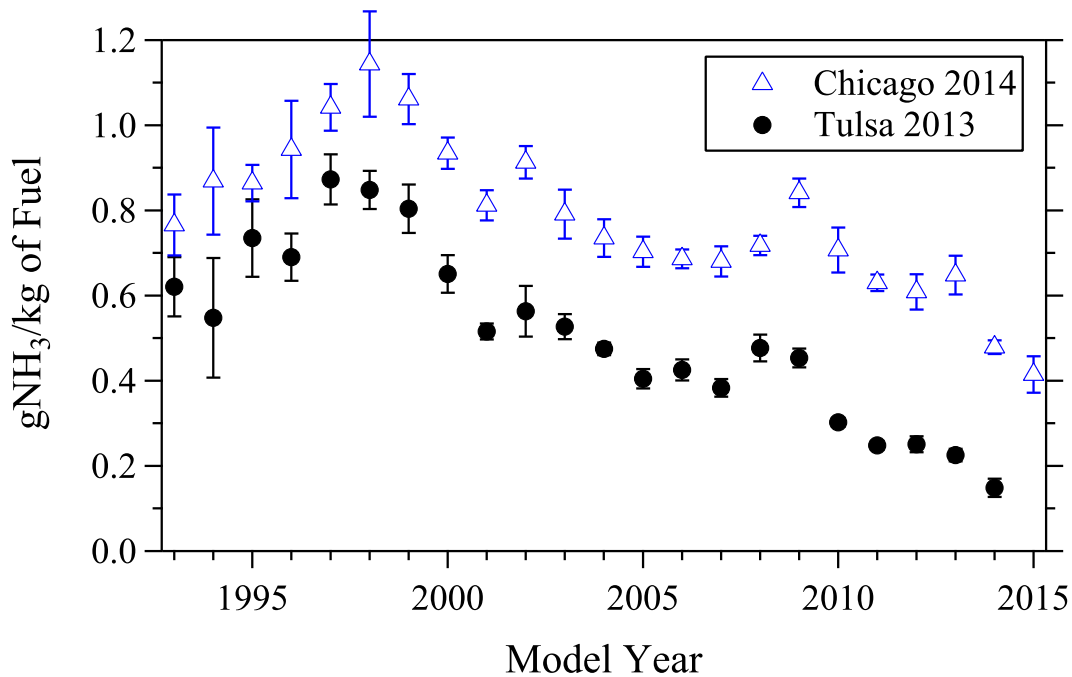
Figure 9. Comparison of gNH₃/kg of fuel emissions by model year for the 2013 Tulsa and the 2014 Chicago data sets. The uncertainties are standard errors of the mean calculated from the daily measurements.
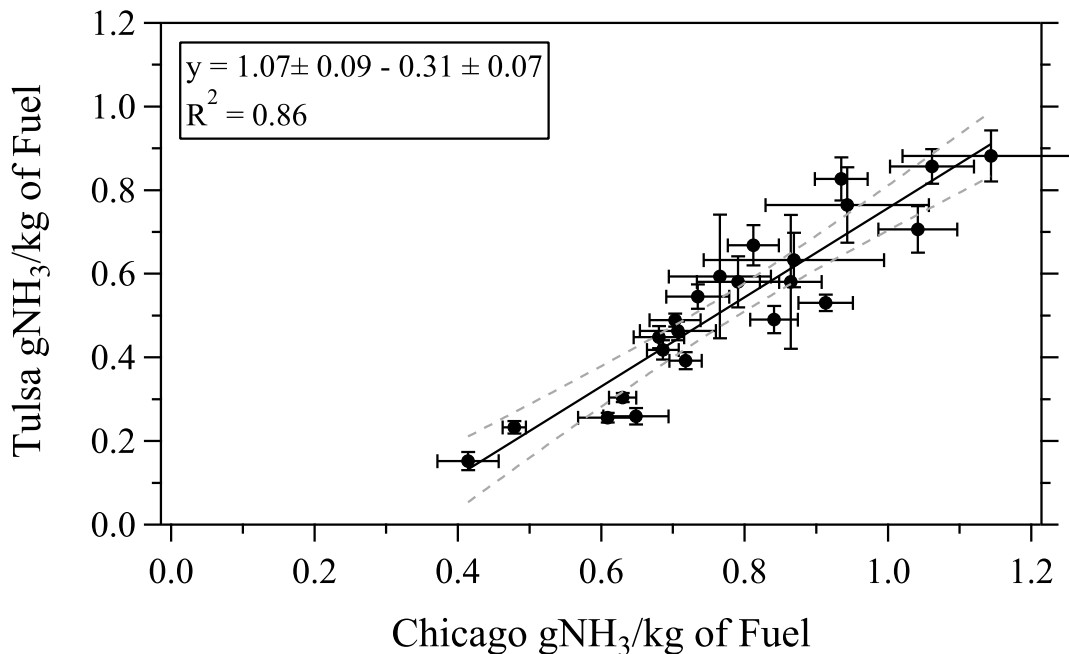
Figure 10. Tulsa gNH₃/kg of fuel plotted against the Chicago gNH₃/kg of fuel emissions grouped by model year and graphed against one another for vehicles of the same age. Zero year vehicles represent 2014 model year vehicles in Tulsa and 2015 models in Chicago. The uncertainties plotted are the standard errors of the mean calculated from the daily means. The results for the least squares best-fit line is in the legend and the dashed lines represent the 95% confidence intervals for the fit.

negative y intercept that reflects the emissions offset of the Chicago data. The dashed lines delineate the 95% confidence intervals for the least squares fit. When vehicle age is taken into account, the correlation for the first 22 model years is good with an R^2 of 0.86. Both data sets have NH_3 emissions which peak with 17 year-old vehicles (1998 models in Chicago and 1997 models in Tulsa), and both data sets show an uptick in emissions for 6 year-old vehicles. This unexplained feature was also observed in the Denver data set but not in the LA data set. The uncertainties are larger in Chicago than in Tulsa. A potential contributing factor is that Chicago weather issues caused inconsistent daily sample times with shortened days on Wednesday (only the afternoon) and Friday (only before mid-afternoon).

The percent ammonia of total fixed nitrogen was analyzed to see if the percentage of ammonia increased as total fixed nitrogen decreased with decreasing age, as shown previously in the analysis of the Tulsa and Denver fleets. The gNO_x/kg of fuel was calculated by converting gNO/kg of fuel to gNO_2/kg of fuel equivalents and summing with the measured gNO_2/kg of fuel. The percent of ammonia in the total fixed nitrogen (FN_2), in g/kg, was calculated as shown by Burgard et al.[18] All of the N factors were converted to mole/kg.

$$\text{Molar \% } NH_3 \text{ in Total Fixed Nitrogen} = \frac{100 \times N_{NH_3}}{N_{NH_3} + N_{NO_x}} \qquad (5)$$

Figure 11 shows the results of these calculations for Chicago. The molar $\%NO_x$ and $\%NH_3$ which total 100%, are percentages of the gFN_2/kg of fuel values plotted by model year. The noise increases for the molar percentages in newest model years because the amount of fixed nitrogen emissions diminishes. The total fixed nitrogen (filled diamonds, right axis) species have decreased significantly over the last 23 model years. The percent contributed by ammonia (filled circles, left axis) has steadily increased and now dominates the small amount of fixed nitrogen being emitted by the newest model year vehicles. The crossover point in Chicago is with ten year-old vehicles. This compares with eight to nine year-old vehicles in Tulsa, nine year-old vehicles in LA and four to five year-old vehicles at the Denver site measured in 2013.

At the Chicago site, 47% of the measurements are multiple measurements on the same vehicle, similar to the statistics observed in Tulsa. This is higher than most of the sites sampled. For instance, the Denver and LA sites have much lower repeat rates of 9% and 39% respectively.

Figures 12, 13 and 14 are plots showing the mean emissions and standard error of the mean for Chicago vehicles measured at least four times for which the CO, HC and NO emissions were all valid. Figures 12 and 13 are correlation plots for CO and HC and CO and NO; Figure 14 shows the same data rank-ordered by mean emissions. Most vehicles are low-emitting and show little emissions variability when measured more than once. In general, as mean emissions increase, the observed variability also increases. This relationship has also been observed in multiple FTP and IM240 tests, which emphasize that the source of the variability is the vehicle and not the testing
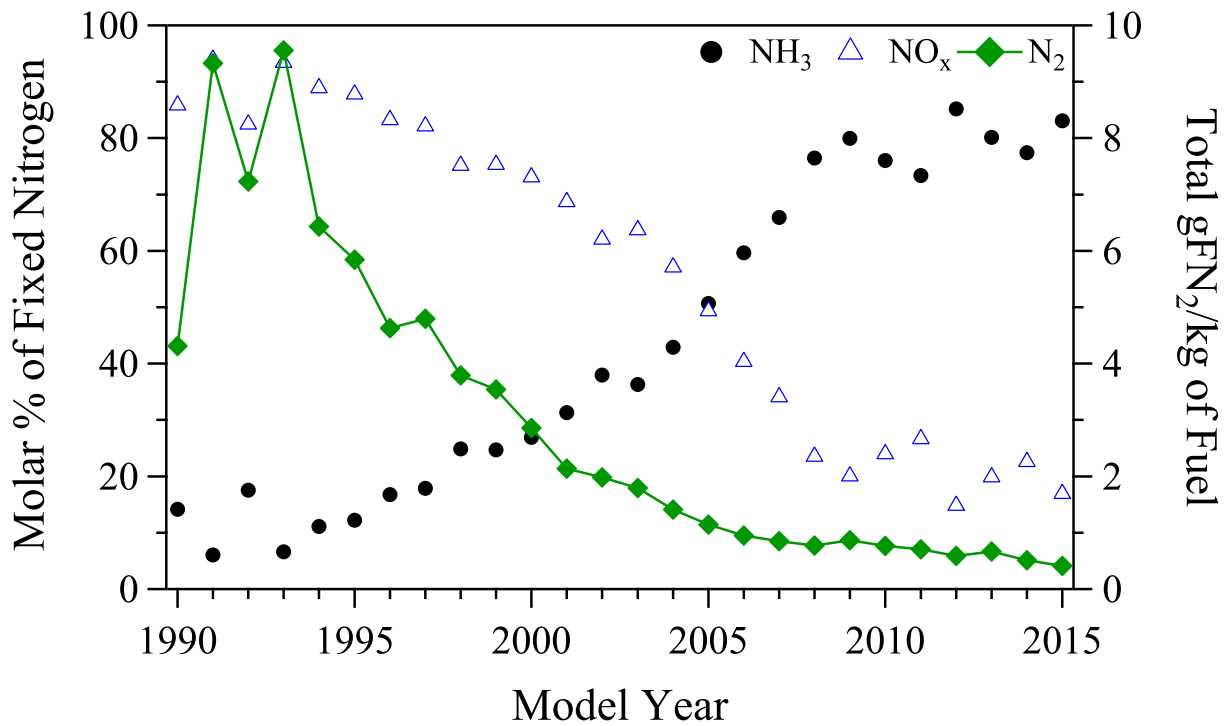
Figure 11. Total fixed nitrogen in g/kg of fuel (diamonds, right axis) with the molar percent composition distributed between the molar %NO_x (triangles, left axis) component and the molar %NH_3 component (circles, left axis).
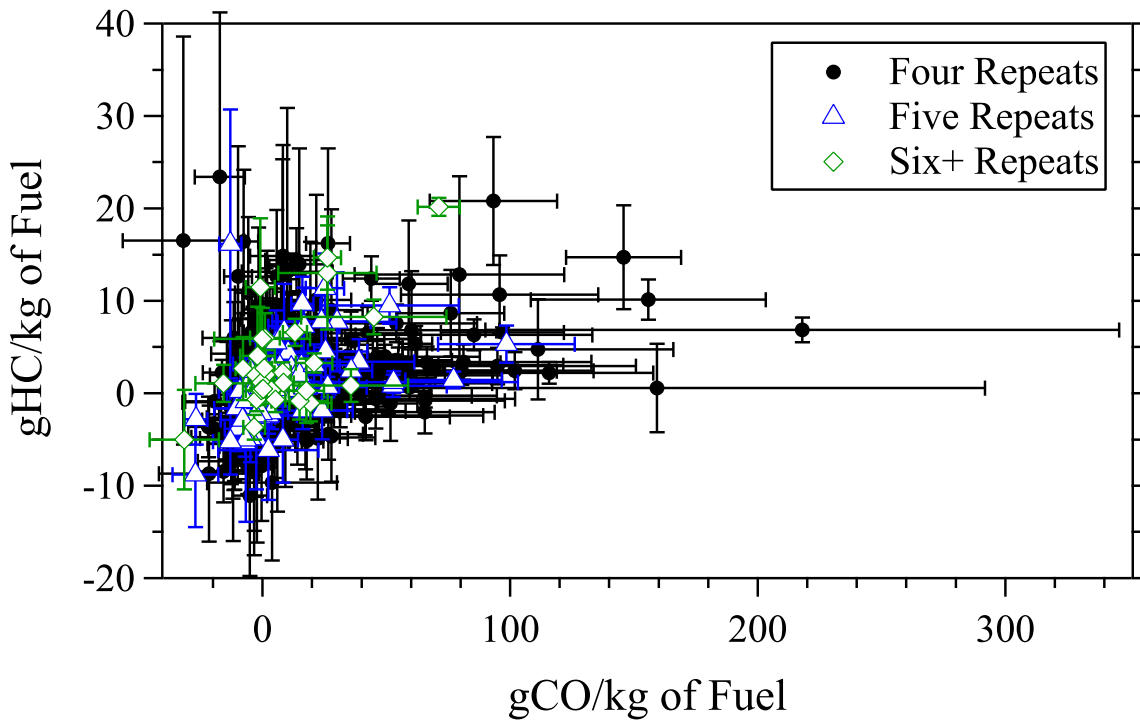
Figure 12. Mean gHC/kg of fuel emissions plotted against mean gCO/kg of fuel emissions for vehicles measured four or more times. Standard errors of the mean are the uncertainties shown.
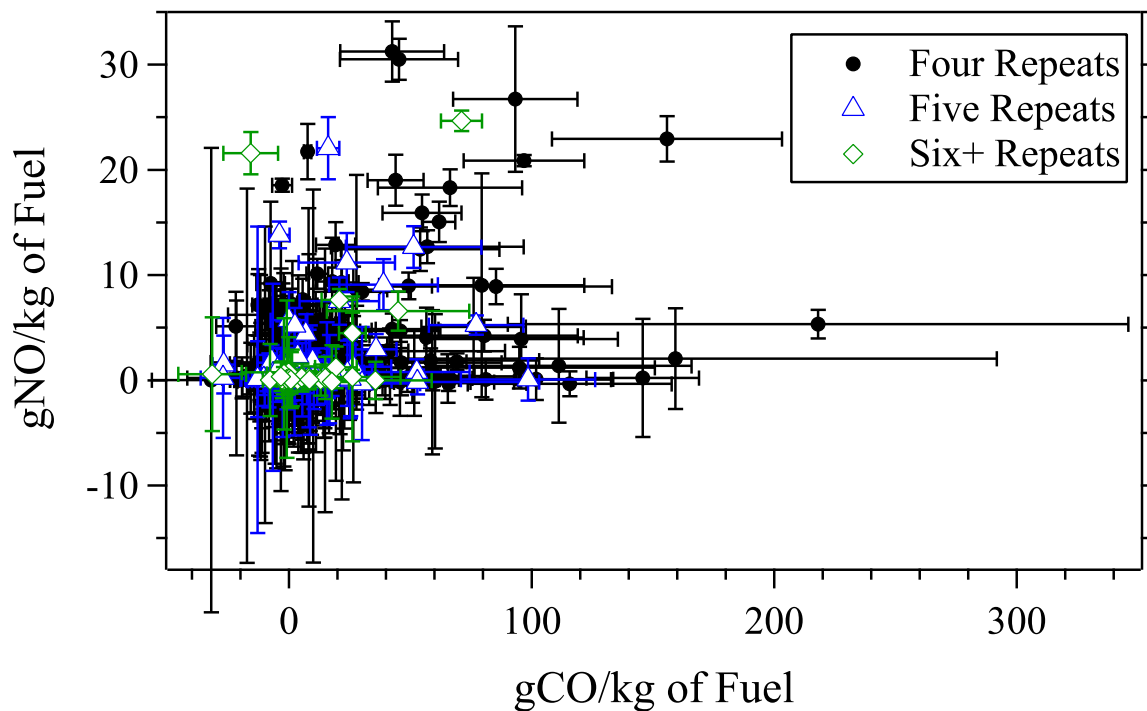
Figure 13. Mean gNO/kg of fuel emissions plotted against mean gCO/kg of fuel emissions for vehicles measured four or more times. Standard errors of the mean are the uncertainties shown.

method.[19] Pullover studies in California demonstrate that even one high reading identifies vehicles with a >90% probability of failing an alternative I/M test if performed immediately.[20]

The number of these "high reading" vehicles has dropped considerably over the last two decades which is attributable to the quality and reliability of the engine and emission control systems built into modern vehicles.[6] In Chicago in 2014, the 99th percentile is responsible for 34%, 42% and 25% of the total CO, HC and NO respectively. These values are 2.5 times larger for CO (14%) and NO (9%) than results measured in 1997 and two times larger for HC (21%). This variability in the emissions of broken cars means that the emissions distribution obtained from any snapshot of fleet emissions (remote sensing or I/M testing) is bound to be more skewed than the results of constant monitoring of the emissions of all vehicles at all times. This phenomenon does not affect the means measured by these snapshots, but it does imply that the overlap between species and the high emitter fractions would show less skewness were one able to fully characterize all vehicles and their variability.

Instrument noise was measured by looking at the slope of the negative portion of the log plots in the same manner described in the Phoenix, Year 2 report.[21] Such plots were constructed for all of the measured species. Linear regression gave best fit lines whose slopes correspond to the inverse of the Laplace factor, which describes the noise present in the measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to obtain a description of noise. The Laplace factors were 9, 3.4, 0.2, 0.01 and 0.7 for CO, HC, NO, NH₃
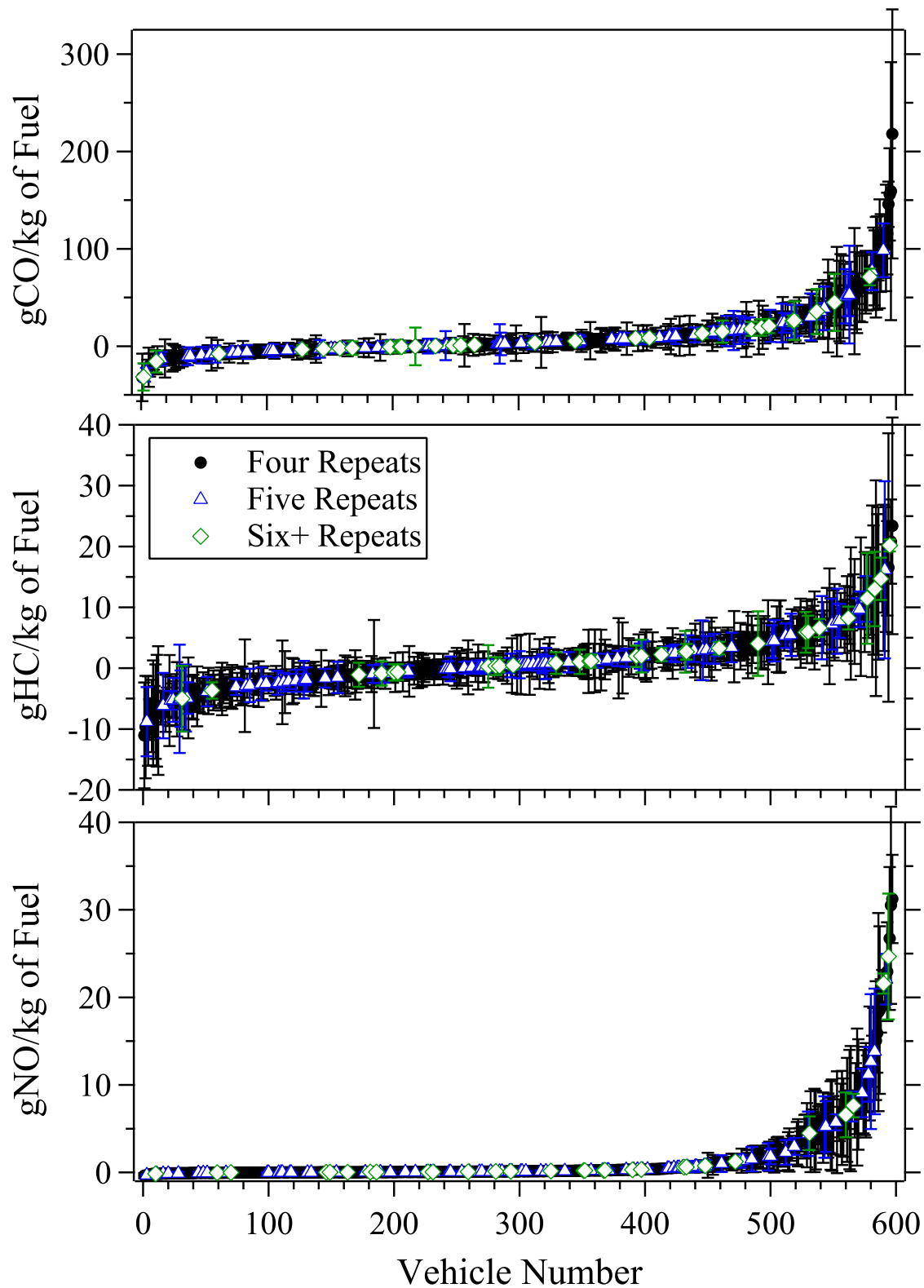
Figure 14. Rank ordered plots of mean gCO/kg of fuel (top panel), gHC/kg of fuel (middle panel) and gNO/kg of fuel (bottom panel) emissions for vehicles with at least 4 repeat measurements where all three specie measurements are valid. The standard errors of the mean are the uncertainties plotted.

and NO$_2$ respectively. These values indicate standard deviations of 12.7 gCO/kg (0.1%), 4.8 gHC/kg (114 ppm), 0.3 gNO/kg (41 ppm), 0.02 gNH$_3$/kg (4 ppm) and1 gNO$_2$/kg (45 ppm) for individual measurements of CO, HC, NO, NH$_3$ and NO$_2$ respectively. In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with an average of 100 measurements, the uncertainty reduces by a factor of 10. Thus, the uncertainties in the averages reduce to 0.9 gCO/kg, 0.3 gHC/kg, 0.02 gNO/kg, 0.001 gNH$_3$/kg and 0.1 gNO$_2$/kg, respectively.

ACKNOWLEDGEMENTS

LITERATURE CITED

1. Clean Air Act Text. U. S. Environmental Protection Agency. http://www.epa.gov/air/caa/text.html.

2. National Ambient Air Quality Standards. U. S. Environmental Protection Agency. http://www.epa.gov/air/criteria.html.

3. U. S. Environmental Protection Agency, *Our Nation's Air: Status and trends through 2010*; 2012; http://www.epa.gov/airtrends/2011/.

4. Heywood, J. B., *Internal combustion engine fundamentals*. McGraw Hill: New York, **1988**.

5. Lefohn, A. S.; Shadwick, D. S.; Ziman, S. D., Peer Reviewed: The Difficult Challenge of Attaining EPA's New Ozone Standard. *Environ. Sci. Technol.* **1998,** 32, (11), 276A-282A, DOI: 10.1021/es983569x.

6. Bishop, G. A.; Stedman, D. H., A decade of on-road emissions measurements. *Environ. Sci. Technol.* **2008,** 42, (5), 1651-1656, DOI: 10.1021/es702413b.

7. Bishop, G. A.; Stedman, D. H., Measuring the emissions of passing cars. *Acc. Chem. Res.* **1996,** 29, 489-495.

8. Popp, P. J.; Bishop, G. A.; Stedman, D. H., Development of a high-speed ultraviolet spectrometer for remote sensing of mobile source nitric oxide emissions. *J. Air Waste Manage. Assoc.* **1999,** 49, 1463-1468, DOI: 10.1080/10473289.1999.10463978.

9. Burgard, D. A.; Bishop, G. A.; Stadtmuller, R. S.; Dalton, T. R.; Stedman, D. H., Spectroscopy applied to on-road mobile source emissions. *Appl. Spectrosc.* **2006,** 60, 135A-148A, DOI: 10.1366/000370206777412185.

10. Burgard, D. A.; Dalton, T. R.; Bishop, G. A.; Starkey, J. R.; Stedman, D. H., Nitrogen dioxide, sulfur dioxide, and ammonia detector for remote sensing of vehicle emissions. *Rev. Sci. Instrum.* **2006,** 77, (014101), 1-4, DOI: 10.1063/1.2162432.

11. Singer, B. C.; Harley, R. A.; Littlejohn, D.; Ho, J.; Vo, T., Scaling of infrared remote sensor hydrocarbon measurements for motor vehicle emission inventory calculations. *Environ. Sci. Technol.* **1998,** 32, 3241-3248, DOI: 10.1021/es980392y.

12. Lawson, D. R.; Groblicki, P. J.; Stedman, D. H.; Bishop, G. A.; Guenther, P. L., Emissions from in-use motor vehicles in Los Angeles: A pilot study of remote sensing and the inspection and maintenance program. *J. Air Waste Manage. Assoc.* **1990,** 40, 1096-1105, DOI: 10.1080/10473289.1990.10466754.

13. Ashbaugh, L. L.; Lawson, D. R.; Bishop, G. A.; Guenther, P. L.; Stedman, D. H.; Stephens, R. D.; Groblicki, P. J.; Johnson, B. J.; Huang, S. C. On-road remote rensing of carbon monoxide and hydrocarbon emissions during several vehicle operating conditions, In *Proceedings of the A&WMA International Specialty Conference on PM10 Standards and Non-traditional Source Control*, Phoenix, **1992**.

14. Bishop, G. A.; Stedman, D. H., The recession of 2008 and it impact on light-duty vehicle emissions in three western US cities. *Environ. Sci. Technol.* **2014,** 48, 14822-14827, DOI: 10.1021/es5043518.

15. Ashbaugh, L. L.; Croes, B. E.; Fujita, E. M.; Lawson, D. R. Emission characteristics of California's 1989 random roadside survey, In *Proceedings of the 13th North American Motor Vehicle Emissions Control Conference*, Tampa, **1990**.

16. Jimenez, J. L.; McClintock, P.; McRae, G. J.; Nelson, D. D.; Zahniser, M. S. Vehicle specific power: A useful parameter for remote sensing and emission studies, In *Proceedings of the Ninth CRC On-road Vehicle Emissions Workshop*, Coordinating Research Council, Inc.: Atlanta, **1999**; pp 7-45 - 7-57.

17. Huai, T.; Durbin, T. D.; Miller, J. W.; Pisano, J. T.; Sauer, C. G.; Rhee, S. H.; Norbeck, J. M., Investigation of NH_3 emissions from new technology vehicles as a function of vehicle operating conditions. *Environ. Sci. Technol.* **2003,** 37, 4841-4847, DOI: 10.1021/es030403+.

18. Burgard, D. A.; Bishop, G. A.; Stedman, D. H., Remote sensing of ammonia and sulfur dioxide from on-road light duty vehicles. *Environ. Sci. Technol.* **2006,** 40, 7018-7022, DOI: 10.1021/es061161r.

19. Bishop, G. A.; Stedman, D. H.; Ashbaugh, L., Motor vehicle emissions variability. *J. Air Waste Manage. Assoc.* **1996,** 46, 667-675.

20. Burnette, A.; Manne, G. Impact of vsp filtering on RSD prediction of roadside ASM failure, In *Proceedings of the 16th CRC On-road Vehicle Emissions Workshop*, San Diego, **2006**;

21. Pokharel, S. S.; Bishop, G. A.; Stedman, D. H., *On-road remote sensing of automobile emissions in the Phoenix area: Year 2*; Coordinating Research Council, Inc: Alpharetta, **2000**.

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

Not measured:

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

2) Vehicle which drives completely through during the 0.1 seconds "thinking" time (relatively rare).

Invalid :

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

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

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

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

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

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

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

8) Excessive error on NH3/CO2 slope, equivalent to +50ppm.

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

10) Excess error on NO2/CO2 slope, equivalent to +20% for NO2 > 200ppm, 40ppm for NO2 < 200ppm

11) Reported NO2 < -500ppm or > 7000ppm. NO2 "invalid".

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

APPENDIX B: Explanation of the ill_2014.dbf database.

The ill_2014.dbf is a Microsoft Foxpro database file, and can be opened by any version of MS Foxpro, Excel, Access or Filemaker Pro, regardless of platform. The following is an explanation of the data fields found in this database:

License   Illinois license plate.

Date   Date of measurement, in standard format.

Time   Time of measurement, in standard format.

Percent_co   Carbon monoxide concentration, in percent.

Co_err   Standard error of the carbon monoxide measurement.

Percent_hc   Hydrocarbon concentration (propane equivalents), in percent.

Hc_err   Standard error of the hydrocarbon measurement.

Percent_no   Nitric oxide concentration, in percent.

No_err   Standard error of the nitric oxide measurement.

PercentNH3   Ammonia concentration, in percent.

NH3_err   Standard error of the ammonia measurement.

PercentNO2   Nitrogen dioxide concentration, in percent.

NO2_err   Standard error of the nitrogen dioxide measurement.

Percent_co2   Carbon dioxide concentration, in percent.

Co2_err   Standard error of the carbon dioxide measurement.

Opacity   Opacity measurement, in percent.

Opac_err   Standard error of the opacity measurement.

Restart   Number of times data collection is interrupted and restarted by a close-following vehicle, or the rear wheels of tractor trailer.

HC_flag   Indicates a valid hydrocarbon measurement by a "V", invalid by an "X".

NO_flag   Indicates a valid nitric oxide measurement by a "V", invalid by an "X".

NH3_flag   Indicates a valid ammonia measurement by a "V", invalid by an "X".

NO2_flag   Indicates a valid nitrogen dioxide measurement by a "V", invalid by an "X".

Opac_flag   Indicates a valid opacity measurement by a "V", invalid by an "X".

Max_co2   Reports the highest absolute concentration of carbon dioxide measured by the remote sensor; indicates the strength of the observed plume.

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

Speed   Measured speed of the vehicle, in mph.

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

Tag_name   File name for the digital picture of the vehicle.

Exp_month   Indicates the month the current registration expires.

Exp_year   Indicates the year the current registration expires.

Year   Model year of the vehicle.

Make   Manufacturer of the vehicle.

Body_style   Type of vehicle.

Vin   Vehicle identification number.

Zipcode   Zip code of the owners address.

Zip_4   Zip code +4 of the owners address.

Owner_code   Illinois DMV ownership codes (1 – individual, 2 – multiple individuals same last name, 3 – multiple individuals different last names, 4 – corporate owner, 5 – combined corporate and individual, 6 – multiple corporate ownership, 7 – local government, 8 – state government and 9 – Federal government).

Make_abrv   Abbreviated manufacturer.

APPENDIX C: Temperature and Humidity Data from Chicago O'Hare Int. Airport.

Time (CDT)	1997									
	Sept. 15		Sept. 16		Sept. 17		Sept. 18		Sept. 19	
	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)
0700	64	100	68	87	68	81	64	78	71	84
0800	69	78	71	84	69	70	71	68	-	-
0900	73	68	75	73	71	61	75	57	77	76
1000	75	68	78	71	75	46	77	46	78	73
1100	78	61	80	66	77	39	78	44	80	73
1200	80	57	84	60	78	38	82	36	82	69
1300	80	57	82	62	80	32	82	36	80	73
1400	80	57	84	60	80	29	82	36	77	76
1500	80	62	84	58	80	29	82	32	73	87
1600	78	66	82	58	80	27	80	32	71	93
1700	75	73	82	58	78	32	78	38	71	100
1800	73	78	80	68	78	38	77	39	71	93

Time (CDT)	1998							
	Sept. 21		Sept. 22		Sept. 23		Sept. 24	
	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)
0700	57	66	57	80	51	68	53	89
0800	59	62	62	72	55	54	55	83
0900	60	59	62	72	59	51	57	77
1000	64	51	64	67	60	49	59	72
1100	64	55	66	56	62	42	60	77
1200	64	55	62	67	64	39	64	72
1300	66	48	62	67	64	39	64	72
1400	64	60	64	60	64	36	66	67
1500	64	62	64	51	66	34	64	72
1600	64	62	62	60	66	36	64	72
1700	62	67	62	55	62	51	64	78
1800	62	67	59	53	55	61	62	83

Time (CDT)	Sept. 20 T (°F)	Sept. 20 RH (%)	Sept. 21 T (°F)	Sept. 21 RH (%)	Sept. 22 T (°F)	Sept. 22 RH (%)	Sept. 23 T (°F)	Sept. 23 RH (%)
0700	54	87	48	89	46	80	54	65
0800	55	80	49	80	54	56	58	56
0900	57	75	53	74	59	43	62	51
1000	60	62	57	67	63	37	70	42
1100	62	56	57	64	66	34	74	36
1200	62	52	59	58	66	33	77	31
1300	60	53	60	58	71	33	78	31
1400	60	50	59	56	72	32	79	31
1500	63	43	60	53	72	33	80	31
1600	62	43	59	58	72	33	78	36
1700	59	51	57	62	71	35	77	37
1800	58	60	55	69	67	40	75	40

Table title: 1999

Time (CDT)	Sept. 11 T (°F)	Sept. 11 RH (%)	Sept. 12 T (°F)	Sept. 12 RH (%)	Sept. 13 T (°F)	Sept. 13 RH (%)	Sept. 14 T (°F)	Sept. 14 RH (%)
0800	76	85	63	76	62	60	64	96
0900	79	79	65	70	66	50	63	93
1000	82	71	67		69	47	60	96
1100	84	66	68	53	71	44	65	81
1200	87	61	69	45	74	41	68	63
1300	77	73	71	41	76	39	70	53
1400	74	78	71	47	77	36	73	38
1500	66	95	70	46	78	36	72	38
1600	67	95	70	47	79	34	72	44
1700	68	89	68	47	77	36	71	42
1800	69	84	66	49	73	48	67	47
1900	69	87	64	52	64	70	64	52

Table title: 2000

	2002									
Time (CDT)	Sept. 16		Sept. 17		Sept. 18		Sept. 19		Sept. 20	
	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)
0700	57	90	60	84	62	100	73	96	71	94
0800	63	70	66	72	64	93	74	94	70	100
0900	67	55	71	63	68	87	75	94	70	100
1000	69	55	74	60	70	76	76	91	70	100
1100	70	53	75	52	72	73	77	90	71	96
1200	72	50	77	50	72	79	76	97	70	90
1300	73	44	76	52	75	79	79	88	69	
1400	75	40	79	47	78	74	79	82	69	90
1500	75	42	79	42	79	74	78	85	69	87
1600	76	39	77	45	79	74	78	79	69	87
1700	74	41	74	52	78	74	79	77	69	84
1800	67	57	73	57	77	79	77	79	67	87

	2004							
Time (CDT)	Sept. 20		Sept. 21		Sept. 22		Sept. 23	
	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)
0800	63	54	67	61	69	57	70	61
0900	67	47	72	46	73	50	75	50
1000	71	42	75	37	76	43	79	44
1100	72	41	77	35	78	37	80	39
1200	74	38	80	34	78	37	81	38
1300	76	33	80	34	80	35	83	37
1400	77	28	81	32	80	35	84	35
1500	78	29	82	28	78	40	84	32
1600	77	30	81	30	80	38	84	33
1700	75	39	80	33	76	43	82	34
1800	71	49	70	55	68	63	78	39
1900	67	59	67	59	70	57	76	42

2006								
Time (CDT)	Sept. 12		Sept. 13		Sept. 14		Sept. 15	
	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)
0751	67	93	60	93	64	70	65	87
0851	68	93	60	93	66	70	69	76
0951	68	90	61	93	68	68	72	66
1051	68	97	61	90	71	61	72	59
1151	68	97	62	84	71	64	77	52
1251	70	90	62	87	71	64	75	52
1351	70	87	63	84	71	61	77	50
1451	71	84	62	87	72	57	78	47
1551	68	93	63	81	71	61	74	60
1651	66	90	63	81	69	66	73	64
1751	65	90	63	81	67	68	71	68
1851	65	90	62	81	65	75	69	76

2014												
Time (CDT)	Sept. 8		Sept. 9		Sept. 10		Sept. 11		Sept. 12		Sept. 13	
	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)	T (°F)	RH (%)
0851	70	51	70	66	71	90	50	66	52	61	47	74
0951	72	46	71	66	73	90	51	69	52	64	49	69
1051	74	43	75	60	73	90	51	69	54	59	51	61
1151	75	40	77	54	74	82	52	64	54	67	53	59
1251	76	43	79	52	78	71	52	64	52	83	54	57
1351	76	42	77	60	79	67	53	62	51	90	57	51
1451	76	43	78	58	78	64	53	64	49	93	56	53
1551	75	46	78	58	77	64	52	66	48	89	56	53
1651	74	48	77	62	76	64	51	66	47	89	57	51
1751	72	50	75	66	68	81	51	69	46	93	54	59
1851	70	51	76	62	63	78	51	69	46	89	52	64

APPENDIX D: Calculation of Vehicle Specific Power Adjusted Vehicle Emissions

1997 (Measured)	VSP Bin	Mean NO (ppm)	No. of Measurements	Total Emissions
	-5	236	225	53200
	0	224	1609	360090
	5	307	4985	1531000
	10	431	6146	2648020
	15	548	2624	1438060
	20	590	456	269180
			16045	6299550
			Mean NO (ppm)	**93**

1998 (Measured)	VSP Bin	Mean NO (ppm)	No. of Measurements	Total Emissions
	-5	233	137	31951
	0	239	784	187394
	5	265	3613	956613
	10	385	6685	2576433
	15	475	6012	2856195
	20	483	2392	1156320
			19623	7764906
			Mean NO (ppm)	**396**

1998 (Adjusted)	VSP Bin	'98 Mean NO (ppm)	'97 No. of Meas.	Total Emissions
	-5	233	225	52474
	0	239	1609	384588
	5	265	4985	1319877
	10	385	6146	2368700
	15	475	2624	1246616
	20	483	456	220436
			16045	5592691
			Mean NO (ppm)	**349**

Note that the Mean NO readings listed here have been rounded to the nearest ppm values which results in the Total Emissions column appearing to not be a direct multiplication product. The -5 to 20 kw/tonne bins are chosen to preclude any "off-cycle" emissions.

The object of this adjustment is to have the 1998 fleet's emissions calculated as if they drove (VSP wise) like the 1997 fleet. This is accomplished by first binning and averaging the 1997 and 1998 data (the top two tables). The mean NO values from the 1998 fleet are combined with the numerical VSP bin distribution from the 1997 fleet in the bottom table. The product of these two columns is summed, and the sum total emissions are divided by the number of 1997 vehicles to produce the 1998 adjusted mean NO average. For this example, it shows that the 1998 fleet when driven like the 1997 fleet has lower NO emissions than the 1997 fleet.

APPENDIX E: Calculation of Model Year Adjusted Fleet Emissions

1997 (Measured)	Model Year	Mean NO (ppm)	No. of Measurements	Total Emissions
	83	690	398	274620
	84	720	223	160560
	85	680	340	231200
	86	670	513	343710
	87	690	588	405720
	88	650	734	477100
	89	610	963	587430
	90	540	962	519480
	91	500	1133	566500
	92	450	1294	582300
	93	460	1533	705180
	94	370	1883	696710
	95	340	2400	816000
	96	230	2275	523250
	97	150	2509	376350
			17748	7266110
		Mean NO (ppm)		**409**

1998 (Measured)	Model Year	Mean NO (ppm)	No. of Measurements	Total Emissions
	83	740	371	274540
	84	741	191	141531
	85	746	331	246926
	86	724	472	341728
	87	775	557	431675
	88	754	835	629590
	89	687	1036	711732
	90	687	1136	780432
	91	611	1266	773526
	92	538	1541	829058
	93	543	1816	986088
	94	418	2154	900372
	95	343	2679	918897
	96	220	2620	576400
	97	177	3166	560382
			20171	9102877
		Mean NO (ppm)		**451**

1998 (Adjusted)	Model Year	'98 Mean NO (ppm)	'97 No. of Meas.	Total Emissions
	83	740	398	294520
	84	741	223	165243
	85	746	340	253640
	86	724	513	371412
	87	775	588	455700
	88	754	734	553436
	89	687	963	661581
	90	687	962	660894
	91	611	1133	692263
	92	538	1294	696172
	93	543	1533	832419
	94	418	1883	787094
	95	343	2400	823200
	96	220	2275	500500
	97	177	2509	444093
			17748	8192167
		Mean NO (ppm)		**462**

APPENDIX F: Field Calibration Record.

1997				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/15	9:35	1.42	1.35	1.07
9/15	14:30	1.26	1.18	0.94
9/16	9:20	1.33	1.25	1.02
9/16	12:40	1.12	1.08	0.86
9/17	8:10	1.39	1.27	1.11
9/17	11:55	1.19	1.12	0.97
9/18	8:15	1.49	1.41	1.20
9/18	12:30	1.15	1.10	0.86
9/19	11:00	1.24	1.16	0.95

1998				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/21	8:15	1.38	1.26	1.21
9/21	13:00	1.31	1.17	1.15
9/22	7:40	1.48	1.36	1.46
9/22	11:40	1.26	1.15	1.27
9/23	8:00	1.64	1.52	1.26
9/23	10:45	1.32	1.25	1.13
9/24	9:00	1.46	1.33	1.41
9/24	12:30	1.30	1.19	1.12

1999				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/20	9:50	1.32	1.05	1.21
9/20	14:30	1.25	0.99	1.15
9/21	8:15	1.45	1.19	1.46
9/21	10:30	1.33	1.07	1.27
9/22	8:30	1.47	1.13	1.32
9/22	11:10	1.22	1.01	1.201
9/23	8:15	1.46	1.16	1.41
9/23	10:30	1.25	0.97	1.12

2000				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/11	8:50	1.22	0.94	1.22
9/11	11:20	1.12	0.87	1.10
9/11	18:05	1.28	0.98	1.35
9/12	8:35	1.29	0.99	1.49
9/13	8:10	1.41	1.11	1.38
9/13	10:35	1.18	0.94	1.13
9/14	8:25	1.36	1.03	1.49
9/14	10:25	1.35	1.07	1.49
9/14	12:35	1.19	0.93	1.25

2002				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/16	11:10	1.35	1.07	1.59
9/17	9:35	1.52	1.19	1.82
9/17	12:00	1.35	1.07	1.46
9/18	9:00	1.51	1.19	1.67
9/18	12:45	1.36	1.07	1.44
9/19	9:20	1.59	1.31	1.60
9/19	12:35	1.39	1.16	1.40
9/20	12:30	1.31	1.17	1.68

2004				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/20	9:00	1.66	1.45	1.47
9/20	11:15	1.37	1.14	1.26
9/21	8:45	1.58	1.32	1.35
9/21	11:10	1.31	1.11	1.19
9/22	8:00	1.77	1.50	1.58
9/22	10:00	1.39	1.19	1.23
9/23	8:00	2.24	1.66	1.87
9/23	10:00	1.43	1.22	1.27

2006				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
9/12	9:05	1.69	1.41	1.52
9/13	10:00	1.58	1.30	1.51
9/13	11;50	1.75	1.38	1.48
9/13	13:50	1.48	1.20	1.19
9/14	8:00	1.59	1.30	1.41
9/14	11:00	1.43	1.19	1.22
9/15	8:00	2.32	91	2.35
9/15	9:30	1.69	1.42	1.56
9/15	11:15	1.46	1.22	1.31

2014					
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	NH$_3$ Cal Factor	NO$_2$ Cal Factor
9/8	10:00	1.58	1.44	1.44	0.99	0.72
9/8	12:30	1.34	1.23	1.33	0.99	0.6
9/9	9:25	1.62	1.46	1.58	0.96	0.72
9/9	11:30	1.41	1.30	1.37	0.96	0.67
9/10	13:45	1.34	1.24	1.35	0.91	0.69
9/11	9:15	1.83	1.66	1.79	0.98	1.03
9/11	12:20	1.75	1.59	1.73	1.0	0.97
9/11	16:15	1.83	1.63	1.77	0.98	1.04
9/12	9:20	1.85	1.65	1.78	1.02	1.09
9/12	12:15	1.76	1.57	1.68	1.03	0.98
9/13	9:25	1.90	1.70	1.82	0.99	1.13
9/13	12:00	1.75	1.55	1.67	1.03	0.92
9/13	14:35	1.66	1.49	1.62	1.04	0.99