2018

On-Road Remote Sensing of Automobile Emissions in the Denver Area: Winter 2017

Gary A. Bishop

Molly J. Haugen

CRC Report No. E-123

ON-ROAD REMOTE SENSING OF AUTOMOBILE EMISSIONS IN THE DENVER AREA: WINTER 2017

August 2018

COORDINATING RESEARCH COUNCIL, INC.
5755 NORTH POINT PARKWAY • SUITE 265 • ALPHARETTA, GA 30022

The Coordinating Research Council, Inc. (CRC) is a non-profit corporation supported by the petroleum and automotive equipment industries. CRC operates through the committees made up of technical experts from industry and government who voluntarily participate. The four main areas of research within CRC are: air pollution (atmospheric and engineering studies); aviation fuels, lubricants, and equipment performance; heavy-duty vehicle fuels, lubricants, and equipment performance (e.g., diesel trucks); and light-duty vehicle fuels, lubricants, and equipment performance (e.g., passenger cars). CRC's function is to provide the mechanism for joint research conducted by the two industries that will help in determining the optimum combination of petroleum products and automotive equipment. CRC's work is limited to research that is mutually beneficial to the two industries involved. The final results of the research conducted by, or under the auspices of, CRC are available to the public.

On-Road Remote Sensing of Automobile Emissions in the Denver Area: Winter 2017

Gary A. Bishop and Molly J. Haugen

Department of Chemistry and Biochemistry
University of Denver
Denver, CO 80208

August 2018

Prepared for:

Coordinating Research Council, Inc.
5755 North Point Parkway, Suite 265
Alpharetta, Georgia 30022
Contract No. E-123

EXECUTIVE SUMMARY

The University of Denver conducted five days of remote sensing in the Denver, Colorado area in December of 2017 and January of 2018. The remote sensor used in this study measures the ratios of CO, HC, NO, SO_2, NH_3 and NO_2 to CO_2 in motor vehicle exhaust. From these ratios, one can calculate the percent concentrations of CO, CO_2, HC, NO, SO_2, NH_3 and NO_2 in the exhaust that would be observed by a tailpipe probe, corrected for water and any excess oxygen not involved in combustion. Mass emissions per mass or volume of fuel can also be determined and are generally the preferred units for analysis. The equipment used in this study was configured to determine vehicle speed and acceleration, and included a video system to record license plate information. The latter was subsequently used to obtain non-personal vehicle registration information. Since fuel sulfur has been nearly eliminated in US fuels SO_2 emissions have followed suit and while vehicle SO_2 measurements are collected they were not calibrated and the measurements are not included in the discussion of the results.

Measurements were made on five weekdays, Friday December 15, Tuesday December 19, Wednesday December 20 2017, Tuesday January 9 and Thursday January 18 2018 on the interchange ramp from northbound I-25 to westbound US6. Since this is a winter measurement program only days with mild temperatures were used to collect measurements (high temperatures >50° F) and as such the sampling does not always occur on consecutive days. This is the same location previously used for the Denver measurements in the winters of 1999-2001, 2003, 2005, 2007, 2013 and 2015. However, between the 2013 and 2015 measurements this ramp was completely redesigned. Previously it was a tightly curved uphill (4.6°) interchange ramp with average speeds around 21 mph. The redesigned interchange reduced both the curvature and the steepness (1°) of the ramp allowing average speeds to increase above 30 mph and loads to decrease.

A database was compiled for the Denver data containing 22,266 records for which the State of Colorado provided registration information. All of these records contained valid measurements for at least CO and CO_2, and most records contained valid measurements for the other species as well. The database, as well as others compiled by the University of Denver, can be found at www.feat.biochem.du.edu.

The 2017 mean CO, HC, NO, NH_3 and NO_2 emissions for the fleet measured in this study were 8.0 ± 0.2 g/kg of fuel (0.06%), 2.6 ± 0.2 g/kg of fuel (65 ppm), 1.77 ± 0.05 g/kg of fuel (125 ppm), 0.37 ± 0.01 g/kg of fuel (46 ppm) and 0.11 ± 0.02 g/kg of fuel (5 ppm) respectively. When compared with the previous measurements from 2015 there are decreases for mean CO (g/kg of fuel) (-37%), HC (-10%), NO (-10%), NH_3 (-12%) and NO_2 (-21%) and the differences are all statistically significant at the 95% confidence interval. The percent of emissions contributed by the highest emitting 1% of the fleet (the 99th percentile) increased for CO, NO, NH_3 and slightly decreased for HC and NO_2.

Figure ES1 graphs the mean fuel specific emissions for CO (○, left axis), HC (▲, right axis) and NO (□, right axis) versus measurement year for all the data sets collected at the Denver site using the E-23 protocols. Uncertainties are standard errors of the mean calculated using the daily means. Since 1999 the fuel specific CO emissions have decreased by 86%, HC by 48% and NO by 79%. The rates of decreases for all of the species has slowed since the measurements were

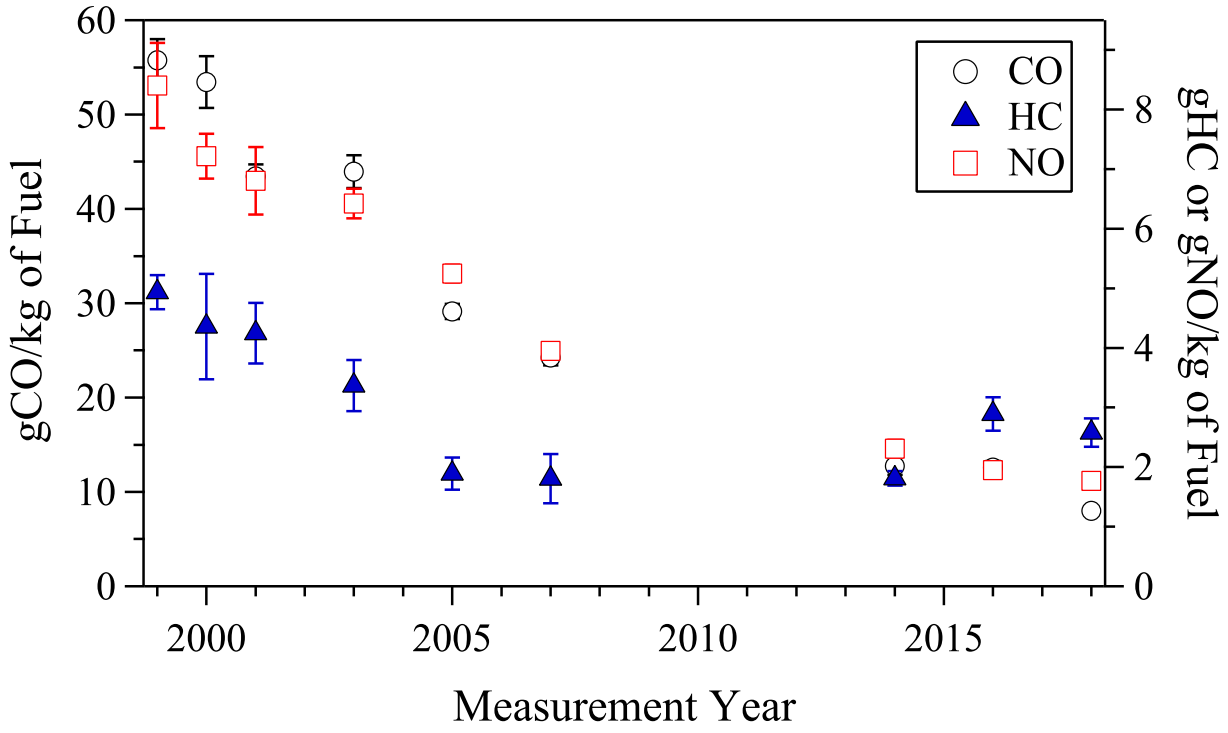

Figure ES1. Denver 6th Avenue historical fuel specific fleet mean emissions for CO (○, left axis), HC (▲ , right axis) and NO (□, right axis) by measurement year. Uncertainties are standard errors of the mean calculated using the daily measurements. The fuel specific HC means have been adjusted as described in the report.

collected in 2013 and mean fuel specific HC emissions increased between 2014 and 2016 when the interchange ramp was reconstructed.

The average age of the Denver fleet at this location has remained constant at 9.2 years old (2009.2 average model year in 2017) since 2013. This is still an increase of almost 2 years relative to the age of the fleet at this location prior to the 2008 recession. Fleet mean emissions remain dominated by a few high emitting vehicles. For the 2017 data set the highest emitting 1% of the measurements (99th percentile) are responsible for 47%, 29%, 26%, 17 % and 41% of the overall fleet CO, HC, NO, NH_3 and NO_2 emissions, respectively.

The history of NH_3 emission measurements at the Denver 6th Avenue site include measurements collected in a separate summer campaign of 2005 and winter CRC measurements in 2013, 2015 and 2017. Mean emissions were 0.45 ± 0.09, 0.44 ± 0.02, 0.42 ± 0.01 and 0.37 ± 0.008 gNH_3/kg of fuel respectively. This is an overall 18% reduction in emissions since 2005 or a 16% reduction since measurements resumed in 2013. Figure ES2 shows the fuel specific NH_3 emissions versus model year for the four data sets collected. Uncertainties are standard errors of the mean determined using the daily measurements. The peak for the NH_3 emissions in this plot continues to extend into older models with the 2017 measurements suggesting the peak occurs in 19 year old vehicles. However, the increased uncertainty due to fewer measurements in the older model

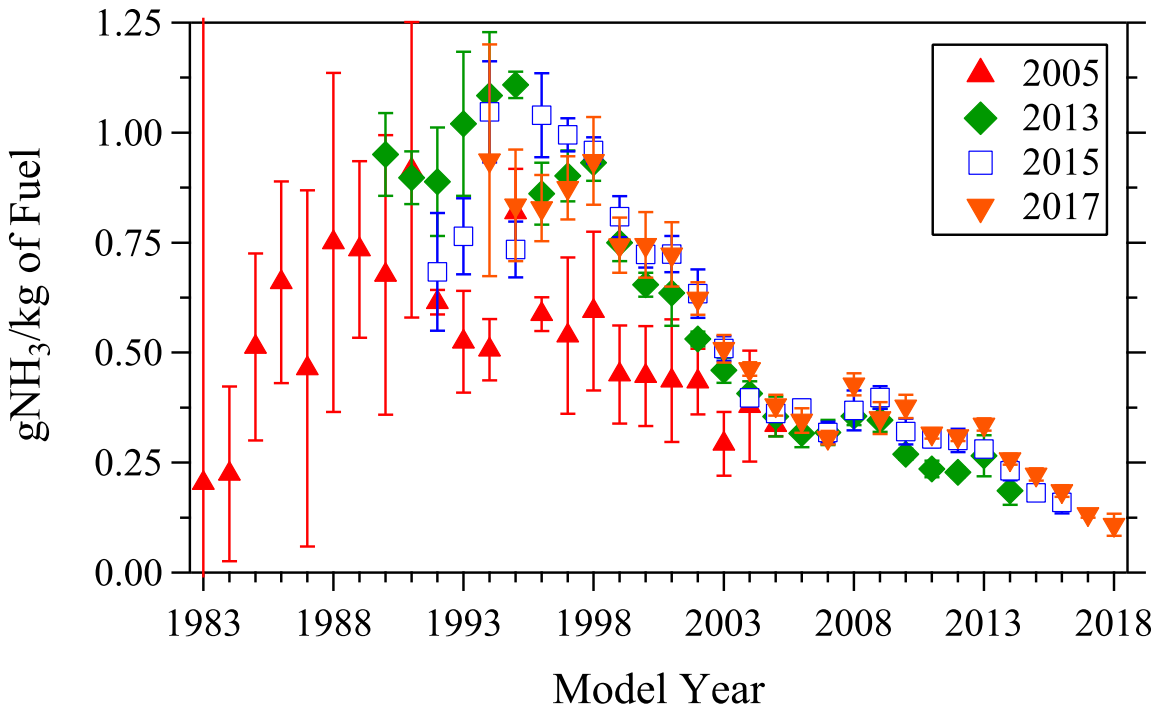

Figure ES2. Mean gNH_3/kg of fuel emissions plotted against vehicle model year for the four measurement data sets collected at the Denver site. Uncertainties are standard errors of the mean determined using the daily measurements.

year vehicles makes an exact assignment difficult but illustrates the fact that catalytic converters in modern gasoline vehicles continue to show improved durability. The NH_3 fleet reduction rates continue to be smaller than observed for tailpipe NO emissions, which at the Denver site have decreased 51% (3.7 gNO/kg in the summer of 2005 to 1.8 gNO/kg) over the same time period. The large uncertainties in the 2005 measurements shown in Figure ES2 stem from the small sample size (3,680 total measurements).

The total fixed nitrogen in g/kg of fuel for the Denver 2017 measurements are shown in Figure ES3 (◆, right axis) with the molar percent composition distributed between NH_3 (●, left axis) and the NO_x (▲, left axis) component versus model year for non-diesel vehicles. The total fixed nitrogen calculation neglects any unmeasured nitrous oxide (N_2O) and nitrous acid (HONO) that may account for a few percent of the total. Total fixed nitrogen emissions have been on a steep decline since the mid-nineties in the gasoline fleet and are continuing to show decreases in the newest model years in this data set as well. The percent of measured fixed nitrogen made up of NH_3 had been on the rise but in this latest Denver data set that rise appears to have leveled out soon after the introduction of Tier 2 vehicles and starting around the 2015 models it has declined. The start of this decline was also observed in the percent of fixed nitrogen which is NH_3 in the 2017 measurements collected in Tulsa, OK but there were not enough vehicle model years to establish the decline with any certainty. It is not known what if anything is behind this preference now for nitrogen oxidation (NO_x) at the tailpipe over reduced nitrogen (NH_3) in the newest vehicles but catalyst formulation is an important factor that can influence NH_3 production and may indicate formulation changes.

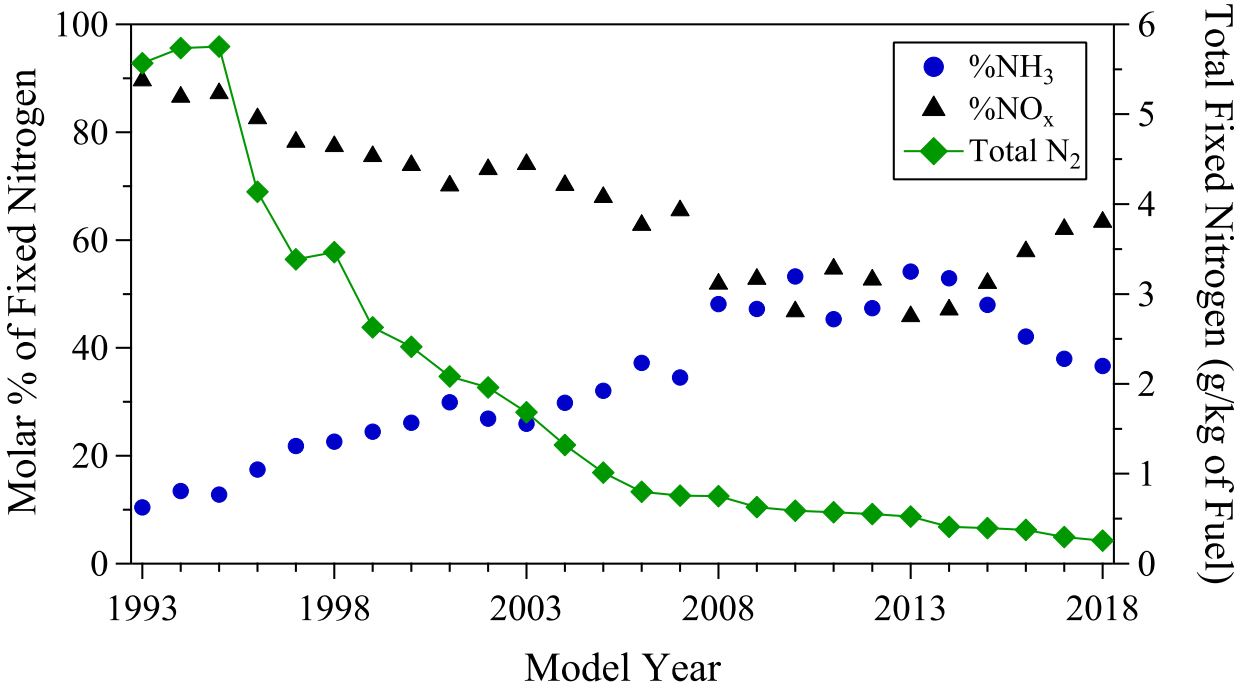

Figure ES3. Total fixed nitrogen in g/kg of fuel (◆, right axis) with the molar percent composition distributed between the NH_3 (●, left axis) and NO_x (▲, left axis) component versus model year for non-diesel vehicles.

INTRODUCTION

Since the early 1970's many heavily populated cities in the United States have been unable to comply with the National Air Quality Standards (NAAQS) that have been 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. 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 (NO_2). As of 2015, on-road vehicles continued to be estimated as one of the larger sources for major atmospheric pollutants, contributing approximately 39% of the CO, 14% of the volatile organic carbons, 3% of the ammonia (NH_3) and 36% of the NO_x to the national emission inventory.[3]

The use of the internal combustion engine and the combustion of carbon based fuels as one of our primary means of transportation accounts for it being 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, hydrocarbons (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 are difficult to quantify. Many areas remain in non-attainment for ozone. The further reduction of the federal eight-hour ozone standards (first introduced by the EPA in 1997 and subsequently lowered in 2008 (75ppb) and again in 2015 (70ppb)) means that many new locations are likely to have difficulty meeting the standards in the future.[5]

Beginning in 1997 the University of Denver began conducting on-road tailpipe emission surveys at selected sites in the U.S. to follow long term vehicle emission trends. A site northwest of Chicago IL, in Arlington Heights, was the first to be established but over the years 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 and the data have been used by many additional researchers to establish fleet emission trends and inventories.[7-13]

Reflecting a desire to continue evaluating the historical and recent emissions trends, several of the previous E-23 sites were chosen for additional data collection. As part of the E-106 program two additional measurement campaigns were conducted in Denver, CO in the winter of 2013 and 2015. CRC E-123 continues these measurements and this report describes the on-road emission measurements collected in Denver, CO in the winter of 2017. Measurements were made on five separate weekdays, Friday December 15, Tuesday December 19, Wednesday December 20 2017,

Tuesday January 9 and Thursday January 18 2018, between the hours of 9:00 and 16:00 on the interchange ramp from northbound I-25 to westbound US6.

Measurements were previously collected at this location beginning in 1995 and measurements collected using the E-23 protocol in 1999, 2000, 2001, 2003 and 2005 and 2007. E-106 measurements have been collected every other year since 2013, however, between the 2013 and 2015 measurements this ramp was completely redesigned. Previously it was a tightly curved uphill (4.6°) interchange ramp with average speeds around 21 mph. The redesigned interchange reduced both the curvature and the steepness (1°) of the previous ramp allowing average speeds to increase above 30 mph and loads to decrease.

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, and has previously been described in the literature.[14-16] The instrument consists of a non-dispersive infrared (NDIR) component for detecting CO, CO_2, and HC, and twin dispersive ultraviolet (UV) spectrometers for measuring oxides of nitrogen (NO and NO_2), SO_2 and NH_3 (0.26 nm/diode resolution). The source and detector units are positioned on opposite sides of the road in a bi-static arrangement. Collinear beams of infrared (IR) and UV light are passed across the roadway into the IR detection unit, and are then focused through a dichroic beam splitter, which serves to separate the beams into their IR and UV components. The IR light is then passed onto a spinning polygon mirror, which spreads the light across the four infrared detectors: CO, CO_2, HC and reference.

The UV light is reflected from the surface of the dichroic mirror and is focused onto the end of a quartz fiber bundle that is mounted to a coaxial connector on the side of the detector unit. The quartz fiber bundle is divided in half to carry the UV signal to two separate spectrometers. The first spectrometer was adapted to expand its UV range down to 200nm in order to measure the peaks from SO_2 and NH_3 and continue to measure the 227nm peak from NO. 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 in order 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.[17] Since the removal of sulfur from gasoline and diesel fuel in the US SO_2 emissions have become negligibly small and as such, 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 are dependent upon, 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 only directly measures 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, and on their own are useful parameters for describing a hydrocarbon combustion system. This study reports measured emissions 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. But 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.[18] To calculate mass emissions as described below, the %HC values reported first have to be multiplied by 2.0 to account for these "unseen" hydrocarbons as shown below, assuming that the fuel used is regular gasoline. These percent emissions can be directly converted into mass emissions by the equations shown below.

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

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 close to 100% NO in the case of gasoline fueled vehicles.

Another useful relationship is the conversion from percent emissions to grams pollutant per kilogram (g/kg) of fuel. This is directly 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 (this translates to 860 gC/kg of 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.[18]

$$\text{gm CO/kg} = (28Q^{CO} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \quad (3a)$$
$$\text{gm HC/kg} = (2(44Q^{HC}) / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \quad (3b)$$
$$\text{gm NO/kg} = (30Q^{NO} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \quad (3c)$$
$$\text{gm } NH_3\text{/kg} = (17Q^{NH3} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \quad (3d)$$
$$\text{gm } NO_2\text{/kg} = (46Q^{NO2} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \quad (3e)$$

Quality assurance calibrations are performed at least twice daily in the field unless observed voltage readings or meteorological changes are judged to warrant additional calibrations. For the multi-species instrument three calibration cylinders are needed. The first contains CO, CO_2, propane and NO, the second contains NH_3 and propane and the final cylinder contains NO_2 and CO_2. A puff of gas is released into the instrument's path, and the measured ratios from the instrument are then compared to those certified by the cylinder manufacturer (Air Liquide and PraxAir). 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.

Double blind 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.[19, 20] The NO channel used in this study has been extensively tested by the University of Denver, but has not been subjected to an extensive double blind study and instrument inter-comparison to have it independently validated. 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.[15] Comparison of fleet average emission by model year versus IM240 fleet average emissions by model year show correlations between 0.75 and 0.98 for data from Denver, Phoenix and Chicago.[21] Appendix A gives a list of criteria for determining data validity.

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, as well as a time and date stamp, is 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 0.1mph) 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. From these two speeds, and the time difference between the two speed measurements, acceleration is calculated (reported to 0.001 mph/sec). Appendix B defines the database format used for the data set.

RESULTS AND DISCUSSION

Measurements were made on five weekdays, Friday December 15, Tuesday December 19, Wednesday December 20 2017, Tuesday January 9 and Thursday January 18 2018, between the hours of 9:00 and 16:00 on the interchange ramp from northbound I-25 to westbound US6. Since this is a winter measurement program only days with mild temperatures were chosen to collect measurements (high temperatures >50° F) and as such the sampling does not always occur on

consecutive days. A satellite image of the measurement location is shown in Figure 1 and a photograph of the setup from the 2015 campaign is shown in Figure 2. Appendix C gives temperature and humidity data for the study dates.

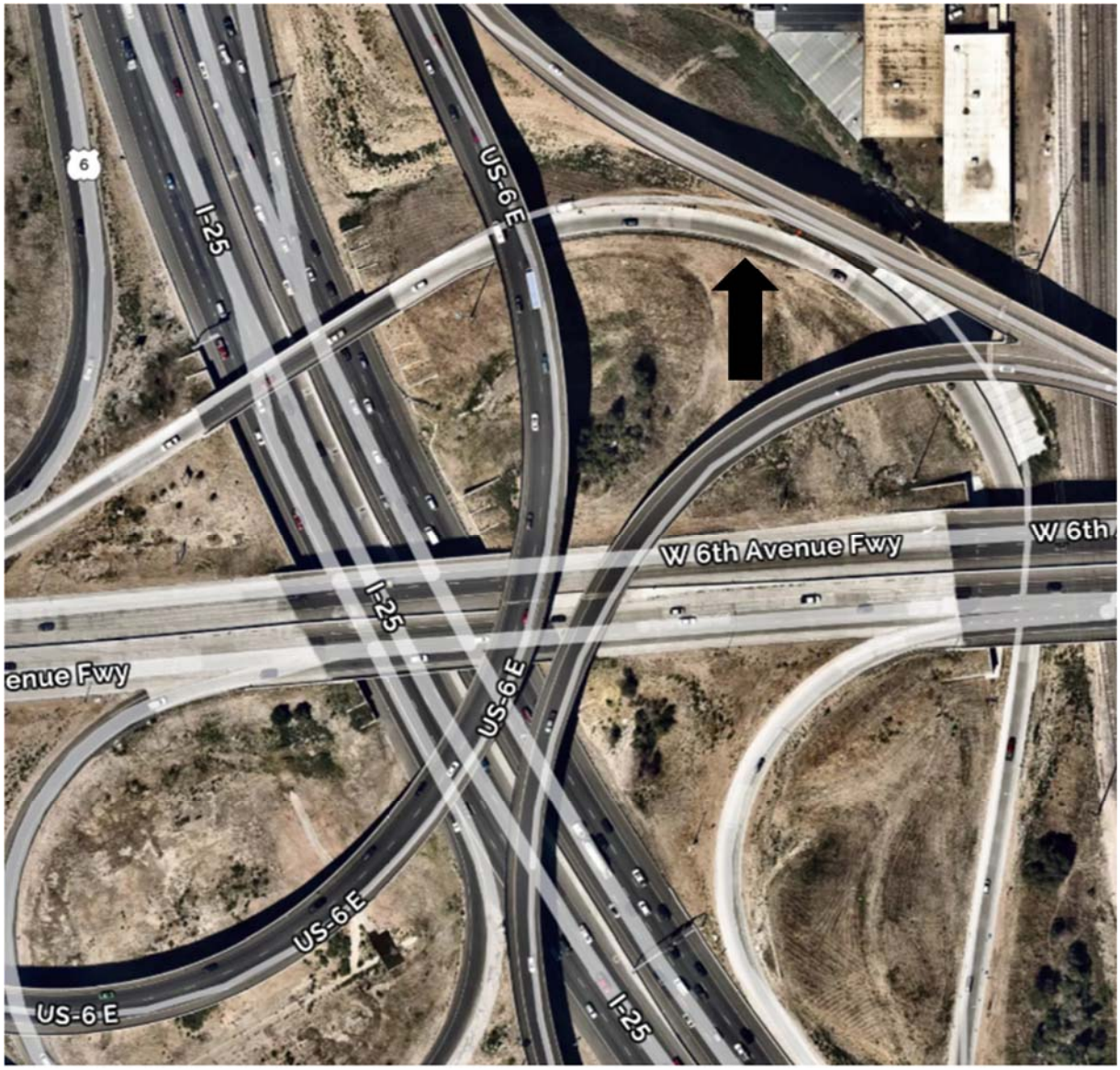

Figure 1. A satellite picture of the Denver interchange ramp from Northbound I-25 to Westbound US6 (labeled W 6th Avenue Fwy. in this image). The large black arrow marks the approximate sampling location.

The digital video images of the license plates were subsequently transcribed for license plate identification. Colorado license plates were transcribed and submitted to the state for matching against registration records for all non-personal vehicle information. The resulting 2017 database contains 22,266 records with make and model year information and valid measurements for at

Figure 2. The Denver US6 monitoring site looking west toward the mountains.

least CO and CO_2. Most of these records also contain valid measurements for HC, NO, NH_3 and NO_2. This database and all previous databases compiled for the CRC E-23 and E-106 campaigns can be found at www.feat.biochem.du.edu.

The validity of the attempted measurements is summarized in Table 1. The table describes the data reduction process 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 closely following vehicle, that measurement attempt is aborted and an attempt is made at measuring the second vehicle. 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 absent (elevated, electric/hybrid engine off operation or rapid deceleration from foot off the throttle), or the reported error in the ratio of the pollutant to CO_2 exceeds a preset limit (see Appendix A). For the Denver site this represents the largest loss of measurements as the higher speeds at the redesigned ramp allow vehicles the opportunity to coast through the measurement beam. Additional data losses occur during the plate reading process, when out-of-state vehicles, vehicles with unreadable plates (obscured, missing, dealer, out of camera field of view) are

Table 1. Validity Summary.

	CO	HC	NO	NH_3	NO_2
Attempted Measurements	35,189				
Valid Measurements	27,967	27,935	27,962	27,939	27,784
Percent of Attempts	79.5%	79.4%	79.5%	79.4%	79.0%
Submitted Plates	23,083	23,057	23,078	23,060	22,930
Percent of Attempts	65.6%	65.5%	65.6%	65.5%	65.2%
Percent of Valid Measurements	82.5%	82.3%	82.5%	82.5%	82.5%
Matched Plates	22,266	22,240	22,261	22,243	22,124
Percent of Attempts	63.3%	63.2%	63.3%	63.2%	62.9%
Percent of Valid Measurements	79.6%	79.6%	79.6%	79.6%	79.6%
Percent of Submitted Plates	96.5%	96.5%	96.5%	96.5%	96.5%

omitted from the database. Colorado, like Oklahoma, has expanded the use of Q's in its plates and combined with D's and O's makes it difficult to successfully transcribe some plates. To combat mistaken matches all of the plates with Q's, D's and O's in them were visually rechecked for the DMV matched vehicle make and records with mismatched makes were deleted.

Table 2 provides an analysis of the number of vehicles that were measured repeatedly, and the number of times they were measured. Of the 22,266 records used in this fleet analysis, 17,793 (79.9%) were contributed by vehicles measured only once, and the remaining 4,473 (20.1%) records were from vehicles measured at least twice. The combination of high traffic volumes and fewer consecutive days of sampling at this site increases the number of unique vehicle measurements.

Table 2. Number of measurements of repeat vehicles.

Number of Times Measured	Number of Vehicles
1	17,793
2	1,563
3	319
4	72
5	18
6	2

Table 3 summarizes the data for the current and all of the previous winter CRC remote sensing campaigns conducted at this site. The measurements that were collected in the years following reconstruction of the exit ramp at the 6th Avenue site are delineated in the table by the double lines separating the columns labeled 2013 and 2015. The average HC values have been adjusted for this comparison to remove an artificial offset in the measurements. This offset, restricted to the HC channel, has been reported in earlier CRC E-23-4 reports. Calculation of the offset is accomplished by computing the mode and means of the newest model year and vehicles, and assuming that these vehicles emit negligible levels of hydrocarbons and that the median of these group's emissions distribution should be very close to zero, using the lowest of either of these

Table 3. Winter Campaign Data Summary.

Study Year	1999	2000	2001	2003	2005	2007	2013	2015	2017
Mean CO (%) (g/kg of fuel)	0.45 (56)	0.43 (54)	0.34 (43)	0.35 (44)	0.23 (29)	0.19 (24)	0.10 (12.6)	0.10 (12.6)	0.06 (8.0)
Median CO (%)	0.09	0.11	0.06	0.08	0.05	0.05	0.02	0.03	0
99th Percentile Contribution	15.4	16.4	19.6	19.2	23.1	25.7	33.6	32.5	47.2
Mean HC (ppm)[a] (g/kg of fuel)[a] Offset (ppm)	125 (5.0) 5	115 (4.6) 60	112 (4.6) -50	88 (3.4) 20	50 (1.9) 10	46 (1.8) 0	45 (1.8) 45	77 (2.9) 11	65 (2.6) 26
Median HC (ppm)[a]	75	50	80	40	20	30	31	42	31
99th Percentile Contribution	22.7	25.7	29.0	30.8	42.3	33.1	26.5	30.4	29.2
Mean NO (ppm) (g/kg of fuel)	600 (8.4)	511 (7.2)	483 (6.8)	456 (6.5)	371 (5.3)	278 (4.0)	193 (2.7)	138 (2.0)	125 (1.8)
Median NO (ppm)	240	165	133	113	76	40	17	8	10
99th Percentile Contribution	7.4	8.6	9.4	9.8	11.0	12.6	17.6	23.3	25.6
Mean NH_3 (ppm) (g/kg of fuel)	NA	NA	NA	NA	NA	NA	55 (0.44)	53 (0.42)	46 (0.37)
Median NH_3 (ppm)	NA	NA	NA	NA	NA	NA	16	15	13
99th Percentile Contribution	NA	NA	NA	NA	NA	NA	15.0	15.8	16.7
Mean NO_2 (ppm) (g/kg of fuel)	NA	NA	NA	NA	NA	NA	11 (0.24)	6 (0.14)	5 (0.11)
Median NO_2 (ppm)	NA	NA	NA	NA	NA	NA	4	2	2
99th Percentile Contribution	NA	NA	NA	NA	NA	NA	44.8	43.1	41.1
Mean Model Year	1992.4	1993.4	1994.6	1996.4	1998.1	2000	2005.2	2007.2	2009.2
Mean Fleet Age[b]	6.9	6.9	6.7	6.9	7.2	7.3	9.2	9.2	9.2
Mean Speed (mph)	20.6	21.9	22.3	20.2	23.5	22.5	22.9	32.8	32.5
Mean Acceleration (mph/s)	0.21	0.08	-0.77	0.12	-0.47	0.07	0.01	-1.0	0.33
Mean VSP (kw/tonne) Slope (degrees)	9.9 4.6°	10.1 4.6°	5.9 4.6°	10.7 4.6°	8.1 4.6°	10.4 4.6°	10.4 4.6°	-1.4 1.0°	8.9 1.0°

[a]Indicates values that have been HC offset adjusted as described in text.
[b]Assumes new vehicle model year starts September 1.

values as the offset. The offset adjustment is subtracted or added to the individual hydrocarbon measurements. This normalizes each data set to a similar emissions zero point since it is assumed that the cleanest vehicles emit few hydrocarbons. Such an approximation will err only slightly towards clean because the true offset will be a value somewhat less than the average of the cleanest model year and make. This adjustment facilitates comparisons with the other E-23 sites and/or different collection years for the same site. The offset adjustments have been performed where indicated in the analyses in this report and a detailed example of how it is calculated is included in Appendix D.

The 2017 Denver measurements show reductions for all of the species measured when compared with the 2015 values. Fuel specific emission factors (g/kg of fuel) decreased for CO (-37%), HC (-10%), NO (-10%), NH_3 (-12%) and NO_2 (-21%) and the differences were all statistically significant at the 95% confidence interval. The percent of emissions contributed by the highest emitting 1% of the fleet (the 99th percentile) increased for CO, NO, NH_3 and slightly decreased for HC and NO_2. Increases in congestion on the ramp results in increases in the mean acceleration observed during the measurements and accounts for the changes in VSP observed between 2015 and 2017.

An inverse relationship between vehicle emissions and model year is shown in Figure 3 for the nine periods sampled during the winters of 1999 – 2001, 2003, 2005, 2007, 2013, 2015 and 2017. The HC data have been offset adjusted here for comparison. There is a noticeable increase in the mean HC emissions for all the model years beginning with the 2015 measurements after reconstruction of the ramp and increases in the number of measured vehicle deceleration events (foot off the gas motoring as well as braking). CO and NO mean emissions by model year are not affected by this change in driving mode and the dominate feature for these two species is the gradual increases in fleet average emissions, year over year, beginning around model years 2002 and older. Note that there is considerable uncertainty in the mean emission levels for model years 1993 and older in the newest data sets because of the small sample sizes (in the 2017 measurements there are only 42 1993 model year vehicle measurements). All three species graphed in Figure 3 show an ever increasing number of model years with emission levels that do not change from the initial model year average. NO emissions are the first to show increases but the Tier II certified vehicles (2009 & newer) have now eliminated fleet average NO emissions deterioration.

Following the data analysis and presentation format originally shown by Ashbaugh et al.,[22] the vehicle emissions data by model year from the 2017 study were divided into quintiles and plotted. The results are shown in Figures 4 - 6. The bars in the top plot represent the mean emissions for each model year's quintile, but do not account for the number of vehicles in each model year. The middle graph shows the fleet fraction by model year for the newest 22 model years showing the impacts the last recession had on car sales between 2009 and 2010 and the recovery that has followed. Model years older than 1997 and not graphed account for 2.8% of the measurements and contribute between 11.8% (HC) and 23.4% (CO) of the total emissions. The bottom graph for each species is the combination of the top and middle figures. These figures illustrate that the lowest emitting 60% of the on-road fleet, regardless of model year, make an

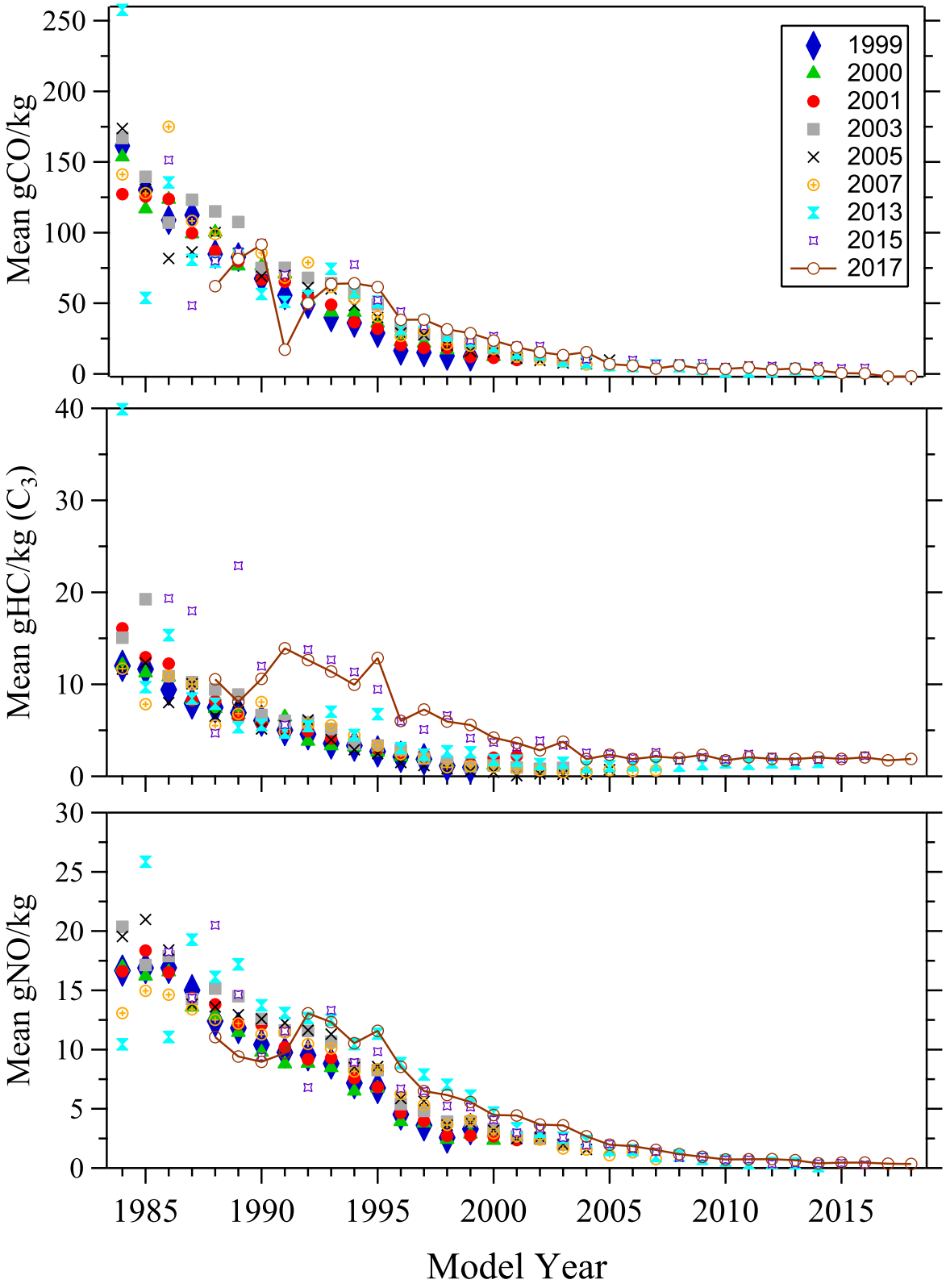

Figure 3. Mean fuel specific vehicle emissions plotted as a function of model year for all the collected Denver data sets. HC data have been offset adjusted as described in the text.

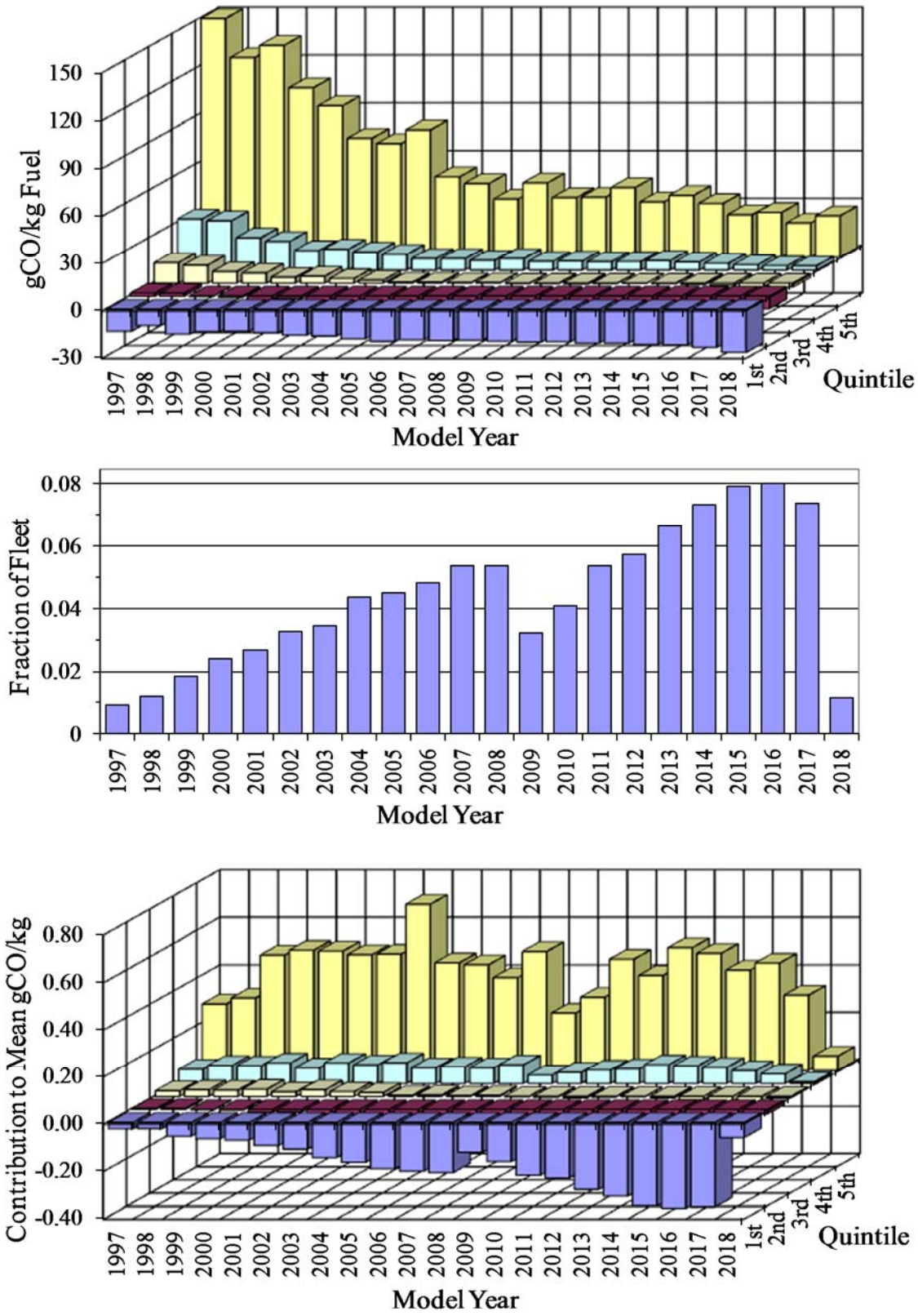

Figure 4. Mean gCO/kg of fuel emissions by model year and quintile (top), fleet distribution (middle) and their product showing the contribution to the mean gCO/kg of fuel emissions by model year and quintile (bottom).

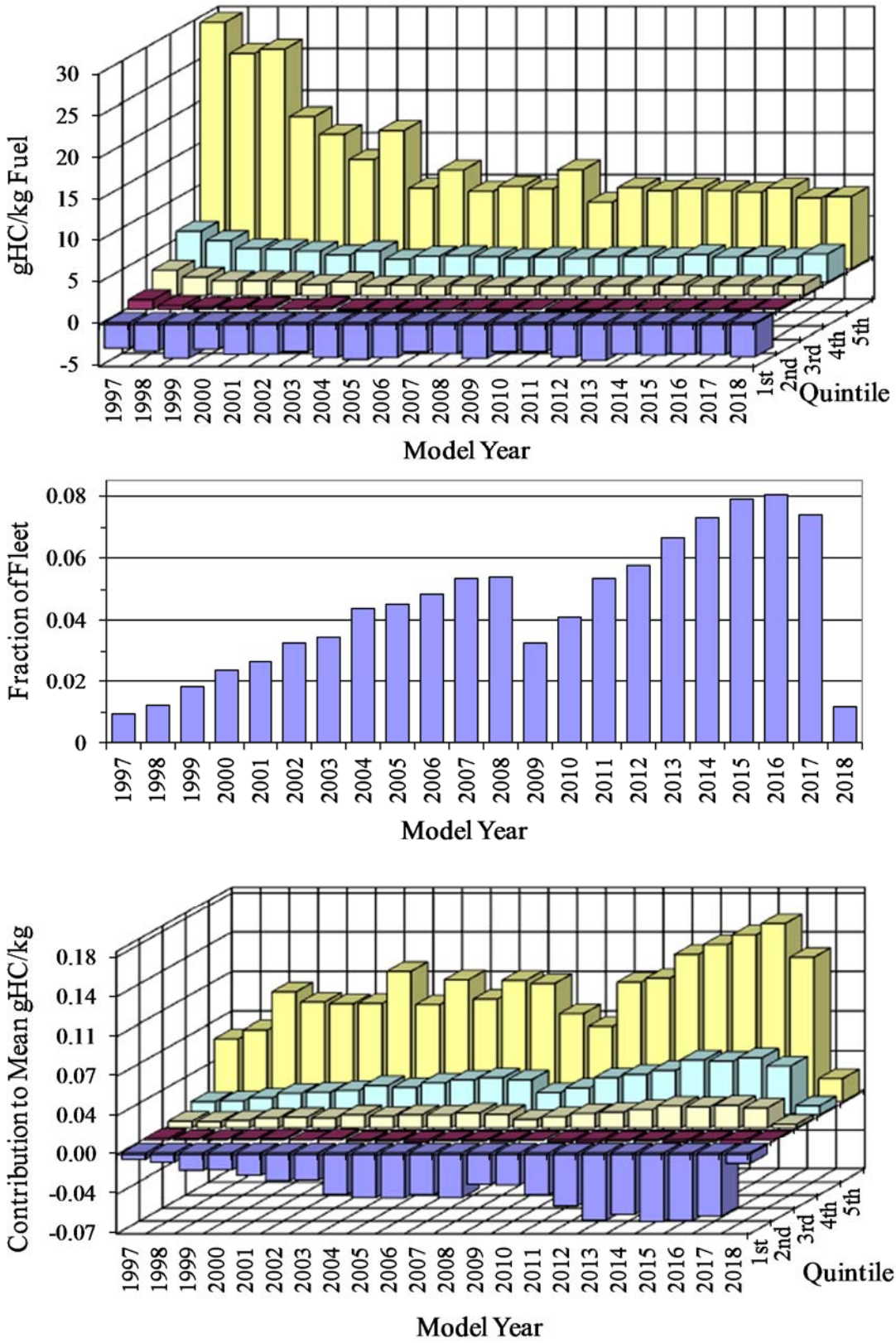

Figure 5. Mean gHC/kg of fuel emissions by model year and quintile (top), fleet distribution (middle) and their product showing the contribution to the mean gHC/kg of fuel emissions by model year and quintile (bottom).

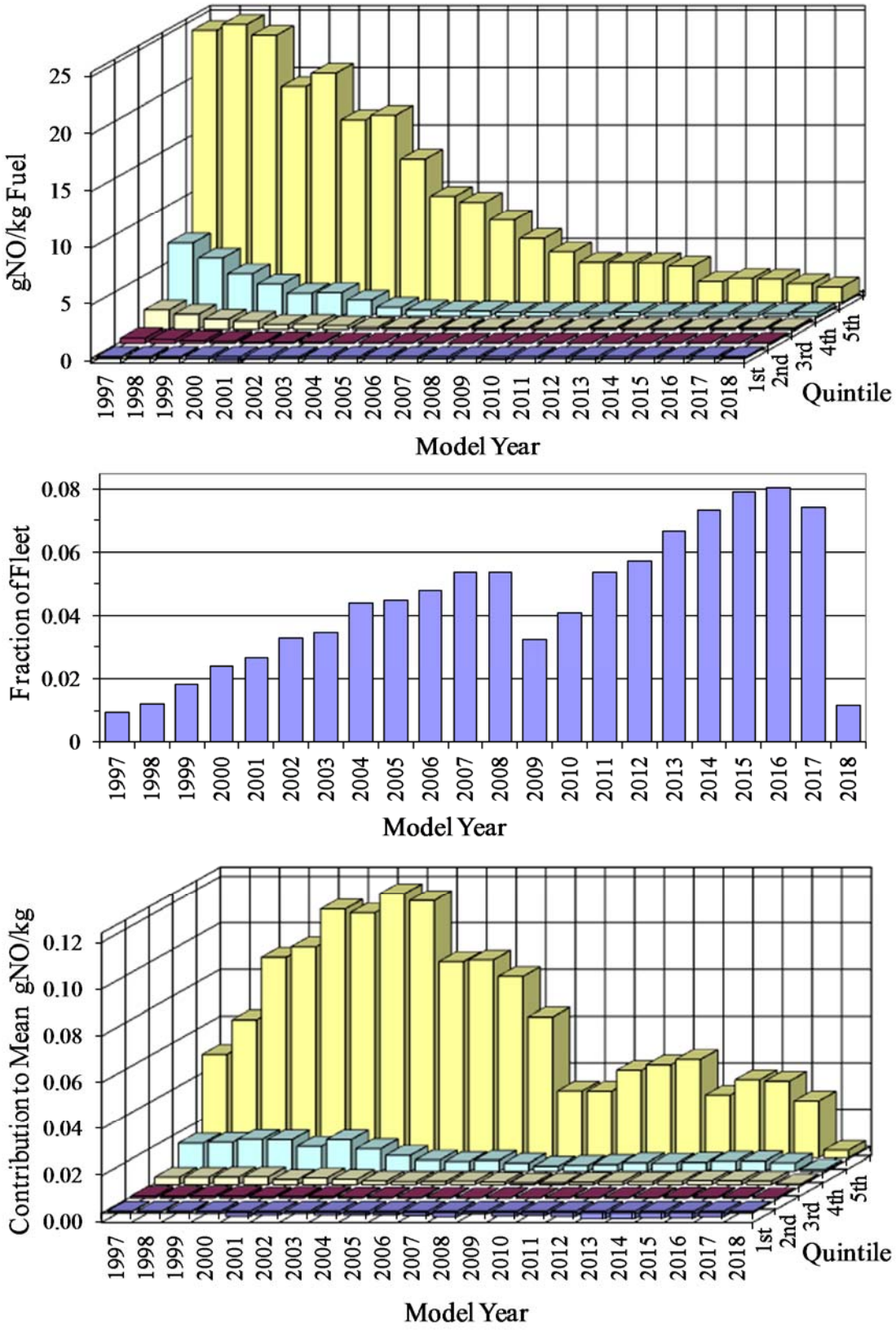

Figure 6. Mean gNO/kg of fuel emissions by model year and quintile (top), fleet distribution (middle) and their product showing the contribution to the mean gNO/kg of fuel emissions by model year and quintile (bottom).

essentially negligible contribution to the overall fleet mean emissions. The accumulations of negative emissions in the first two quintiles are the result of ever decreasing emission levels. Our instrument is designed such that when measuring true zero emission plumes (a ratio of zero), approximately half of the readings will be negative and half will be positive. As the lowest emitting segments of the fleets continue to trend toward zero emissions, the negative emission readings will continue to grow toward half of the measurements. This is evident for approximately the first 10 model years for CO (bottom panel) where the negative height of the first quintile is generally equal to the positive height of the last quintile.

The middle graph in Figures 4 – 6 shows the fleet fractions by model year for the 2017 Denver database. The impact of the reduction in light-duty vehicle sales during the 2008 recession is still a prominent feature of the 2017 data.[23] In both Denver and Los Angeles the 2008 recession increased average fleet ages by 2 full model years. Table 3 shows that the average age of the Denver fleet observed at this ramp has remained constant at 9.2 years since 2013 despite the recovery in vehicle sales following the 2008 recession. For comparison in the winter 2006 – 2007 (~7.3 year old fleet) the first 11 model years (2007 – 1997) accounted for 79% of the measurements. In the winter 2017 – 2018 (~9.2 year old fleet) the first 11 model years (2018 – 2008) now only accounts for 62% of the measurements.

As emissions of CO and HC have been drastically reduced over the past two decades, generally all those that contribute to the means are found in the last quintile (as shown in the bottom graphs of Figures 4 and 5). For CO these contributions to the fleet mean emissions are generally evenly distributed across the first twenty model years (refer to bottom graph Figure 4). For HC the contributions by model year to the fleet mean follows the pattern of the fleet fractions with the numerical superiority of the newest seven model years accounting for greater shares with more equal influences attributed to the older model years. NO is the exception. The large reductions in NO emissions in the Tier 2 vehicles combined with lower vehicle sales when they were introduced into the fleet has shifted the bulk of the contributions to the NO mean to 2008 and older models (see the bottom graph of Figure 6). In addition, the small numbers of diesel powered vehicles in the fleet also contribute to the last quintile for NO.

While NH_3 is not a regulated pollutant it is a necessary precursor for the production of ammonium nitrate and sulfates which are often a significant component of secondary aerosols found in urban areas.[24] Ammonia is most often associated with farming and livestock operations but it can also be produced by 3-way catalyst equipped gasoline and natural gas vehicles.[25] The production of exhaust NH_3 emissions is contingent upon the vehicle's ability to produce NO in the presence of a catalytic convertor that has enough hydrogen available to reduce the NO to NH_3. The absence of either of these species precludes the formation of exhaust NH_3. Dynamometer studies have shown that the hydrogen stores can be increased when acceleration events are preceded by a deceleration event though not necessarily back to back.[26] Previous on-road ammonia emissions have been reported by Baum *et al.* for a Los Angeles site in 1999, by Burgard *et al.* in 2005 from gasoline-powered vehicles for this Denver site, our E-106 site in Tulsa and by Kean et al in 1999 and 2006 from the Caldecott tunnel near Oakland.[27-30] The University of Denver collected NH_3 measurements at three California, (San Jose, Fresno and

West LA) sites in 2008 and from a Van Nuys, California site in 2010.[31, 32] In addition air borne measurements of ammonia were collected in 2010 over the South Coast Air Basin as part of the CalNex campaign.[11] Most recently we have reported on ammonia emissions collected in 2013 from West LA, Tulsa and this Denver site.[33]

With the collection of the 2017 data set there are now 4 Denver data sets that can be used to look at the changes in NH_3 emissions. The 2005 data were collected in a non-CRC measurement campaign during the summer while the remaining data sets were collected during the winter. Figure 7 compares gNH_3/kg of fuel emissions collected at the Denver site for all four measurement campaigns by model year. The uncertainties plotted are standard errors of the mean determined using the daily means (see Appendix E). The 2005 data set has considerably more measurement uncertainty owing to its significantly smaller size (~3700 total measurements). With each data set collected we find that the newest model year vehicles continue to have lower NH_3 emissions.

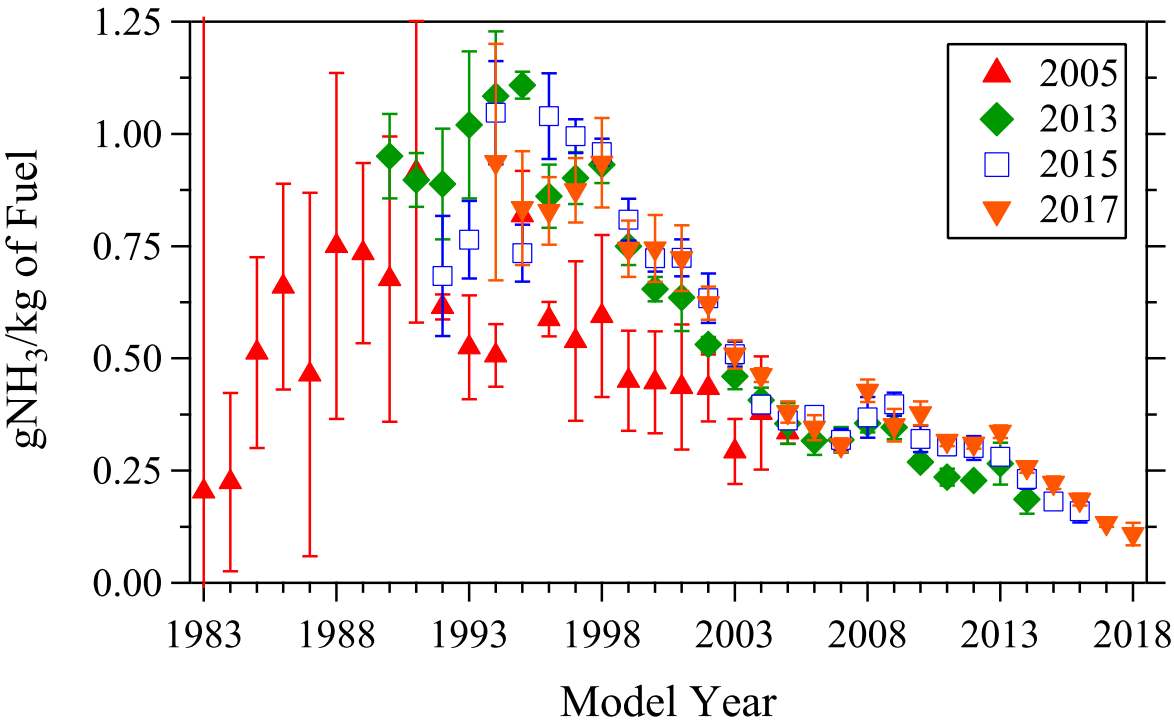

Figure 7. Mean gNH_3/kg of fuel emissions plotted against vehicle model year for the four measurement data sets collected at the Denver site with uncertainties plotted as standard errors of the mean determined using the daily means.

Because NH_3 emissions are sensitive to vehicle age it often helps to plot the data against vehicle age as opposed to model year. Figure 8 compares the four Denver data sets in this way where year 0 vehicles are 2018, 2016, 2014 and 2006 models for the 2017, 2015, 2013 and 2005 data sets, respectively. The uncertainties plotted are standard errors of the mean calculated from distributing the daily means for each year's data (see Appendix E). Most noticeable in the 2005 data set is the characteristic shape with NH_3 emissions increasing with model year until the

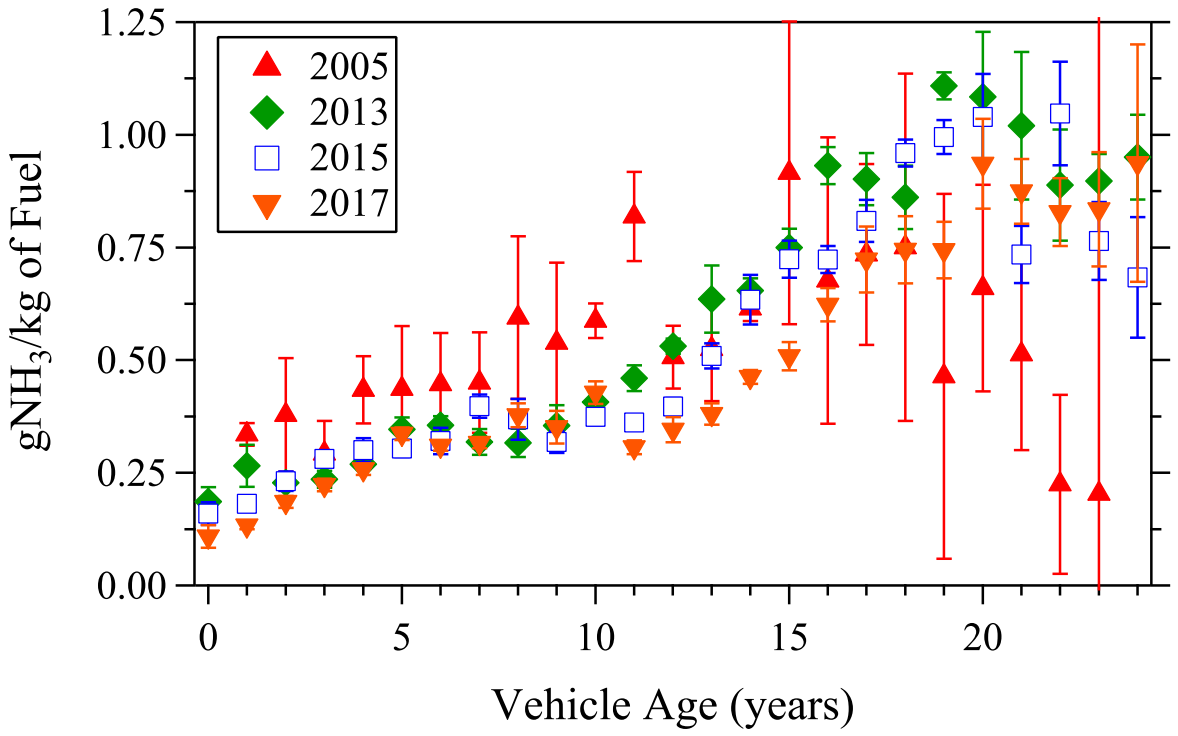

Figure 8. Mean gNH_3/kg emissions plotted against vehicle age for the 2017, 2015, 2013 and 2005 measurements at the Denver site. The uncertainties plotted are the standard error of the mean determined using the daily means.

vehicles reach an age where the catalytic converters lose their ability to reduce NO emissions and then the emissions start decreasing to levels approaching zero.

The differences between the 4 data sets are more obvious when NH_3 emissions are plotted as a function of vehicle age instead of model year as shown in Figure 8. For the same age vehicles, which are manufactured to significantly different standards, substantial emissions reductions relative to 2005 measurement campaign have occurred for the first 10 years. In addition there is a lower rate of increase in NH_3 emissions as a function of vehicle age, seen initially with the 2013 data set, which is still a feature of the 2017 data. While the rate of increase has slowed it appears that the average vehicle age at which NH_3 emissions peak and then begin to decrease keeps getting older as previously mentioned. The period of increasing NH_3 emissions has grown considerably since 2005, though it is debatable as to the exact point in the 2005 data that the emissions peak. The 2005 data increases for approximately 10 years (1996 model year was the introduction of Tier 1 vehicles) and starts to decline before it reaches the 15 year old vehicles (1991 models). The 2013 data set rises for approximately 17 years (1997 models) and then declines. This is consistent with several other data sets collected since 2008.[32] The 2015 data set appears to not peak until approximately 19 year old vehicles; though there is increased uncertainty about assigning the exact point because the small sample sizes of these older model years complicates that determination. For the 2017 Denver data set it is arguable whether NH_3 shows any decline through the first 24 model years (the remaining 1994 model year vehicles).

Certainly declining fuel sulfur levels have improved the longevity of catalytic converters which is a factor in these NH_3 emission trends.

The total fixed nitrogen in g/kg of fuel for the Denver 2017 measurements is shown in Figure 9 (◆, right axis) with the molar percent composition distributed between NH_3 (●, left axis) and the NO_x (▲, left axis) component versus model year for non-diesel vehicles. The total fixed nitrogen calculation neglects any unmeasured nitrous oxide (N_2O) and nitrous acid (HONO) that may account for a few percent of the total. Total fixed nitrogen emissions have been on a steep decline since the mid-nineties in the gasoline fleet and are continuing to show decreases in the newest model years in this data as well. The percent of fixed nitrogen made up of NH_3 had been on the rise but in this latest data set that increase appears to have leveled out soon after the introduction of Tier 2 vehicles and starting around the 2015 models it has declined. The start of this decline in the percent of fixed nitrogen as NH_3 was also observed in the 2017 Tulsa, OK measurements but at that time there were not enough vehicle model years to establish the decline with any certainty. It is not known what if anything is behind this preference now for nitrogen oxidation (NO_x) at the tailpipe over reduced nitrogen (NH_3) in the newest vehicles but catalyst formulation is an important factor that can influence NH_3 production.

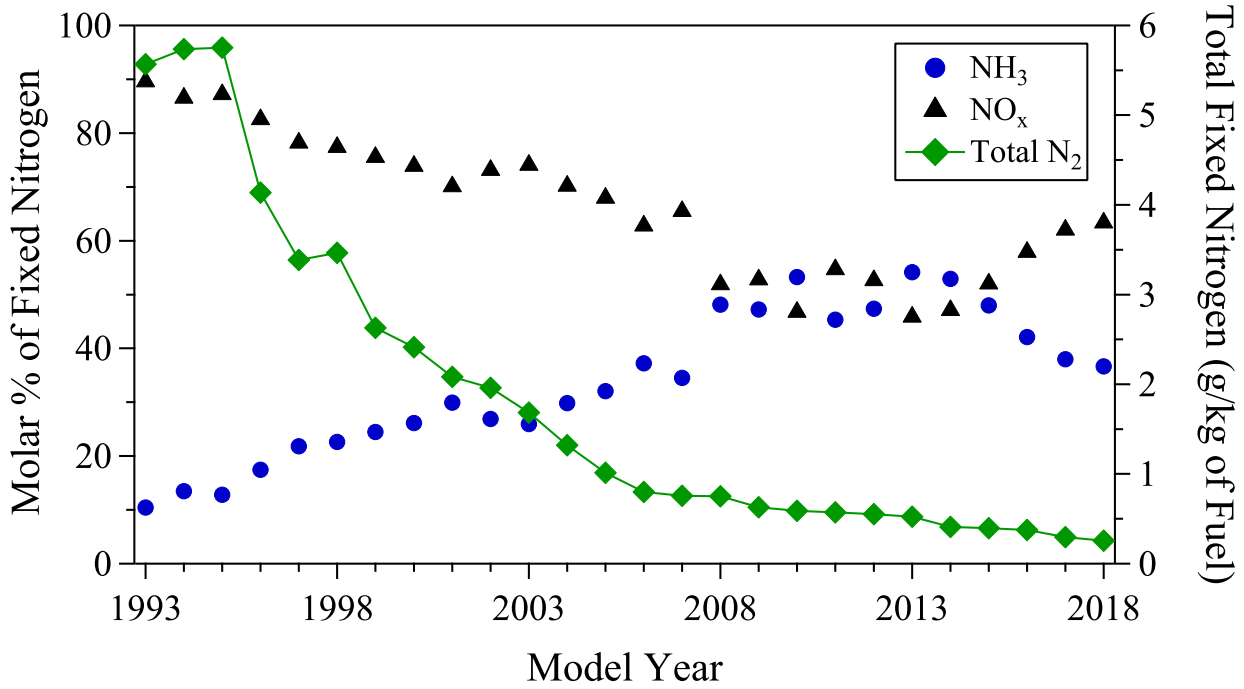

Figure 9. Total fixed nitrogen in g/kg of fuel (◆, right axis) with the molar percent composition distributed between the NH_3 (●, left axis) and NO_x (▲, left axis) component versus model year for non-diesel vehicles.

The history of NH_3 emission measurements at the Denver 6th Avenue site include measurements collected in a separate summer campaign of 2005 and winter CRC measurements in 2013, 2015 and 2017. Mean emissions were 0.45 ± 0.09, 0.44 ± 0.02, 0.42 ± 0.01 and 0.37 ± 0.008 gNH_3/kg of fuel respectively. This is an overall 18% reduction in emissions since 2005 or a 16% reduction

since measurements resumed in 2013. One interesting observation is that NH_3 mean emissions likely increased after 2005 despite the fact that newer model year vehicles were being introduced into the fleet with lower emissions due to the increasing longevity of the catalytic converters in the older model vehicles (see Figures 7 & 8) that continued to reduce NO to NH_3. Over this same period NO emissions in Denver have decreased by 51% (3.7 gNO/kg in the summer of 2005 to 1.8 gNO/kg in 2017). Further research is necessary to understand why NO emissions have decreased dramatically more during this twelve year period than NH_3 since they have a common origination point in engine out NO emissions. Fuel changes might be a contributing factor, as fuel sulfur levels have decreased significantly during this period, but laboratory research on the fuel effects of NH_3 emissions is contradictory, due in part to the small number of vehicles tested.[25, 34] Driving mode and catalyst age are two additional factors discussed in the literature that impact NH_3 emissions and might be involved.[26, 34] Also as previously mentioned NH_3 emissions are not regulated while NO emissions are and one can speculate that engine operating conditions that minimize tailpipe NO emissions will be emphasized by the manufacturer.

An equation for determining the instantaneous power of an on-road vehicle by Jimenez takes the form

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

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.[35] Derived from dynamometer studies, and 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. Using equation 4, VSP was calculated for all measurements in each of the five years' databases. This equation, in common with all dynamometer studies, does not include any load effects arising from road curvature. The emissions data were binned according to vehicle specific power, and graphed in Figure 10. Each of the specific power bins contains at least 125 measurements, except for the 25 VSP bin in 2005 which only contains 57 measurements, and the HC data have been offset adjusted for this comparison. The uncertainty bars included in the plot are standard errors of the mean calculated using the daily means (see Appendix E). The solid line in the bottom graph is the frequency count distribution of vehicles in the 2017 dataset sorted by specific power bin.

Within each vehicle specific power bin there have been significant year over year reductions in mean fuel specific emissions of all the species between the 1999 and 2017 datasets. The redesigned ramp effects can also be seen in the increase in the range of positive and negative VSP values observed. The increases are the result of the increased speeds and the potential for significant decelerations they afford when congestion on the road occurs ahead. In addition to the emissions reductions all of the species show a decreasing dependency on VSP where the emissions trend has slowly flattened out since the early campaigns. HC emissions still show increasing emissions with decelerations though in the Denver data that dependence seems to flatten out at the largest VSP bins. Keep in mind that the lack of an influence of VSP for CO and

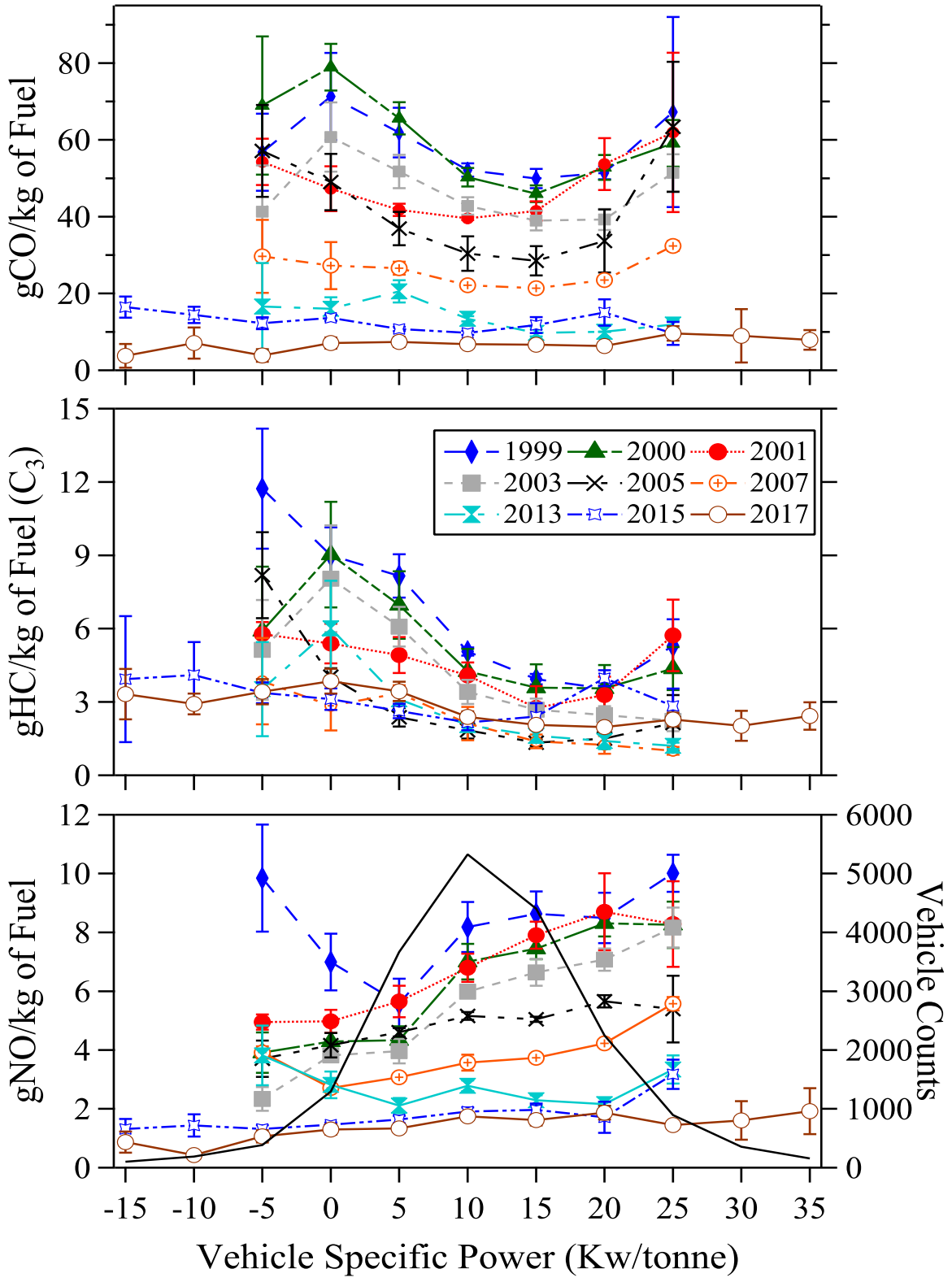

Figure 10. Vehicle emissions as a function of vehicle specific power for all of the Denver data sets. Uncertainties plotted are standard errors of the mean calculated using the daily samples. The solid line without markers in the bottom graph is the vehicle count profile for the 2017 data.

NO are for fuel specific emissions and likely is not the case for distance specific emissions as the fuel economy changes by a factor of 3 or more across the range of VSP's plotted.

Instrument noise was measured by looking at the slope of the negative portion of the log plots in the same manner as described in the Phoenix, Year 2 report.[36] Such plots were constructed for all of the measured species (not shown). 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 8.7, 2.8, 0.3, 0.02 and 0.2 for CO, HC, NO, NH_3 and NO_2 respectively. These values indicate standard deviations of 12.4 gCO/kg of fuel (0.1%), 4.0 gHC/kg of fuel (89 ppm), 0.46 gNO/kg of fuel (59 ppm), 0.03 gNH_3/kg of fuel (3 ppm) and 0.3 gNO_2/kg of fuel (14 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 of a hundred measurements reduce to 1.2 gCO/kg of fuel, 0.4 gHC/kg of fuel, 0.05 gNO/kg of fuel, 0.003 gNH_3/kg of fuel and 0.03 gNO_2/kg of fuel, respectively.

CONCLUSIONS

The University of Denver carried out five days of remote sensing study in the Denver, Colorado area in December of 2017 and January of 2018. Measurements were made on five weekdays, Friday December 15, Tuesday December 19, Wednesday December 20 2017, Tuesday January 9 and Thursday January 18 2018 on the interchange ramp from northbound I-25 to westbound US6. This is the same location previously used for measurements in the winter of 1999-2001, 2003, 2005, 2007, 2013 and 2015. A database was compiled containing 22,266 records for which the State of Colorado provided registration information. All of these records contained valid measurements for at least CO and CO_2, and most records contained valid measurements for the other species as well.

The 2017 mean CO, HC, NO, NH_3 and NO_2 emissions for the fleet measured in this study were 8.0 ± 0.2 g/kg of fuel (0.06%), 2.6 ± 0.2 g/kg of fuel (65 ppm), 1.77 ± 0.05 g/kg of fuel (125 ppm), 0.37 ± 0.01 g/kg of fuel (46 ppm) and 0.11 ± 0.02 g/kg of fuel (5 ppm) respectively. When compared with the previous measurements from 2015 there are decreases for mean CO (g/kg of fuel) (-37%), HC (-10%), NO (-10%), NH_3 (-12%) and NO_2 (-21%) and the differences are all statistically significant at the 95% confidence interval. The percent of emissions contributed by the highest emitting 1% of the fleet (the 99th percentile) increased for CO, NO, NH_3 and slightly decreased for HC and NO_2.

The average age of the Denver fleet at this location has remained constant at 9.2 years old (2009.2 average model year) since 2013. This is still an increase of almost 2 years relative to the age of the fleet at this location prior to the 2008 recession. Fleet mean emissions remain dominated by a few high emitting vehicles. For the 2017 data set the highest emitting 1% of the

measurements (99th percentile) are responsible for 47%, 29%, 26%, 17 % and 41% of the overall fleet CO, HC, NO, NH_3 and NO_2 emissions, respectively.

The history of NH_3 emission measurements at the Denver 6th Avenue site include measurements collected in a separate summer campaign of 2005 and winter CRC measurements in 2013, 2015 and 2017. Mean emissions were 0.45 ± 0.09, 0.44 ± 0.02, 0.42 ± 0.01 and 0.37 ± 0.008 gNH_3/kg of fuel respectively. This is an overall 18% reduction in emissions since 2005 or a 16% reduction since measurements resumed in 2013. The peak NH_3 emissions continue to extend into older models with the 2017 measurements suggesting the peak is around 19 year old vehicles but the increased uncertainty, due to fewer measurements in the older model year vehicles makes, an exact assignment difficult but illustrates the fact that catalytic converters in modern gasoline vehicles continue to show improved durability. The NH_3 fleet reduction rates continue to be smaller than observed for tailpipe NO emissions which at the Denver site have decreased 51% (3.7 gNO/kg in the summer of 2005 to 1.8 gNO/kg) over the same time period. Total fixed nitrogen emissions have been on a steep decline since the mid-nineties in the gasoline fleet and are continuing to show decreases in the newest model years in this data set as well. The percent of measured fixed nitrogen made up of NH_3 had been on the rise but in this latest Denver data set that rise appears to have leveled out soon after the introduction of Tier 2 vehicles and starting around the 2015 models it has declined. The start of this decline was also observed in the percent of fixed nitrogen which is NH_3 in the 2017 measurements in Tulsa, OK but there were not enough vehicle model years to establish the decline with any certainty. It is not known what if anything is behind this preference now for nitrogen oxidation (NO_x) at the tailpipe over reduced nitrogen (NH_3) in the newest vehicles but catalyst formulation is an important factor that can influence NH_3 production.

ACKNOWLEDGEMENTS

The successful outcome of this project would not be possible without the assistance of Kevin Wallace of the Colorado Department of Revenue, Rob Dawson of the Colorado Department of Public Health and Environment and Mrs. Annette Bishop for plate transcription. Comments from the various reviewers of this report were also invaluable and appreciated.

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. Our Nation's Air: Status and trends through 2015. U. S. Environmental Protection Agency. http://www.epa.gov/air/trendsreport/2016/.

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

5. Cooper, O. R.; Langford, A. O.; Parrish, D. D.; Fahey, D. W., Challenges of a lowered U.S. ozone standard. *Science* **2015,** 348, (6239), 1096-1097, DOI: 10.1126/science.aaa5748.

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. Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Lunden, M. M.; Kirchstetter, T. W.; Kean, A. J.; Strawa, A. W.; Stevenson, E. D.; Kendall, G. R., Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles. *Atmos. Environ.* **2008,** 42, 220-232, DOI: 10.1016/j.atmosenv.2007.09.049.

8. McDonald, B. C.; Dallmann, T. R.; Martin, E. W.; Harley, R. A., Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales. *J. Geophys. Res. Atmos.* **2012,** 117, (D18), 1-11, DOI: 10.1029/2012jd018304.

9. Pollack, I. B.; Ryerson, T. B.; Trainer, M.; Neuman, J. A.; Roberts, J. M.; Parrish, D. D., Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010. *Journal of Geophysical Research, [Atmospheres]* **2013,** 118, 1-19, DOI: 10.1002/jgrd.50472.

10. Hassler, B.; McDonald, B. C.; Frost, G. J.; Borbon, A.; Carslaw, D. C.; Civerolo, K.; Granier, C.; Monks, P. S.; Monks, S.; Parrish, D. D.; Pollack, I. B.; Rosenlof, K. H.; Ryerson, T. B.; von Schneidemesser, E.; Trainer, M. C. G. L., Analysis of long-term observations of NO_x and CO in megacities and application to constraining emissions inventories. *Geophys. Res. Lett.* **2016,** 43, (18), 9920-9930, DOI: 10.1002/2016gl069894.

11. Nowak, J. B.; Neuman, J. A.; Bahreini, R.; Middlebrook, A. M.; Holloway, J. S.; McKeen, S.; Parrish, D. D.; Ryerson, T. B.; Trainer, M., Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation. *Geophys. Res. Lett.* **2012,** 39, L07804, DOI: 10.1029/2012GL051197.

12. McDonald, B. C.; Goldstein, A. H.; Harley, R. A., Long-Term Trends in California Mobile Source Emissions and Ambient Concentrations of Black Carbon and Organic Aerosol. *Environ. Sci. Technol.* **2015,** 49, (8), 5178-5188, DOI: 10.1021/es505912b.

13. Dallmann, T. R.; Harley, R. A., Evaluation of mobile source emission trends in the United States. *Journal of Geophysical Research, [Atmospheres]* **2010,** 115, D14305-D14312, DOI: 10.1029/2010JD013862.

14. Bishop, G. A.; Stedman, D. H., Measuring the emissions of passing cars. *Acc. Chem. Res.* **1996,** 29, 489-495, DOI: 10.1021/ar950240x.

15. 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.

16. 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.

17. 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.

18. 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.

19. 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.

20. 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 sensing 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;

21. Pokharel, S. S.; Stedman, D. H.; Bishop, G. A. RSD Versus IM240 Fleet Average Correlations, In *Proceedings of the 10th CRC On-Road Vehicle Emissions Workshop*, San Diego, 2000;

22. 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;

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

24. Kim, E.; Turkiewicz, K.; Zulawnick, S. A.; Magliano, K. L., Sources of fine particles in the south coast area, California. *Atmos. Environ.* **2010,** 44, 3095-3100, DOI: 10.1016/j.atmosenv.2010.05.037.

25. Durbin, T. D.; Wilson, R. D.; Norbeck, J. M.; Miller, J. W.; Huai, T.; Rhee, S. H., Estimates of the emission rates of ammonia from light-duty vehicles using standard chassis dynamometer test cycles. *Atmos. Environ.* **2002,** 36, 1475-1482.

26. 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+.

27. Kean, A. J.; Littlejohn, D.; Ban-Weiss, G. A.; Harley, R. A.; Kirchstetter, T. W.; Lunden, M. M., Trends in on-road vehicle emissions of ammonia. *Atmos. Environ.* **2009,** 43, (8), 1565-1570, DOI: 10.1016/j.atmosenv.2008.09.085.

28. Baum, M. M.; Kiyomiya, E. S.; Kumar, S.; Lappas, A. M.; Kapinus, V. A.; Lord III, H. C., Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. Direct on-road ammonia measurements. *Environ. Sci. Technol.* **2001,** 35, 3735-3741, DOI: 10.1021/es002046y.

29. 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.

30. Kean, A. J.; Harley, R. A.; Littlejohn, D.; Kendall, G. R., On-road measurement of ammonia and other motor vehicle exhaust emissions. *Environ. Sci. Technol.* **2000,** 34, 3535-3539, DOI: 10.1021/es991451q.

31. Bishop, G. A.; Peddle, A. M.; Stedman, D. H.; Zhan, T., On-road emission measurements of reactive nitrogen compounds from three California cities. *Environ. Sci. Technol.* **2010,** 44, 3616-3620, DOI: 10.1021/es903722p.

32. Bishop, G. A.; Schuchmann, B. G.; Stedman, D. H.; Lawson, D. R., Multispecies remote sensing measurements of vehicle emissions on Sherman Way in Van Nuys, California. *J. Air Waste Manage. Assoc.* **2012,** 62, (10), 1127-1133, DOI: 10.1080/10962247.2012.699015.

33. Bishop, G. A.; Stedman, D. H., Reactive Nitrogen Species Emission Trends in Three Light-/Medium-Duty United States Fleets. *Environ. Sci. Technol.* **2015,** 49, (18), 11234-11240, DOI: 10.1021/acs.est.5b02392.

34. Durbin, T. D.; Miller, J. W.; Pisano, J. T.; Younglove, T.; Sauer, C. G.; Rhee, S. H.; Huai, T., *The effect of fuel sulfur on NH_3 and other emissions from 2000-2001 model year vehicles*; Coordinating Research Council, Inc: Alpharetta, 2003.

35. 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 *Ninth Coordinating Research Council On-road Vehicle Emissions Workshop*, Coordinating Research Council, Inc.: San Diego, CA, 1999; Vol. 2, pp 7-45 - 7-57.

36. 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 exhaust. The restart number appears in the database.

2) Vehicle which drives completely through during the 0.4 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 heavy-duty diesel trucks, bicycles.

2) Too much 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) Too much 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) Too much 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 NH_3/CO_2 slope, equivalent to $\pm$50ppm.

9) Reported NH_3 < -80ppm or > 7000ppm. NH3 "invalid".

10) Excessive error on NO_2/CO_2 slope, equivalent to $\pm$20% for NO_2 > 200ppm, 40ppm for NO_2 < 200ppm

11) Reported NO_2 < -500ppm or > 7000ppm. NO_2 "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 Denver_17.dbf database.

The Denver_17.dbf is a Microsoft FoxPro database file, and can be opened by any version of MS FoxPro. The file can be read by a number of other database management programs as well, and is available on our website at www.feat.biochem.du.edu. The following is an explanation of the data fields found in this database:

License	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.
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”.
CO2_max	Reports the highest absolute concentration of carbon dioxide measured by the remote sensor over an 8 cm path; indicates plume strength.
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.
Veh_type	Colorado plate type classification.
Vin	Vehicle identification number.

Year	Model year.
Make	Manufacturer of the vehicle.
Model	Oklahoma model designation.
Body	Oklahoma designated body style
Legal_City	Registrant's mailing city.
Legal_Zip5	Registrant's zip code.
County	Colorado county number where vehicle is registered.
Exp_date	Date that current vehicle registration expires.
Im_flag	I/M flag: 'Y', 'N', 'X'.
Im_status	I/M status: E – exempt, P, C
Fuel	Fuel type: 'G' gasoline, 'D' diesel, 'Z' hybrid.
Im_test	Previous I/M test date.
IM_next	Due date for next I/M inspection.
CO_gkg	Grams of CO per kilogram of fuel using 860 gC/kg of fuel.
HC_gkg	Grams of HC per kilogram of fuel using 860 gC/kg of fuel and the molecular weight of propane which is our calibration gas.
NO_gkg	Grams of NO per kilogram of fuel using 860 gC/kg of fuel.
NH3_gkg	Grams of NH_3 per kilogram of fuel using 860 gC/kg of fuel.
NO2_gkg	Grams of NO_2 per kilogram of fuel using 860 gC/kg of fuel.
NOx_gkg	Grams of NO_x per kilogram of fuel using 860 gC/kg of fuel.
HC_offset	Percent hydrocarbon concentration after offset adjustment.
Hcgkg_off	Grams of HC per kilogram of fuel using 860 gC/kg of fuel and using the HC_offset value for this calculation.
VSP	Vehicles specific power calculated using the equation provided in the report. Kw/metric tonne

APPENDIX C: Temperature and Humidity Data

Denver 1999 Temperature Data							
1/14 Time	1/14 °F	1/15 Time	1/15 °F	1/18 Time	1/18 °F	2/1 Time	2/1 °F
14:16	57	9:25	47	8:30	40	8:00	26
15:50	56	9:45	48	9:30	45	8:33	30
		10:24	58	10:20	50	9:11	33
		11:08	58	10:50	55	9:29	33
		11:25	58	11:30	50	10:00	40
				12:00	46	10;25	46
						11:07	54
						11:56	55

Denver 1999/2000 Temperature and Humidity Data											
12/30 Time	12/30 °F	12/30 %RH	1/11 Time	1/11 °F	1/11 %RH	1/13 Time	1/13 °F	1/13 %RH	1/14 Time	1/14 °F	1/14 %RH
11:23	48	38	9:33	54	38	8:43	35	61	7:53	32	69
12:03	51	32	10:3	54	32	9:43	35	61	8:42	35	65
13:06	54	29	11:5	55	28	10:4	35	62	9:53	43	50
14:02	55	28	12:3	52	30	11:0	36	61	11:1	51	36
15:14	64	26	13:3	49	37	12:0	39	59			
16:00	57	26	14:3	50	39	13:0	41	56			
16:54	52	27	15:5	49	41	14:1	42	52			
			16:0	48	41	15:0	45	48			

Denver 2001 Temperature and Humidity Data								
1/5 Time	1/5 °F	1/5 %RH	1/6 Time	1/6 °F	1/6 %RH	1/8 Time	1/8 °F	1/8 %RH
7:42	33	60	7:12	41	44	7:50	27	38
8:57	37	59	8:13	42	46	10:18	43	28
9:45	43	51	10:12	50	38	11:19	46	24
11:49	59	28	11:30	51	38	12:27	51	21
13:05	64	24	12:30	52	37	13:27	53	<20
14:10	66	20	13:33	61	21	14:27	54	<20
			14:43	61	<20	15:27	53	<20
			15:47	61	25			

Denver 2002/2003 Temperature and Humidity Data											
12/31 Time	12/31 °F	12/31 %RH	1/7 Time	1/7 °F	1/7 %RH	1/8 Time	1/8 °F	1/8 %RH	1/31 Time	1/31 °F	1/31 %RH
9:45	34	31	9:05	43	38	9:27	48	32			
10:45	39	30	10:09	48	36	10:40	57	26	10:15	55	37
11:19	43	29	11:09	54	30	11:16	61	25	11:15	64	31
11:38	41	29	12:12	59	25	12:16	68	17	12:03	63	26
12:38	50	26	12:39	61	21	13:17	70	14	12:15	64	24
13:16	50	26	13:09	64	18	14:19	73	11	13:15	64	24
14:16	52	26	14:09	66	15	15:25	68	15			
15:16	52	26	15:09	68	15	15:50	66	15			
16:00	48	27	16:02	66	15						

Denver 2005 Temperature and Humidity Data								
1/8 Time	1/8 °F	1/8 %RH	1/10 Time	1/10 °F	1/10 %RH	1/11 Time	1/11 °F	1/11 %RH
12:06	52	34	8:44	41	51	8:00	37	77
13:22	54	33	9:11	36	65	9:01	39	77
14:06	55	33	10:11	37	64	10:03	37	76
15:06	54	34	11:11	45	57	11:01	41	70
16:06	50	36	12:11	45	53	12:25	46	56
			13:11	45	57	13:19	54	56
			14:16	48	50	14:19	39	72
			15:11	46	54	15:19	39	71
			16:12	45	57	16:19	39	74
			16:46	45	60	16:45	37	75

Denver 2007 Temperature and Humidity Data								
1/10 Time	1/10 °F	1/10 %RH	1/25 Time	1/25 °F	1/25 %RH	2/27 Time	2/27 °F	2/27 %RH
8:56	45	26	8:46	36	48	7:56	34	52
9:45	48	23	9:45	39	45	8:55	39	43
10:46	52	26	10:45	41	49	10:55	45	35
11:45	54	24	11:45	45	42	11:45	46	37
12:58	55	23	12:48	46	44	12:48	46	34
13:46	61	19	13:46	46	37	13:55	50	32
14:45	63	12	14:52	50	32	14:45	46	50
15:45	63	11	15:45	50	32	15:45	46	50
16:46	59	10	16:45	46	37	16:45	45	51

Denver 2013 / 2014 Temperature and Humidity Data								
12/12 Time	12/12 °F	12/12 %RH	12/13 Time	12/13 °F	12/13 %RH	1/3 Time	1/3 °F	1/3 %RH
8:55	30	43	8:47	41	30	8:53	54	20
9:47	39	36	9:47	45	26	9:47	55	21
10:47	45	31	10:45	46	23	10:55	57	18
11:47	46	30	11:47	48	21	11:55	59	16
12:50	52	20	12:45	50	19	12:47	59	17
13:47	54	17	13:50	46	30	13:50	59	16
14:47	50	28	14:45	45	31			
15:47	46	33	15:45	43	34	15:50	59	16
16:47	45	34	16:50	37	46	16:50	55	18

Denver 2015/2016 Temperature and Humidity Data												
Time	12/9		12/10		1/13		1/27		1/28		1/29	
	°F	%RH	°F	%RH	°F	%RH	°F	%RH	°F	%RH	°F	%RH
8:53	53	26	50	24	35	48	38	46	37	50	45	37
9:53	57	22	54	19	42	41	43	40	44	41	47	31
10:53	58	22	54	22	44	41	50	32	47	37	49	28
11:53	58	23	57	21	49	31	48	34	51	29	51	24
12:53	59	19	59	20	50	29	49	33	54	24	52	22
13:53	63	17	61	15	48	34	49	35	56	22	54	18
14:53	61	19	65	15	51	28	50	36	56	24	55	16
15:53	58	23	60	19	47	36	49	35	55	28	54	17
16:53	57	23	56	22	43	45	44	45	53	28	48	27

Denver 2017/2018 Temperature and Humidity Data										
Time	12/15		12/19		12/20		1/9		1/18	
	°F	%RH	°F	%RH	°F	%RH	°F	%RH	°F	%RH
8:53	42	27	38	48	48	23	48	46	37	33
9:53	47	24	46	32	55	19	54	40	52	13
10:53	51	21	48	33	59	16	57	36	55	12
11:53	55	16	50	29	61	14	60	41	59	9
12:53	58	14	49	32	63	13	64	26	61	10
13:53	60	13	50	30	63	13	65	26	63	10
14:53	60	14	50	29	64	12	65	26	64	9
15:53	57	21	51	29	60	16	63	28	63	10
16:53	51	21	41	41	55	18	56	34	59	11

APPENDIX D: Methodology to Normalize Mean gHC/kg of fuel Emissions

The hydrocarbon channel on FEAT has the lowest signal to noise ratio of all the measurement channels in large part because the absorption signals are the smallest (millivolt levels). FEAT 3002 uses one detector for the target gas absorption and a second detector for the background IR intensity (reference). These channels are ratioed to each other to correct for changes in background IR intensities that are not the result of gas absorption. The detector responses are not perfectly twinned and for the low signal HC channel this lack of perfect intensity correction can result in small systematic artifacts, which can be a positive or negative offset of the emissions distribution, being introduced into the measurement. In addition the region of the infrared spectrum that is used for HC absorption measurements is overlapped by an absorption band for liquid water. Normally this is not an issue as fully warmed up vehicles emit little if any liquid water at the tailpipe. However, there are times when low temperatures and high dew points cause water vapor to condense at the tailpipe and create an additional absorption artifact in the measurements that are not related to HC emissions. In these cases the normalization value calculated will be larger because it includes an additional adjustment for the liquid water emissions.

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 and that their emissions distribution should have a median value very near zero, using the lowest of either of these values as the offset. The offset value is then added (for negative offsets) or subtracted from all of the hydrocarbon measurements adjusting the zero point of the emissions distribution. Since it is assumed that the newest vehicles are the lowest emitting this approximation will slightly over correct because the true offset will be a value somewhat less than the average of the cleanest model year and make.

As an example of the process the calculation is demonstrated using data collected in Chicago in 2014 and shown in Table D1. The Chicago 2014 measurement included a correction for both of the previously discussed issues as the first three days of measurements were with normal temperatures and low humidity while the last three days experienced the exact opposite. FEAT ratios are first reported as percent emissions and the normalization calculations are performed using these percent values. Below are the data tables used for estimating the HC normalization value for the 2014 Chicago measurements.

For the Monday through Wednesday time slot Honda's vehicles had the lowest average HC emissions with a mean %HC of 0.0013. In Table S2 the mode calculation has two values that are very close to each other 0.001 and 0.0015. It was decided to average those two values and the HC normalization value for the first time period used was 0.00125% which is approximately 0.5 gHC/kg of fuel.

For the Thursday through Saturday time period Honda vehicles again had the lowest HC emission. The average of 2009 – 2014 Honda vehicles is 0.003% which is the same as the mode shown in Table S2. This is approximately 1.25 gHC/kg of fuel.

2014 Chicago Mode Calculations
For model year 2009 and newer vehicles

Table D1. HC Normalization Mode Calculation.

Monday – Wednesday		Thursday - Saturday	
%HC	Counts	%HC	Counts
-0.0015	129	-0.0015	73
-0.001	147	-0.001	59
-0.0005	138	-0.0005	75
0	125	0	67
0.0005	126	0.0005	79
0.001	152	0.001	69
0.0015	155	0.0015	75
0.002	143	0.002	85
0.0025	104	0.0025	51
0.003	131	0.003	94
0.0035	129	0.0035	68
0.004	120	0.004	77
0.0045	115	0.0045	80
0.005	124	0.005	88

This method will successfully normalize the fleet HC means but may over or under correct smaller sub-fleets.

APPENDIX E: How standard errors of the mean for our reported uncertainties are estimated

Vehicle emissions from US vehicle fleets are not normally distributed, thus 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, result in uncertainties that are unrealistically too small due to the large number of samples. The Central Limit Theorem in general indicates that the means of multiple samples, randomly collected, from a larger parent population will be normally distributed, irrespective of the parent populations underlying distribution. Since multiple days of emission measurements are almost always collected at each site, these daily measurements are used as our randomly collected multiple samples from the larger population and the reported uncertainties are based on their distribution. Next the means, standard deviations and standard errors of the mean for this group of daily measurements is calculated. Next an error percentage is calculated from the ratio of the standard error of the mean for the daily measurements divided by the daily measurement mean. The fleet weighted means for all of the emission measurements are reported and the standard error of the fleet mean is calculated by multiplying the error percentage obtained previously against the fleet mean. An example of this process is provided below for the 2017 Denver gCO/kg of fuel and gNO/kg of fuel measurements. While this example is for a fleet mean this technique is also used when reporting uncertainties for other statistics such as individual model years, specific fuel or technology types, and VSP. For example each model year will have its daily means averaged and then its standard error of the mean for the daily average computed and that percent uncertainty (Daily STD Error MY/Daily MY average) will be applied to that entire model year's mean emissions.

Denver 2017 Date	Mean gCO/kg of fuel	Counts	Mean gNO/kg of fuel	Counts
12/15/17	8.72	4300	1.80	4299
12/19/17	7.48	5430	1.92	5429
12/20/17	8.37	5027	1.77	5027
1/9/17	7.48	4910	1.60	4908
1/18/17	8.17	2599	1.75	2598
Average for Daily Mean	8.04		1.77	
Standard Error for the daily means	0.25		0.05	
Weighted Fleet Mean	8.00		1.77	
Standard Error calculated for the fleet means	0.24		0.05	
As reported	8.0 ± 0.2		1.77 ± 0.05	

APPENDIX F: Field Calibration Record.

1999				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
1/15	8:30	1.54	1.73	1.53
1/15	10:15	1.31	1.50	1.35
1/15	12:30	0.96	1.1	0.78
1/16	8:00	1.27	1.3	0.72
1/18	7:15	1.56	1.6	1.9
2/1	7:45	1.76	2.0	1.66
2/1	12:15	1.20	1.32	1.25

1999 / 2000				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
12/30	11:20	1.27	1.2	1.67
1/11	9:30	1.14	1.12	1.25
1/13	8:30	1.76	1.74	1.64
1/13	10:55	1.23	1.09	1.34
1/14	7:50	2.45	2.5	3.1
1/14	10:00	1.40	1.40	1.61

2001				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
1/5	7:30	1.96	2.2	3.1
1/5	11:45	1.13	1.05	1.32
1/6	7:00	1.57	1.42	1.84
1/6	11:30	1.41	1.35	1.66
1/8	7:05	1.67	1.6	2.32
1/8	11:30	1.18	1.1	1.6

2002 / 2003				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
12/31	11:14	1.33	1.44	2.22
12/31	13:09	1.258	1.204	1.733
1/7	10:00	1.342	1.204	1.443
1/7	12:35	0.974	0.939	1.084
1/7	15:12	1.157	1.158	1.277
1/8	9:15	1.237	1.191	1.834
1/8	11:10	0.97	1.096	1.493
1/31	10:00	1.124	1.084	1.567
1/31	12:00	0.912	0.932	1.257

2005				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
1/8	8:30	2.6	1.8	4.45
1/8	11:30	1.14	0.96	1.56
1/10	8:30	2.03	1.17	1.43
1/10	12:30	1.44	1.17	1.43
1/11	7:50	1.72	1.45	3.13
1/11	11:10	1.47	1.27	2.65

2007				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
1/10	9:00	1.67	1.51	2.27
1/10	10:10	1.49	1.69	1.76
1/10	12:40	1.16	1.10	1.26
1/25	8:25	2.14	1.87	2.27
1/25	9:20	1.45	1.26	1.35
1/25	12:15	1.35	1.25	1.34
2/27	8:30	1.55	1.47	1.69
2/27	9:35	1.37	1.34	1.35
2/27	11:25	1.19	1.18	1.19

2013 / 2014 Denver						
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
12/12	9:15	1.83	1.85	2.12	1.14	1.06
12/12	11:00	1.49	1.55	1.76	1.11	0.83
12/12	13:00	1.41	1.47	1.68	1.14	0.66
12/13	8:45	2.67	2.78	3.06	1.56	1.37
12/13	9:45	2.07	2.16	2.28	1.19	0.93
12/13	11:00	1.71	1.81	1.88	1.19	0.97
12/13	13:00	1.38	1.47	1.57	1.21	0.90
1/3	8:45	1.73	1.83	1.87	1.35	1.06
1/3	10:10	1.18	1.23	1.30	1.35	0.69

2015 / 2016 Denver						
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
12/9	11:00	1.32	1.54	1.46	1.10	1.25
12/9	13:10	1.27	1.47	1.49	1.12	1.19
12/10	9:50	1.28	1.44	1.08	1.03	1.28
12/10	12:20	1.14	1.29	1	1.06	1.02
1/13	10:15	1.43	1.63	1.70	1.08	1.67
1/13	12:30	1.27	1.47	1.56	1.13	1.25
1/27	9:40	1.72	1.85	1.93	1.06	2.33
1/27	11:45	1.43	1.57	1.60	1.09	1.33
1/27	13:45	1.29	1.45	1.44	1.09	1.27
1/28	9:30	1.72	1.96	1.81	1.07	1.99
1/28	11:50	1.39	1.52	1.56	1.06	1.33
1/28	13:45	1.24	1.43	1.35	0.89	1.18
1/29	9:22	1.48	1.64	1.51	1.09	1.50
1/29	11:41	1.28	1.43	1.34	1.07	1.23

2017 / 2018 Denver						
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
12/15	9:50	1.48	1.62	1.55	1.12	1.33
12/15	11:30	1.33	1.47	1.45	1.11	1.41
12/15	13:30	1.21	1.35	1.37	1.14	1.22
12/19	9:20	1.94	2.10	1.96	1.07	1.73
12/19	10:50	1.72	1.87	1.89	1.11	1.77
12/19	12:30	1.50	1.60	1.65	1.12	1.53
12/20	9:00	1.98	2.20	1.99	1.12	1.82
12/20	10:20	1.33	1.51	1.46	1.13	1.42
12/20	12:00	1.15	1.31	1.28	1.14	1.06
1/9	9:25	2.08	2.40	2.16	1.08	2.26
1/9	11:00	1.35	1.60	1.47	1.09	1.33
1/9	12:40	1.26	1.40	1.37	1.09	1.14
1/18	10:15	1.52	1.66	1.60	1.11	1.43
1/18	11:45	1.29	1.44	1.39	1.12	1.30