Cross road and mobile tunable infrared laser measurements of nitrous oxide emissions from motor vehicles

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Importance of this paper: Novel tunable infrared laser techniques have been used to quantify N_2O/CO_2 emission factors from large numbers of recent on-road US motor vehicles. These data show that N_2O emissions from vehicles equipped with three-way catalysts are significantly lower than some previous estimates, although significant uncertainty remains in the fleet average emissions.

Abstract

Context Abstract: Nitrous oxide (NO_2) is a potent greenhouse gas whose atmospheric budget is poorly constrained. One known atmospheric source is the formation of N_2O on three-way motor vehicle catalytic converters followed by emission with the exhaust. Previous estimates of the magnitude of this N_2O source have varied widely. Two methods employing tunable infrared lasers to measure N_2O/CO_2 ratios from a large number of on-road motor vehicles have been developed. Both methods add support to lower estimates of N_2O emissions from the US motor vehicle fleet, although significant uncertainty remains.

Main Abstract: Two tunable infrared laser differential absorption spectroscopy (TILDAS) techniques have been used to measure the N_2O emission levels of on-road motor vehicle exhausts. Cross road, open path laser measurements were used to assess N_2O emissions from 1361 California catalyst equipped vehicles in November, 1996 yielding an emission ratio of $(8.8 \pm 2.8) \times 10^{-5}$ N_2O/CO_2. A van mounted TILDAS sampling system making on-road N_2O measurements in mixed traffic in June, 1998 in Manchester, New Hampshire yielded a mean N_2O/CO_2 ratio of $(12.8 \pm 0.3) \times 10^{-5}$, based on correlated N_2O and CO_2 concentration peaks attributed to motor vehicle exhaust plumes. The correlation of N_2O emissions with vehicle type, model year and NO emissions are presented for the California data set. It is found that the N_2O emission distribution is highly skewed, with more than 50% of the emissions being contributed by 10% of the vehicles. Comparison of our results with those from four European tunnel studies reveals a wide range of derived N_2O emission indices, with the most recent studies (including this study) finding lower values. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Nitrous oxide (N$_2$O) is both a very efficient and significant greenhouse gas and the major precursor for nitrogen oxides (NO$_x$) in the stratosphere. Significant uncertainties remain in the atmospheric budget of N$_2$O, particularly in identifying sources to balance its stratospheric photolysis and photochemical sinks (Cicerone, 1989; Khalil and Rasmussen, 1992; NRC, 1993; IPCC, 1996). Most atmospheric N$_2$O is believed to be produced by microbial action in soil, fresh water and marine environments. The growing atmospheric burden of N$_2$O is most likely due to the intensification of agriculture, which deposits increased burdens of both synthetic and organic fixed nitrogen into the biosphere (Kroeze et al., 1999).

Motor vehicle exhaust emissions are a second, non-agricultural, anthropogenic source of N$_2$O which is suspected to be increasing steadily. Nitrous oxide is known to be produced as a byproduct of nitric oxide (NO) reduction and carbon monoxide/unburned hydrocarbon (CO/HC) oxidation on noble metal three-way catalysts utilized to reduce pollutants in motor vehicle exhaust emissions (Cant et al., 1998). Attempts to quantify fleet emissions of N$_2$O from motor vehicle exhausts have faced difficulty because N$_2$O emissions are dependent on driving cycle variables, catalyst composition, catalyst age, catalyst exposure to variable levels of sulfur compounds and other poisons in the exhaust, and to the fraction of the fleet equipped with catalytic converters. Thus, measurements on small numbers of selected vehicles may not represent fleet averages (e.g., Dasch, 1992), and fleet averages obtained from tunnel studies have yielded disparate results (Berges et al., 1993; Sjödin et al., 1995, 1998; Becker et al., 1999, 2000).

Atmospheric N$_2$O can be monitored with great accuracy using tunable infrared laser differential absorption spectroscopy (TILDAS). TILDAS methods, currently utilizing lead salt diode lasers, are routinely used to map stratospheric N$_2$O distributions (Poldoske and Lowenstein, 1993; Webster et al., 1994) and to perform micrometeorological measurement of N$_2$O fluxes from agricultural biomass using eddy correlation techniques (Zahniser et al., 1995; Hargreaves et al., 1996). This technique has also been used to monitor N$_2$O levels in directly sampled automotive exhaust (Jobson et al., 1994).

We report on the use of two different TILDAS techniques to better quantify the atmospheric emission of N$_2$O from large numbers of on-road motor vehicles. Cross road (remote sensing) measurements with a laser instrument have yielded emission values for over 1300 identified vehicles. These measurements have enough sensitivity, accuracy, and vehicle specificity to provide emissions distributions as well as averages, and to allow data breakdowns by vehicle class. A second type of

measurement utilized point sampling into a closed multipasss cell on a mobile platform, providing statistics on N$_2$O emissions across an urban area, under various driving conditions. Both of these techniques can be used to derive emissions statistics representative of real-world conditions.

2. Experimental

Two different measurement techniques are employed in the work reported here, both using TILDAS instruments. The first technique is to use open path absorption of a laser beam directed through the exhaust plume of passing vehicles, combined with vehicle identification. This first technique gives specific information on emissions from individual vehicles under well-characterized driving conditions. The second technique is to mount the TILDAS instrument in a mobile lab and drive in traffic, extractively sampling airborne exhaust of other vehicles into a closed-path absorption cell. This second technique gives rapid wide area statistics on emissions from aggregations of vehicles, without confinement in a tunnel environment. Both techniques take advantage of the fast time response and high sensitivity of laser spectroscopic detection.

The two different techniques are complementary. The cross road method links measurements to individual cars, so detailed relations can be developed between emissions and vehicle categories and operating conditions. For example, sets of sampled vehicles can be broken down by categories of model year, catalyst type, and engine power demand. Examples of such results are presented below. Extractive sampling with the mobile instrument is more sensitive than the open path measurements, since it works at lower pressure where the absorption lines are narrow, and the absorption path lengths can be 100 m or more. Although it is difficult to assign measurements to specific vehicles using mobile extractive measurements, the aggregate emissions of a real-world mix of vehicles under a wide range of operating conditions is readily accessible.

2.1. Cross road measurement technique

Cross road measurement of emissions from motor vehicles (often described as ''remote sensing'') is accomplished by sending a sensing beam of light across the road, through the exhaust plumes of passing vehicles, and then analyzing the spectral absorption produced by the exhaust gases. Non-dispersive infrared (NDIR) instruments to measure carbon monoxide (CO) and hydrocarbon (HC) emissions were pioneered by Bishop et al. (1989). Recently, tunable lasers have been applied to cross road emission measurements (Nelson et al., 1998, 1999; Jimenez, 1999; Jimenez et al., 1999). Laser

instruments offer significant increases in sensitivity (of up to 100 times for some molecules) compared to NDIR instruments, giving sensitivities within the range of new low-emission vehicles (e.g., approximately 5 ppmv of the exhaust for NO with our system). Laser systems also offer greater operational range (more than 85 m in our systems) than NDIR instruments. The high sensitivity of laser spectroscopic measurements is especially important for the case of N_2O, where exhaust concentrations are often quite low.

We briefly review the laser instrument for cross road measurements which was developed at Aerodyne Research with more detail given elsewhere (Nelson et al., 1998, 1999; Jimenez, 1999). This instrument has two infrared diode lasers mounted in a liquid nitrogen dewar. The light from the two lasers is combined into a single spatially overlapped diagnostic beam, which is sent across the road to a retroreflector, and back to a telescope and detector at the instrument. The signal for the two lasers is separated by time multiplexing the lasers, at approximately 2 KHz. Each laser is tuned across individual absorption lines, and the column density of the absorbing species is obtained from a non-linear fit to the absorption vs frequency data. The ultimate sensitivity under ideal conditions for trace species with this instrument is approximately 3 ppmv at the tailpipe in $\sim$100 ms. Each laser nominally measures one chemical species, but when close spectral coincidences allow, two species can be measured with a single diode. One of the measured species is always CO_2, as a reference which allows computation of the emission rate of the minor species without knowledge of the exhaust plume location or extent of dilution. The emission ratio is formed from the trace species concentration (above background) and the CO_2 concentration (above background). The background levels are those measured immediately before the passing vehicle interrupts the laser beam. The fast time response of the instrument, 10 ms per independent measurement, allows multiple samples of each plume event. The assignment of an emission ratio for each vehicle is based on a linear regression of the set of independent samples for each plume.

The N_2O emissions of more than 1300 automobiles and light-duty trucks were measured during a experimental campaign in the Los Angeles area in California in November 1996 using the Aerodyne TILDAS instrument. The primary objective of this experiment was the measurement of NO/CO_2 emission indices, with one laser dedicated to CO_2 column density and the other to NO column density. We obtained N_2O column densities with the CO_2 laser by choosing a spectral region with strong, non-overlapping N_2O and CO_2 transitions near 2243 cm^{-1}. The N_2O measurement did not have the best possible spectral selection for that gas, so the sensitivity for N_2O ($\sim$8 ppm in the exhaust, or emission ratio $\sim 6 \times 10^{-5}$) was somewhat higher than for NO ($\sim$5 ppm).

The measurements were conducted with a suite of instruments set up beside a single lane roadway (with 4% grade) leading to an industrial parking lot. In addition to the TILDAS instrument, there were laser devices for measuring vehicle speed and acceleration. We determined if a given vehicle was equipped with a three-way catalyst by decoding the vehicle identification numbers (VINs) provided by the California Department of Motor Vehicles, based on video recorded vehicle license plates. A commercial NDIR cross road sensing system built and operated by Hughes provided information on CO and HC emission ratios for each vehicle (Jack et al., 1995).

2.2. Mobile measurement technique

The mobile measurements were performed as part of a program to characterize urban emissions of a variety of trace gases. It was not a focus of that program to specifically measure N_2O emissions of motor vehicles, however such data could be obtained. We also collected data that yields emission ratios for NO, NO_2, CH_4 and CO. We conducted several measurement campaigns in Manchester, NH, between November 1997 and June 1998. The goals for those campaigns were to develop instrumentation and methodologies, both in terms of measurement protocols and analysis strategies, and to determine the fine scale spatial distributions of trace gases emitted in urban environments (Shorter et al., 1998). Manchester (population $\sim$100 000) was selected as a test-site for several reasons, including its compact size, circumferential highway system, and proximity to Boston while being a distinct urban area. During the June 1998 campaign, (some results of which are discussed here) we focused on measuring greenhouse gases (CO_2, N_2O, CH_4), as well as CO and particulates. In August 1998 and May 1999 we measured photochemical pollution related gases; NO, NO_2, O_3, as well as CO_2 and particulates.

The mobile measurements were conducted with a suite of fast response ($\sim$1 data point/s) trace gas (N_2O, CH_4, CO, CO_2) instruments mounted in a step van. We measured N_2O, CH_4 and CO with the TILDAS instrument described below. CO_2 was measured by a LICOR NDIR instrument with 1 s response time and 1 ppm sensitivity. Calibration gas was used to periodically check the CO_2 instrument performance. A mobile GPS allowed us to tie concentration records to location (accuracy $\sim$0.3 m in 1 s), as well as to derive velocity, acceleration and roadway slope. We conducted measurements while traveling at normal roadway speeds, sampling from a common port at a height of 2 m. Fast response instruments allowed us to sample concentration fluctuations at small spatial scales, and to identify and isolate sharp spikes in concentrations. Mobile data was collected in a variety of conditions and locations,

including different roadway types and speeds, roadway slopes, and degree of congestion. We could prevent data contamination from our own vehicle by setting a minimum speed sampling data cut, or by doing a more sophisticated comparison to the average ground wind speed.

At the heart of the mobile instrument suite is a two-channel TILDAS instrument developed at Aerodyne Research (Zahniser et al., 1995; Nelson et al., 1998). This instrument is similar in some respects to the cross road instrument, starting with the two infrared diode lasers mounted in a single liquid nitrogen dewar. The lasers are scanned across distinct resolved absorption lines, including background to either side of the line, at a rate of 3 KHz. The absorption features are fit in real time using a nonlinear least squares algorithm, HITRAN (Rothman et al., 1992) tabulated line parameters and full Voigt line shapes. We record absolute concentrations of at least two gases, and sometimes a third or fourth when close spectral coincidences allow. In this instrument, the light from the lasers is directed along separate paths through a long multipass (150 m, 5 l) low pressure absorption cell. The instrument sensitivity generally is approximately 1 ppbv at a data rate of 1/s, and the gas flow replacement rate is equal to the data rate. During the June 1998 campaign we used this instrument to measure N_2O and CO (at ~2200 cm^{-1}) with one laser and CH_4 (at ~3000 cm^{-1}) with another.

3. Results

We present in this section the results from a cross road emission measurement experiment in California in 1996, and a mobile emission measurement experiment in New Hampshire in 1998. We generally report data as a molar emission ratio, ER $= \Delta N_2O/\Delta CO_2$ in the vehicle exhaust, since that is a more basic measured quantity. The emission ratio can be converted to an extrapolated concentration as the gas leaves the tailpipe, assuming stoichiometric gasoline combustion, which can be estimated to good approximation by multiplying the emission ratio ($\Delta N_2O/\Delta CO_2$) by an assumed tailpipe CO_2 mixing ratio of 0.143. The cross road technique yields emission ratios for individual vehicles, while the mobile technique yields emission ratios for variable aggregations of vehicles, weighted by the total exhaust volume. For comparison to other studies, the results also can be given in terms of a emission factor per unit distance (e.g., emitted grams per kilometer), if the aggregate vehicle fuel use rate is known.

We obtain sufficient sensitivity and detail in our data to present varied statistical measures of the results. The emission ratio from a single measurement has an uncertainty due to the random noise limits on the measurement of both the CO_2 and the N_2O column

densities. This uncertainty depends on both the pollutant and CO_2 concentrations in the exhaust, and on the strength of the absorption in a particular plume, which in turn depends on vehicle power demand, vehicle speed, and wake dispersion pattern (Nelson et al., 1998; Jimenez, 1999). The set of emission ratios for a substantial number of vehicles yields a value for the mean emission ratio with a low statistical uncertainty. Other types of uncertainty in the mean, such as systematic bias or instrument drift, must be estimated. The emissions from vehicles have a real variability which is captured by the distribution of measured values. The width of the distribution is greater than the measurement uncertainty (noise). Other statistical measures of the distribution may be applied, such as skewness or fits to standard forms of probability distributions.

3.1. Results of cross road measurements

We obtained a total of 1361 valid N_2O emissions measurements with the cross road remote sensor in California. The set of vehicles measured included cars and light trucks, 99% of which had catalytic converters. There were no heavy-duty trucks among the measured vehicles. We estimate that few if any vehicles in cold start condition were sampled due to the minimum distance traveled before the measurement location (1.2 km) and the location in an industrial area away from residences. The average vehicle speed was 13.9 ± 2.6 m/s and the average acceleration was 0.2 ± 0.5 m/s^2. There was an additional effective acceleration of 0.4 m/s^2 due to the 4% roadway grade at the site. Vehicle specific power (VSP), or power per unit mass, is a normalized measure of power demand which can be calculated for each vehicle, and which has been shown to influence emissions of CO, HC, and NO (Jimenez et al., 1999; Jimenez 1999). The average VSP at this site was 10.7 ± 7.7 kW/Metric Ton, which can be compared to the maximum instantaneous level on the federal test procedure (FTP) of 25 kW/Ton and maximum power ratings for new vehicles in the range 50–110 kW/Ton.

We present the distribution and statistical description of the set of measured N_2O emissions, followed by a breakdown of the data according to factors influencing the emissions. The extrapolated tailpipe N_2O concentrations have been corrected for the CO and HC concentration, and are given in terms of the full mix of exhaust gases including H_2O, and not the concentration in dry exhaust. The N_2O concentrations in dry exhaust would be about 14% larger than the values presented here. The data reported here has been corrected for a small systematic bias by using several consistency tests. This bias appeared due to a small optical interference fringe in the CO_2/N_2O spectra, which tended to curve the non-linear fit to the laser power baseline. This resulted in slightly lower reported N_2O concentrations.

This problem can be completely eliminated from future studies by using a pellicle beamsplitter or by dedicating a laser to N_2O measurement. A preliminary report on this experiment was presented at the Seventh CRC On-Road Vehicle Emissions Workshop before the bias had been discovered (Jimenez et al., 1997), resulting in a lower value for the average emissions in that paper than is reported here. The estimated uncertainty in the bias of ± 3.9 ppm ($\pm 2.8 \times 10^{-5}$ ER) is the dominant source of uncertainty in the mean emissions. The uncertainty of individual measurements is estimated to be ± 8 ppm at the tailpipe (ER uncertainty $\pm 6 \times 10^{-5}$).

3.1.1. Distribution of N_2O emissions

A histogram of the distribution of the N_2O emissions for 1361 vehicles is presented in Fig. 1. The distribution is skewed, with most of the readings at low emission values and with a long exponential tail of high values. The maximum reading is 245 ppm (1.7×10^{-3} ER), which is within the range of concentrations reported in the literature (e.g., Prigent et al., 1994). The negative emissions below approximately -0.3 ppm are unphysical, since that would correspond to the destruction of more than the ambient N_2O concentration. The negative emissions in the distribution are due to measurement noise at small emission levels, and these are retained to avoid biasing the average. The statistics of the distribution of the N_2O emissions are presented in Table 1. The mean N_2O emission value of the data set is 12.6 ± 4.0 ppm ($8.8 \pm 2.8 \times 10^{-5}$ ER). The standard deviation for the distribution is 24 ppm (17×10^{-5} ER).

Emissions of CO, HC, and NO from catalyst-equipped light-duty vehicles have been described with the gamma distribution function, $P(x) = P_o x^{\alpha-1} e^{-x/\beta}$, with $x =$ emission ratio (Zhang et al., 1994, 1996; Jimenez et al., 1999). Since N_2O is produced during NO reduction in the catalyst, N_2O could also have a gamma distribution. We can produce a good fit to our experimental
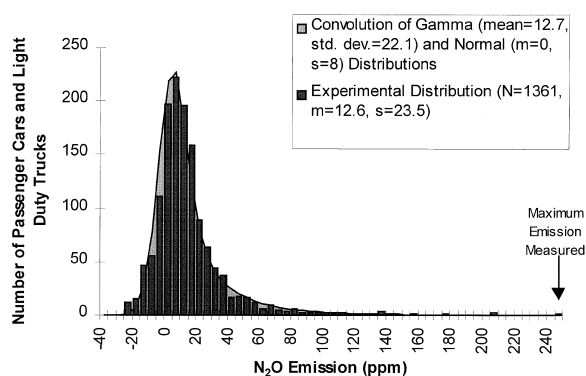
Table 1
Statistics of the cross road N_2O emissions, in terms of tailpipe concentrations

Parameter	Value
N	1361
Mean	12.6 ppm
Median	8.0 ppm
Standard deviation	23.5 ppm
Maximum	245 ppm
Skewness	3.3

distribution using a convolution of a normal distribution (representing measurement noise) and a gamma distribution, as shown in Fig. 1, indicating that the measured N_2O emissions are consistent with a gamma distribution.

A plot of the total emissions vs the fraction of the total sample population, as shown in Fig. 2, emphasizes the importance of the small number of high-emitters. For our sample, in excess of 50% of the N_2O emissions are produced by the 10% highest emitters. We analyzed the correlation between high N_2O emissions and vehicle characteristics in this dataset. We observe a small increase in the high-emitter fraction with vehicle age, but no other statistically significant trends emerged, partially due to the very small high-emitter sample size. In particular, individual high-emitters of N_2O generally are not the same vehicles as the high-emitters of NO, CO, or HC. The large contribution by a few high-emitters is similar to previous results for CO, HC, and NO (Zhang et al., 1994, 1996; Jimenez et al., 1999). The positively skewed distribution of N_2O emission rates that we observe is also seen in several literature reports of driving

Fig. 1. Histogram of N_2O emissions from cross road measurements. Superimposed is a convolution of normal and gamma distributions.
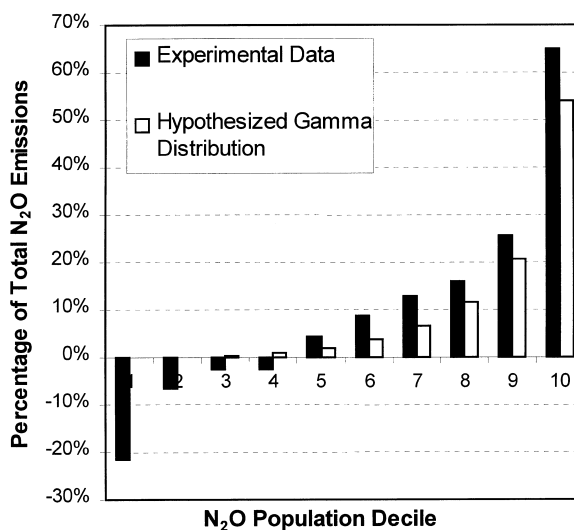

Fig. 2. Contribution to total N_2O emission from each sample decile, from cross road measurements.

cycle tests (Smith and Black, 1980; Laurikko and Aakko, 1995; Michaels 1998). The existence of high N_2O emitters is of practical importance for determining emission factors from small vehicle samples, since the presence or absence of a few N_2O "super-emitters" will heavily influence the resulting average emission factor.

We have analyzed the N_2O emissions as a function of several variables, including vehicle type and model year, vehicle specific power, and the emissions of other gases. The analysis in the following sections utilizes only the measured vehicles that the VIN-decoder identified as equipped with three-way catalysts (TWCs) (93.5% of the measured vehicles), since this is the only catalyst type currently produced. The remaining vehicles had oxidation catalysts (5.4%) or no catalysts (1.1%) and had similar and lower emissions than TWC-equipped vehicles, respectively.

3.1.2. Effect of vehicle type and model year

The emissions data was analyzed in terms of vehicle type and model year (MY), two of the simplest classification methods for the set of measured vehicles. The average N_2O emissions for vehicles equipped with TWC for each model year is shown in Fig. 3. The vehicles have been divided into passenger cars (PC) (713 vehicles) and light-duty trucks (LDT) (281 vehicles), with these classes showing distinct emission patterns. N_2O exhaust concentrations of PCs show little variation between 1985 and 1995, increase for 1983 and 1984 and become very small for 1980–1982. Emissions from LDTs remain constant within the experimental uncertainty, with the exception of MY 1988. Both PCs and LDTs of model year 1988 have significantly higher emissions than those of adjacent model years, for no apparent reason. The strong effect of catalyst aging on N_2O emissions reported for bench aging experiments (Prigent et al., 1991) is not apparent in our data. This may be due to concurrent changes in catalyst technology and composition with model year or to differences between real-world catalyst aging and accelerated bench aging. Accelerated bench aging involves very high engine power for long periods of time which are unlikely to be encountered for most vehicles in the real world, and which could lead to physical and chemical changes of the catalyst.

LDTs have higher concentrations of N_2O in their exhaust, indicating that these vehicles tend to generate more N_2O per unit fuel consumed. The ratio between the emission rates (in mg/mile), obtained by combining the N_2O/CO_2 emission ratios for each model year with the average fuel economy for each model year (Heavenrich and Hellman, 1996), is about a factor of 2 for MY 1990–95, compared to a factor of 1.5 for the ratio of concentrations. Possible reasons for the higher N_2O emission per unit fuel for LDTs include slightly lower average catalyst temperatures due to differences in exhaust system design and mass flows, or differences in catalyst composition and/or precious-metal loading with respect to passenger cars.

The fraction of the total N_2O emissions for each vehicle type and model year is shown in Fig. 4. The fraction has been calculated by adding the emission rates (in mg/mile) of each vehicle observed at every model year and dividing by the sum of the total emissions. All model years from 1984 forward (except 1988) contribute similar fractions, of $\sim 7 \pm 2\%$ of the total N_2O. Passenger cars are the dominant contributor for older model years, while LDTs and cars contribute nearly equal fractions from 1990 on, due to the increase in the fleet percentage of LDT's and their higher N_2O emissions.

3.1.3. Effect of vehicle power demand on N_2O emissions

We also have studied the dependence of the emission of N_2O on instantaneous VSP, or power per unit vehicle
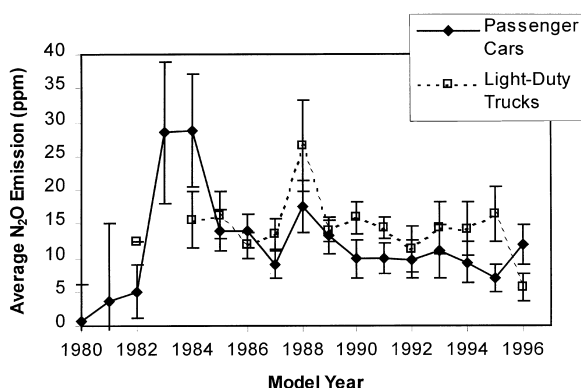
Fig. 3. Average N_2O emissions for each model year of passenger cars and light duty trucks, which are equipped with three-way catalysts, from cross road measurements.
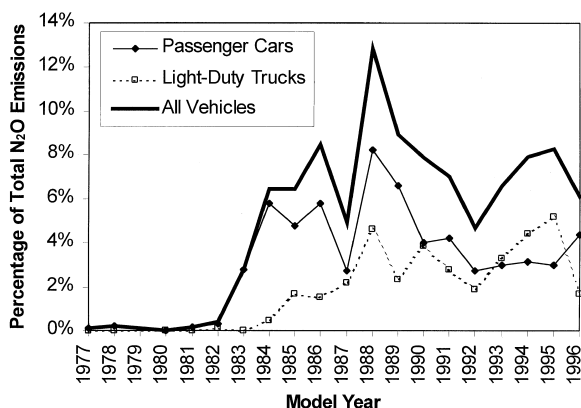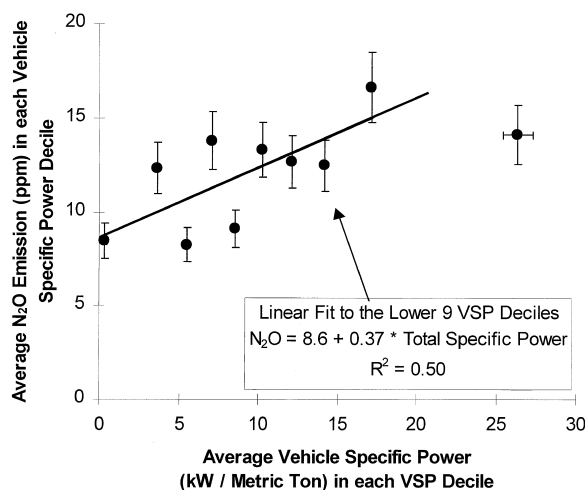
Fig. 4. Fraction of total N_2O emissions for each model year of passenger cars and light duty trucks, which are equipped with three-way catalysts, from cross road measurements.

Fig. 5. N_2O emissions as a function of VSP, for each VSP population decile, from cross road measurements.

Fig. 6. Average N_2O emissions as a function of NO emissions, from cross road measurements.

mass, which can be calculated to good approximation from roadside measurements (Jimenez, 1999). We observe a general trend of increasing N_2O emission as VSP increases. This trend is more apparent when the data is binned in VSP deciles, as shown in Fig. 5. The wide scatter in the emissions on a vehicle-by-vehicle basis makes the trend difficult to observe without binning the data. The general trend of increasing N_2O emission with VSP can be explained by the corresponding increase in engine-out NO with VSP yielding a proportional increase in N_2O. The rate of increase of N_2O with power demand is not as large as that of NO, possibly due to the inhibition of N_2O formation by the higher exhaust temperatures with higher power demands. When VSP exceeds the maximum value in the FTP of 25 kW/Metric Ton, some of the vehicles may be in commanded enrichment operation (Jimenez, 1999; Jimenez et al., 1999). These vehicles produce lower engine-out NO, which means less reduction to N_2O in the catalyst.

3.1.4. Correlation of N_2O with NO, CO and hydrocarbon emissions

Since N_2O is a byproduct of some NO reactions on the catalyst it is interesting to study the relationship between the emissions of these pollutants. The correlation between N_2O and NO is low on a vehicle by vehicle basis ($R^2 = 0.09$) but is statistically significant. There is a tendency to have a larger proportion of the high N_2O emitters for larger values of exhaust NO. Fig. 6 shows the average N_2O vs the average NO binned in 5% increments with respect to NO. There is a consistent trend of increasing N_2O with increasing NO, with somewhat lower values for the last 2 bins, which correspond to the 10% highest NO emitters. This departure from the trend may be due to the highest NO emitters having a very
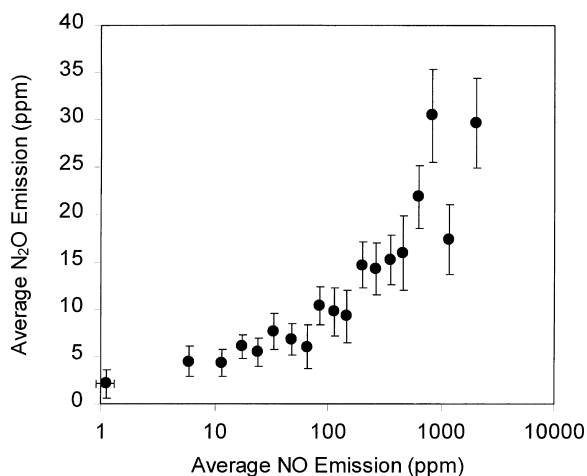
degraded catalyst and/or emission control system. The ratio of the average N_2O to the average NO for the data set is 3.9%. This ratio is heavily influenced by the 10% highest NO emitters (the 2 right-most points in the graph) which produce 50% of the NO and have an average N_2O/NO ratio of only 1.45%.

CO and hydrocarbon emission measurements were obtained simultaneously with NO measurements with a pair of NDIR cross road remote sensors (Jack et al., 1995) through a collaboration with Hughes Santa Barbara Research Center. The trends of N_2O vs CO/HC (described in detail in Jimenez, 1999) mimic those of NO vs CO/HC presented in a previous publication (Jimenez et al., 1999). The N_2O emissions increased with CO and HC for the 80% lowest CO and HC emitters, and decreased for the highest CO and HC emitters.

3.2. Results of mobile measurements

The use of continuous mobile concentration data for emission ratio determination is a new technique. The data collection was guided by the broader goal of examining concentrations of a set of gases across an urban area on fine spatial scales. Determining methods of deriving the emission ratio has been a concern of the analysis reported here. We have considered various methods of grouping the data in time, and of separating contributions of local mobile sources from diffuse sources and background.

The data contains many sharp peaks, with several gases often correlated in time. Correlation with CO_2 generally indicates a combustion source for trace gases. We interpret the sharp peaks as being due to nearby discrete sources, in contrast to distant or diffuse sources which would produce broadened and dispersed plumes.
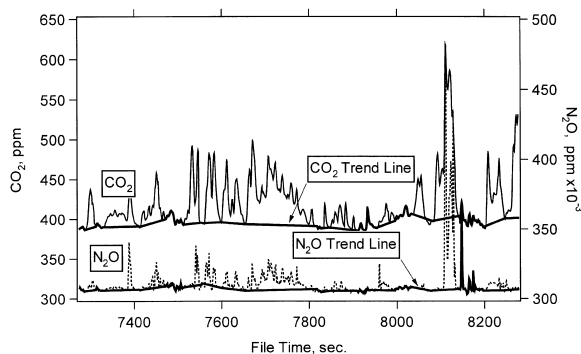
Fig. 7. Mobile real-time data segment, showing N_2O, CO_2, and trend lines.

The slowly varying minimum between peaks is interpreted as a local background. A typical segment of data is shown in Fig. 7, with correlation evident between CO_2 and N_2O.

In contrast to the cross road measurements, there are no clear markers in the mobile data set to indicate emissions from individual vehicles. However, statistical treatments of the data may be used to derive aggregate emission ratios. For short segments of data, over a peak region showing correlation between two gases, the linear regression slope $(d[N_2O]/d[CO_2])$ is interpreted as the emission ratio for the gases. In a longer data segment, a plot of N_2O vs CO_2 will show a large scatter in the points due to the variation in the emission ratio from multiple sources. For example, we show in Fig. 8 a scatterplot of a selection of data from one day (6/16/98), with 14 700 (1 s) data points. The regression slope for the entire data set shown in Fig. 8 is $(8.7 \pm 0.1) \times 10^{-5}$ $(R^2 = 0.25)$. This data is selected to contain both city and highway driving, and to exclude long periods with
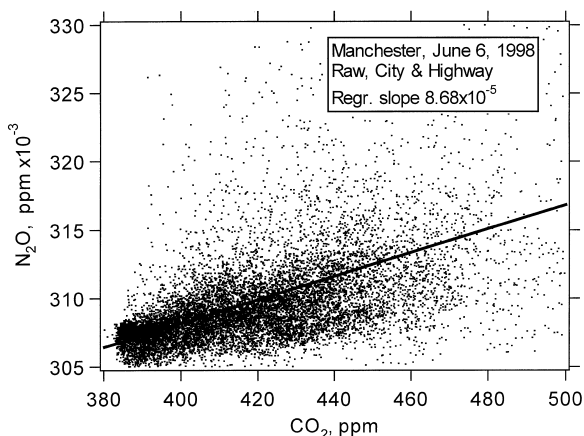

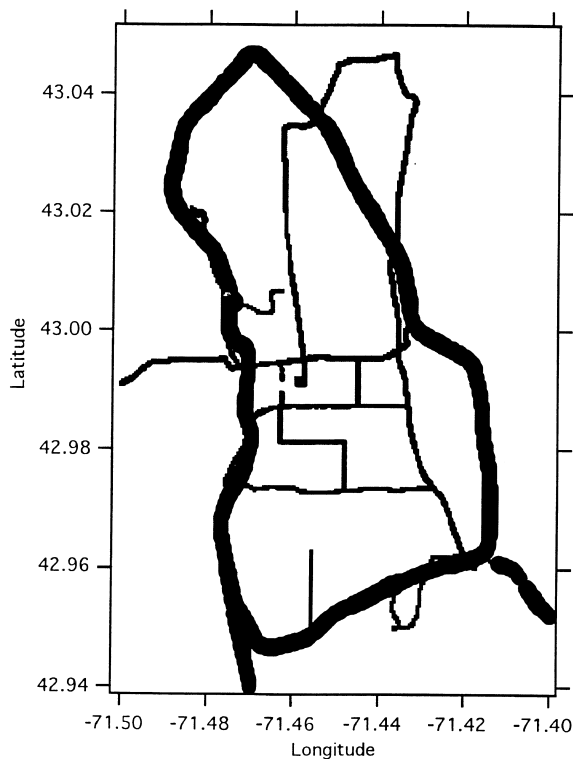Fig. 8. N_2O vs CO_2 concentrations in unprocessed mobile data for Manchester, NH, 16 June 1998.

Fig. 9. GPS locations for mobile data points shown in Fig. 8. The highway data points are thick and the city data points are thin. The vertical scale corresponds to 12 km.

the vehicle stopped or where data is otherwise invalid. The traverses covered in this sampling period cover much of Manchester in a coarse grid, as shown in Fig. 9.

3.2.1. Data separation into peaks and trend line

Using a simple regression slope for the entire data set as an aggregate emission ratio may put too much emphasis on non-local sources. In our long data sets which cover an entire city area, we observe variations in the level of the minimum concentration between peaks, which will affect the aggregate regression slope. The data can be viewed as having two parts, a slowly varying local background and the rapidly changing peaks due to local sources. In computing regression slopes for emission indices, we would like to concentrate on the local sources (i.e., vehicles), rather than the diffuse background which represents more varied sources.

We have used a simple method of separating the data into two parts, a background trend line and peaks above the trend. Local minimum points in CO_2 are identified and a trend line is linearly interpolated between the minima. The times of the CO_2 minima are used to select points in the N_2O data to create a trend line for N_2O. Subtracting the trend line from the data yields the "peak" data, ΔN_2O and ΔCO_2. We show the interpo-

lated trend lines in our typical sample of data in Fig. 7. A similar procedure has been used in a recent aircraft study of emissions in Athens (Klemm and Ziomas, 1997). Drawing a trend line is straightforward for isolated peaks that clearly rise from and return to a flat background. It is less straightforward when there are multiple peaks close together or when there is a fluctuating concentration without a clear background. There is some subjectivity in the selection of minimum points, but the method should give a more accurate representation of the contributions of local sources than the raw data set. The raw data for CO_2 (average 419.7 ± 30.5 ppm), is separated into a trend line part (average 403.1 ± 15.8 ppm) and a peak part (average 16.6 ± 24.7 ppm), where the errors given represent the standard deviation of the data sample. Similarly, the raw data for N_2O (average 309.9 ± 5.3 ppm) is separated into a trend line part (average 307.8 ± 1.7 ppm) and a peak part (average 2.1 ± 4.5 ppm). Thus, the trend line data is the majority of the total gas concentration, but with less statistical variability. The peak fractions are small, with standard deviations greater than their means.

A scatterplot (Fig. 10) of ΔN_2O vs ΔCO_2 for the peak data shows a wide spread of points and a cluster of points near $\Delta N_2O = 0$, $\Delta CO_2 = 0$, but without the dense band of points due to varying background seen in Fig. 8. A linear regression fit to the peak data gives a somewhat higher slope than the raw data set, for an emission ratio from this data aggregation of $(10.9 \pm 0.1) \times 10^{-5}$ ($R^2 = 0.36$). A linear regression for the slowly varying trend line data shows a smaller slope, for a background emission ratio of $(4.41 \pm 0.09) \times 10^{-5}$ ($R^2 = 0.15$).
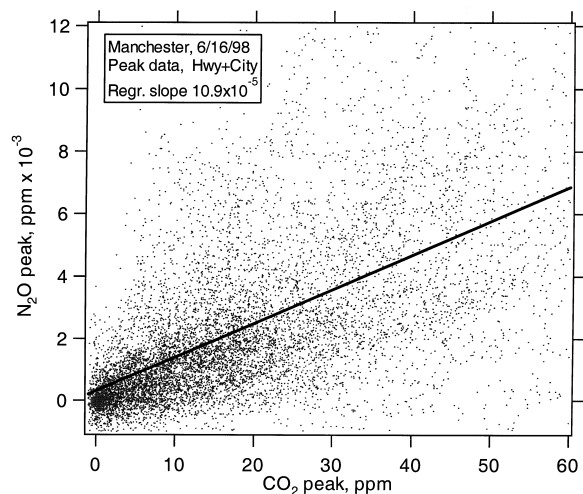
If each pair of ΔN_2O and ΔCO_2 data points is ratioed, we generate a set of $\sim 10^4$ emission ratio samples, which then can be used to form distributions as well as averages. Selections and conditions can be applied easily to the set of pointwise ratios, in order to find the best data subset for emission index determination and to test dependencies. The first selection is to consider the highway plus city roadway data set used in the scatterplots above (Figs. 8 and 10). Next, we select data with ΔCO_2 greater than a minimum level (above the subtracted background). The minimum ΔCO_2 elevation selection excludes data close to the background, which can be negative for either ΔCO_2 or ΔN_2O. Thus, we reduce contamination of the ratio distribution with negative or spuriously large values. We empirically set the ΔCO_2 cutoff to be 15 ppm (close to the average for the whole "peaks" set), which eliminates 52% of the data points, with 5538 remaining. The cutoff value is selected by observing the effect of increasing cutoff on the ratio distribution. There is a large change going from zero cutoff to 10 ppm, but quite small changes from 10 to 20 ppm.

The selected normalized distribution of emission ratios (determined on a point by point basis) from mobile measurements is shown in Fig. 11. From this distribution, we derive our reported average emission ratio of $(12.8 \pm 0.3) \times 10^{-5}$. The uncertainty in the mean is primarily systematic, estimated from the variation in the mean with changes in ΔCO_2 cutoff. The distribution has a similar shape as that observed in cross road measurements. The distribution is skewed, with a peak at low values and an exponentially decreasing tail. The width of the distribution in terms of standard deviation is $\sim 10 \times 10^{-5}$.
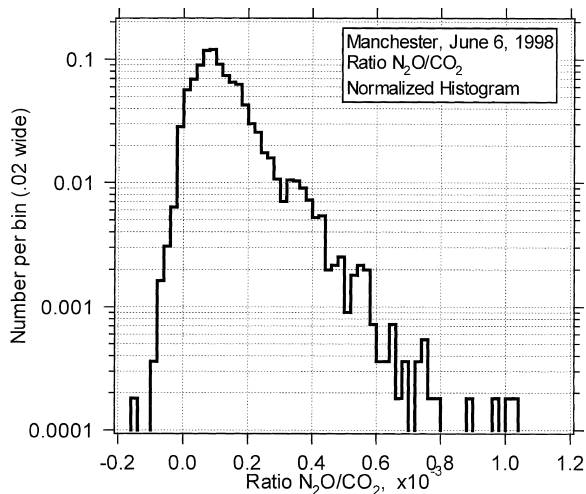

Fig. 10. N_2O vs CO_2 concentrations for the "peak" segment of the mobile data.

Fig. 11. Histogram of pointwise ratios for mobile peak data, $\Delta N_2O/\Delta CO_2$, city and highway, $\Delta CO_2 > 15$ ppm.

The data can be segregated to test the effect of potential controlling variables. For example, if we divide the data contained in Fig. 11 into highway vs city roads, then we observe a difference in the emission ratio: $(10.9 \pm 0.3) \times 10^{-5}$ for the highway vs $(15.6 \pm 0.3) \times 10^{-5}$ for the city roads. A separation of the data into two groups with speed less than or greater than 16 m/s (36 mph) shows a similar difference in the emission ratio, reflecting the traffic speed difference between city and highway roads. Thus, the grouping of data by city-highway or slow-fast represents the same classification, with a robust difference in the N_2O emission ratios. This difference is probably due to the smaller fraction of vehicles in cold start on the highway, and also to the higher catalyst temperatures at higher speeds, both of which result in lower N_2O emissions (Rabl et al., 1997; Odaka et al., 1998). We tested other grouping methods, (positive vs negative acceleration, positive vs negative vertical climb rate) and found much smaller differences in emission ratios.

We have considered the question of possible dependence of our emission index distribution on the method of grouping data. The data might be grouped into larger blocks, each of which contains one (or a few) peaks. The set of minimum points used to identify the local background provides a convenient way to segment the data into relatively small blocks. Some of these segments are individual peaks, and some contain clusters of peaks. We calculated regression slopes ($d[N_2O]/d[CO_2]$) for each of the ~ 250 peak segments contained in the scatterplot (Fig. 10). The peaks have an average width in time of 28 ± 32 s, covering an average distance of 460 ± 680 m, so we expect that many vehicles contribute to each peak. The set of slopes forms a distribution of emission indices, shown in Fig. 12. Also shown in Fig. 12 is the distribution based on point by point analysis.

Similar results are obtained for the two analysis methods, aggregation by peak-segment and point by point ratio analysis, both in terms of average and standard deviation, and in the shape of the distribution. Point by point analysis offers the advantage of the ease of application of cuts based on instantaneous variables, such as speed or location. The point by point ratio distribution can be interpreted as a distribution of the probability of encountering a given emission ratio from local sources in the urban area. Each sample point may contain contributions from more than one vehicle, effectively averaging the measurement to some degree. Averaging will tend to decrease the extremes of the distribution, at both high and low values.

4. Discussion

We have presented vehicular N_2O emissions data which was collected with two different TILDAS instruments utilized in two different experimental configurations (cross road remote sensing and mobile extractive sampling) and in two different settings (southern California and Manchester, New Hampshire). We obtain comparable values for the "raw" average emissions ratios from these two different measurements, i.e., without extrapolating to a consistent traffic mix by taking into account the effects in the mobile data of vehicles without catalytic converters or heavy duty trucks. The emission ratio determined by cross road remote sensing (corresponding to cars with catalytic converters) is $(8.8 \pm 2.8) \times 10^{-5}$ and the mobile extractive sampling value (for all data points, corresponding to mixed traffic) is $(12.8 \pm 0.3) \times 10^{-5}$. The mobile data shows a systematically higher emission ratio for the city roads $((15.6 \pm 0.3) \times 10^{-5})$ than for the highway $((10.9 \pm 0.3) \times 10^{-5})$.

The distributions of the two data sets (cross road and mobile) are similar, especially the exponential tails at high emission values, as seen in Fig. 13. The distributions are more distinct close to zero. The cross road distribution has a more substantial population with "negative" emissions, due to the sensitivity limit (and hence random error) of 8 ppmv of the exhaust (6×10^{-5} emission ratio). The mobile measurements also have a random error, which depends in part on the effect of the peak-trend separation procedure. The basic instrumental noise of the mobile measurements is ~ 1 ppb for N_2O and ~ 1 ppm for CO_2. The presence of negative emission ratios in the mobile measurements
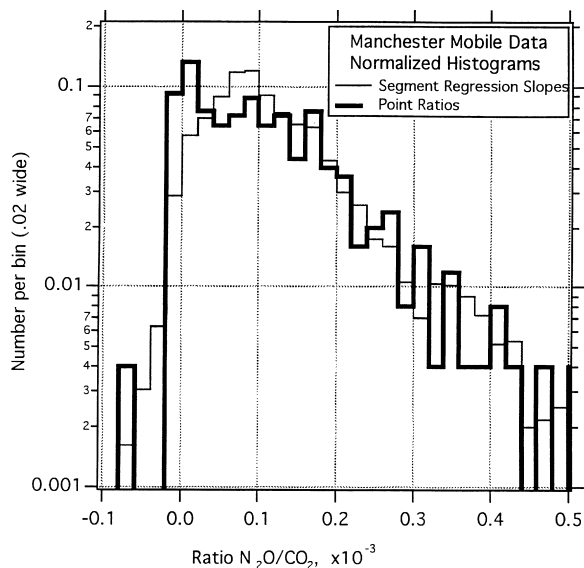

Fig. 12. Histogram of regression slopes, N_2O vs CO_2, for 251 segments of mobile data. The histogram of pointwise ratios is superimposed, dotted line.
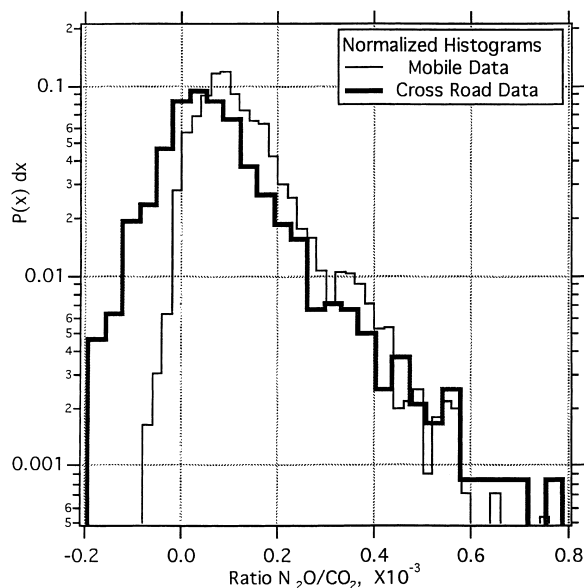
Fig. 13. Normalized histograms of emission ratios from cross road (thick line) and mobile measurements (thin line). Cross road bin widths are 0.035×10^3 and the mobile bin widths are 0.02×10^3.

indicates a random error for each ratio point of $\sim 3 \times 10^{-5}$.

More detailed comparison of our cross road and mobile measurements will involve extrapolations, due to incomplete information and differences in the mix of vehicles, operating conditions and other experimental variables. In the cross road measurements, practically all the vehicles were fully warmed up, the average speed was 13.6 ± 2.6 m/s, $\sim 99\%$ of the vehicles (in the complete data set) had catalytic converters, and there were no heavy duty trucks. The cross road study was conducted in California, where gasoline contained only 30 ppm of sulfur, while the mobile measurement was conducted in an area where gasoline contained sulfur levels near 300 ppm. Michaels (1998) found that lower sulfur content of gasoline resulted in lower N_2O emissions, possibly another reason for the lower result in the cross road study. In the mobile measurements, there may have been vehicles in "cold start" conditions, especially in the city. The mix of vehicles in Manchester was not characterized, but there were certainly large diesel trucks without catalytic converters in the sample. The mobile measurement van had an average speed of 16.5 ± 9.7 m/s, moving with traffic in the city and somewhat slower than traffic on the highway. The range of operating conditions, locations and the variety of vehicles was greater in the mobile measurements. For completeness we note two other differences, the more stringent emissions standards for California as compared to the rest of the country; and the 1.5 year time difference between the studies.

4.1. Comparison with previous work

In order to compare our results to previous work, we must account for the wide variety of the literature on nitrous oxide emissions, in terms of the types of studies, measured quantities, number and type of measured vehicles, and units to express emissions. Previous studies of nitrous oxide emissions from motor vehicles have been of two main types, dynamometer studies and tunnel studies. The dynamometer studies are extensive examinations of a small number of vehicles, with the advantages of known vehicle characteristics and driving conditions, but also with the disadvantage that it is difficult to study enough vehicles to characterize fleet emissions. This is especially true if the emissions distribution is skewed, as we have shown to be the case for nitrous oxide. The tunnel studies sample the emissions from thousands of vehicles, which allows them to acquire statistically robust averages. The tunnel studies also naturally report emission indices (molar ratios of N_2O to CO_2), which are the same quantities that we measure. We therefore focus on comparing our results to the tunnel studies, both in terms of emission indices for mixed traffic and for catalyst equipped automobiles.

The comparison of our work to tunnel studies is complicated by the effects of sampling mixed exhaust from numerous vehicles. Unlike our cross road measurements of individual vehicles, our mobile sampling and previous tunnel studies cannot separate the emissions of catalyst equipped automobiles from those of automobiles and heavy duty vehicles which lack catalysts. The effect of heavy duty trucks in mixed traffic is especially important, since they are strong sources of CO_2 and their N_2O emissions are uncertain. They may constitute $\sim 10\%$ of the traffic, but emit 25–40% of the total exhaust due to their lower fuel economy. To derive emission factors for catalyst equipped vehicles from previous tunnel studies and from our mobile van measurements, one must make assumptions about the N_2O emissions of automobiles without catalysts and of heavy duty vehicles and further assumptions about the relative fuel economy of these vehicles.

In Table 2, we compare our work to four earlier tunnel studies (Berges et al., 1993, counted as two studies, Sjödin et al., 1998 and Becker et al., 2000). We show the measured emission indices for mixed traffic and then derive the emission indices for catalyst equipped vehicles, based on the reported traffic mixtures and two distinct sets of assumptions regarding the vehicles without catalysts. We apply a uniform set of assumptions to different studies in order to clarify the sensitivity of the derived (catalyst equipped vehicle) emission indices to those assumptions, and to see if the variation

Table 2

Comparison of nitrous oxide emission indices from four tunnel studies with this work[a]

Study	Location	Date	Measured EI[b]	Derived EI Case I[c]	Derived EI Case II[d]
Berges (1993)	Sweden	1992	14	28.0	23.5
Berges (1993)	Germany	1992	6	43.9	20.9
Sjödin (1998)	Sweden	1994	4.6	13.3	6.6
Becker (2000)	Germany	1997	4.1	7.6	4.9
This wsrk: Cross road	California	1996	8.8	8.8	8.8
This work: Mobile	New Hampshire	1998	12.8	18.5	17.4

[a] The earlier tunnel study by Sjödin et al. (1995) is not included in the table because a N_2O/CO_2 ratio was not reported.
[b] All emission indices (EI) are multiplied by 10^5, i.e., 14 corresponds to molar ratio $N_2O/CO_2 = 14 \times 10^{-5}$.
[c] Case I emission factors are derived assuming that vehicles without catalysts emit zero nitrous oxide and that the fuel economy of heavy duty trucks is four times smaller than that of light duty vehicles. The traffic mixes are taken from the relevant publications. For our mobile van measurements we assume that the traffic mix is 90% catalyst equipped light duty vehicles and 10% heavy duty vehicles.
[d] Case II emission factors use the same assumptions as Case I except that light duty vehicles without catalysts are assigned an emission index of 4.5×10^{-5} (Jimenez, 1999) and heavy duty vehicles are assigned an emission index of 2.5×10^{-5} (Dietzmann, 1980).

between results is due in part to different assumptions. In analysis Case I, we assume that vehicles without catalysts emit zero nitrous oxide and that the fuel economy of heavy duty vehicles is four times smaller than that of light duty vehicles. Case I is similar to the analysis performed by Berges et al. (1993). In Case II, we make the more realistic assumptions that light duty vehicles without catalysts emit nitrous oxide with an emission index of 4.5×10^{-5} (Jimenez, 1999), and that heavy duty vehicles also emit nitrous oxide with an emission index of 2.5×10^{-5} (Dietzmann et al., 1980), and that the fuel economy of the heavy duty trucks is four times smaller than that of light duty vehicles. Neither case is likely to be exactly correct, nor would any one set of assumptions be perfectly appropriate for all five studies. Still, the two cases show a range of reasonable interpretations based on our current understanding.

The analysis presented in Table 2 produces a derived emission factor for catalyst equipped vehicles from our mobile measurements which is approximately twice as large as our cross road result. Our cross road result is the same in all three columns of the table since we know that that value corresponds to catalyst equipped vehicles. In a study of two tunnels with mixed traffic, Berges et al. (1993) derived an emission index for catalyst equipped vehicles of $(38 \pm 22) \times 10^{-5}$, based on smaller measured molar ratios (6×10^{-5} in Germany in 1992 and 14×10^{-5} in Sweden in 1992), by assuming that vehicles lacking catalysts produced zero nitrous oxide. When we apply our Case II analysis and assumptions to their data we arrive at lower emission indices, but which are still more than twice our cross road value. The more recent studies of Sjödin et al. (1998) and Becker et al. (2000), report smaller emission indices of 4.6×10^{-5} and 4.1×10^{-5}, and our analysis yields extrapolated emission indices closer to our cross road results. The extrapolated emission indices are slightly more variable than the raw

values, so uniform assumptions about traffic mix do not reduce the variation in the results of these studies. We have not been able to reconcile the results of the existing studies with other assumptions about the traffic mixes. It appears that either nitrous oxide emissions of catalyst equipped vehicles are systematically different in these studies or there are significant errors in some of the measurements.

We also compare our results to dynamometer studies, since most of the published studies of N_2O emissions from motor vehicles are of that type. In Fig. 14 we plot the reported results from several dynamometer studies as well as those of the studies with large vehicle samples discussed above, using the common basis for comparison of N_2O emission rate in mg/mile for vehicles with aged TWCs. For the dynamometer studies in Fig. 14 we only include data for passenger cars equipped with TWCs, and only vehicles that have accumulated at least a few thousand miles, if the relevant papers provide mileage information. We have not included the study of Ballantyne et al. (1994) since their emission rates are overestimated due to unsubtracted ambient N_2O levels (Barton and Simpton, 1994). For the tunnel and mobile studies we show our best estimates for aged three-way catalyst vehicles (Case II in Table 2) and assume a fuel economy of 25 miles/gallon (10.6 km/l). In our cross road study, the emission rate is calculated using average fuel consumption rates for each model year of the individual vehicles observed (Heavenrich and Hellman, 1996).

The dynamometer study results plotted in Fig. 14 show higher N_2O emission rates, with an average (weighted by the number of vehicles in each study) of 78 ± 50 mg/mile. The average of the four tunnel studies and our two values (cross road and mobile) is 49 ± 28 mg/mile. The higher average of the dynamometer studies could be because they include cold starts in the driving cycles. The larger apparent variability of the
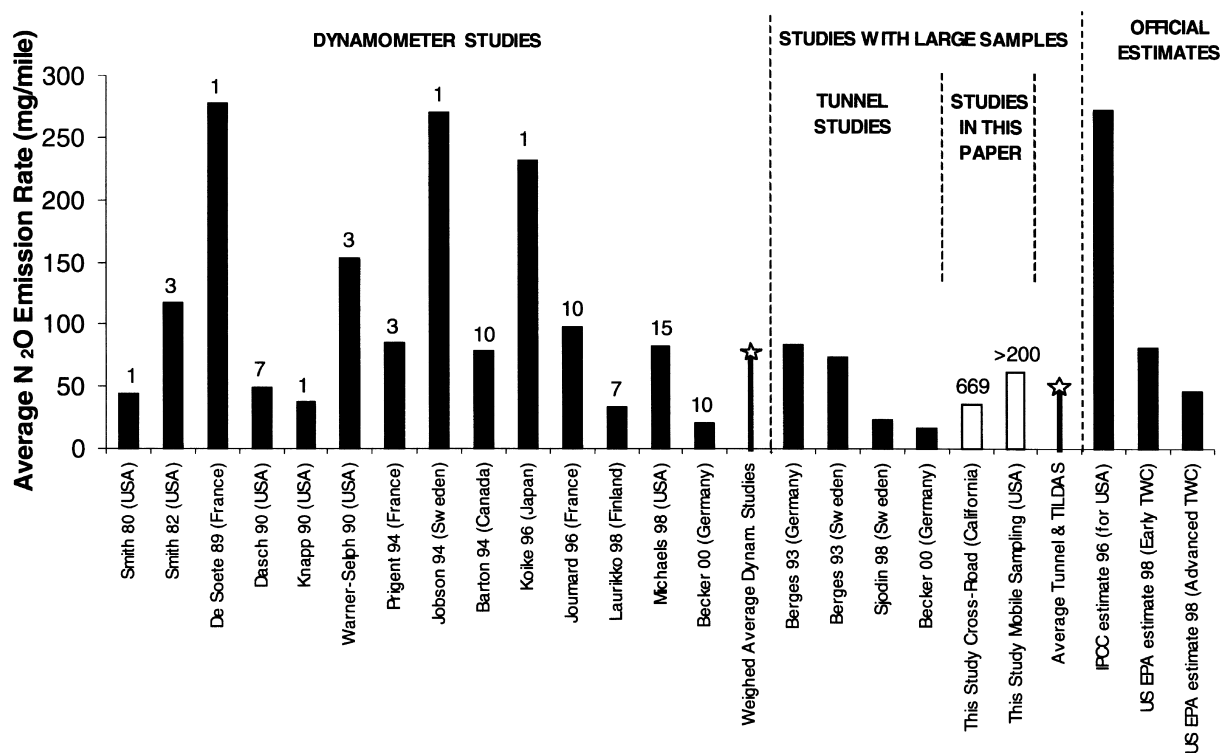
Fig. 14. Comparison of N_2O emission rates for passenger cars with TWC for several dynamometer studies, tunnel studies, the work reported here, and two official estimates. The numbers above the bars indicate the number of vehicles in the studies. The bars with stars represent the average of the dynamometer studies, weighted by the number of vehicles, and the average of the tunnel studies and our two values, equally weighted.

dynamometer studies in Fig. 14 can be explained by small sample sizes. For example, the five studies that only involved one vehicle resulted in most of the extreme (both high and low) emission rates. The study by De Soete (1989) reports a value based on measurements of a single vehicle which is high when compared to the studies summarized in Fig. 14 (cf. Joumard et al., 1996; Knapp, 1990; Koike and Odaka, 1996; Smith and Carey, 1982; Warner-Selph and Harvey, 1990). That high value was essentially adopted as the 1996 IPCC emission factor for the US (IPCC, 1996; Michaels, 1998). The most recent estimates from the US EPA (Michaels, 1998) for cars with "early" and "advanced" TWCs are also shown. Cars with "advanced" TWCs were phased in during 1992–93 in California and 1994–95 in the rest of the U.S. The estimates for both types are within the range spanned by the tunnel, cross road, and mobile studies.

4.2. Implications for the global N_2O budget

An important question is how useful our results can be in predicting the total N_2O emissions of vehicles in the US and throughout the world. Often the first step in

such an estimation is to separately consider the contributions of vehicles with and without catalysts, and to attribute the majority of emissions to vehicles with catalysts. We have generated detailed information on a large number of catalyst equipped vehicles in our cross road study. A model to extrapolate emissions to national or global fleets would take into account the numerous variables which are known to affect N_2O emissions, including vehicle type, power demand, catalyst type and aging, and the sulfur content of the fuel. Also, the emission rate for individual vehicles varies through driving cycles as the catalyst temperature changes, with the highest emissions occurring during the "cold start" phase (Braddock, 1981; Jobson, et al., 1994; Laurikko and Aakko, 1995). Some of these catalyst related effects could alter fleet emission estimates by a factor of two (Jimenez, 1999). Fleet emissions also will have an uncertain contribution from non-catalyst vehicles.

Short of making a detailed model based estimate of fleet emission of N_2O, our data may be useful in setting bounds on fleet emissions. Berges et al. (1993) used a simple analysis of fleet emissions to predict that automobiles would be a large and growing source of

atmospheric N_2O. They calculated that if the entire fleet of existing automobiles were equipped with present day catalysts, and using their emission index of $(38 \pm 22) \times 10^{-5}$, then the nitrous oxide emissions from cars could reach 6–32% of the atmospheric growth rate of nitrous oxide. In this work we find much lower emission indices for catalyst equipped vehicles, of only 9×10^{-5} and 17×10^{-5}, from cross road and mobile measurements. An analysis similar to Berges et al. based on our two values implies that the above scenario would produce a less alarming result, with N_2O emission rates reaching between 4% and 7% of the atmospheric growth rate, using our cross road and mobile emission rates, respectively.

The best way to answer the question of estimating fleet emissions may be to perform many more measurements of vehicles at different locations and under varying conditions. For catalyst equipped vehicles, more work is required to better quantify the effects of vehicle type, driving cycle, catalyst type and age, and fuel chemistry, especially as they apply to real world vehicles and driving patterns. It also is important to better quantify the emissions of vehicles without catalytic converters such as heavy duty diesel trucks.

5. Summary

We have used two different TILDAS based techniques to measure the N_2O/CO_2 emission ratios of on-road motor vehicles. Cross road, open path laser measurements of emissions from 1361 vehicles in California yielded an average emission ratio (N_2O/CO_2) of $(8.8 \pm 2.8) \times 10^{-5}$ for catalyst equipped vehicles. A van-mounted TILDAS sampling system making on-road N_2O measurements in Manchester, New Hampshire yielded an average ratio of $(12.8 \pm 0.3) \times 10^{-5}$ for mixed traffic, including heavy duty vehicles. The mobile data shows a systematically higher emission ratio for the city roads ($(15.6 \pm 0.3) \times 10^{-5}$) than for the highway ($(10.9 \pm 0.3) \times 10^{-5}$). Average N_2O/CO_2 emission ratios for each TILDAS technique are comparable, and their distributions are similar, even though the measurement circumstances were quite different. The average emission rates obtained in both our cross road and mobile measurements are within the range of values reported in recent tunnel studies. Our measured distributions are skewed, with a small number of high N_2O emitters and a majority of low emitters, similar to the distributions of CO, NO and HCs seen in previous studies.

The cross road measurements, when combined with individual vehicle identification, allow detailed analysis of the dependence of N_2O emissions on a variety of factors, including vehicle type and model year, vehicle specific power, and the emissions of other gases. LTDs have higher emissions than passenger cars, which is only partially explained by their lower fuel economy. We observed no significant dependence on vehicle age nor strong correlation between high N_2O emitters and NO, CO, or HC high emitters. We also observed a general trend of increasing N_2O emission as the vehicle specific power increases.

The mobile measurements provide data on the emissions of a large number of vehicles across an urban area in real world driving situations. Average emission ratios and probability distributions can be derived for different conditions. The clearest distinction we see is between emission ratios for city roads (at low speed) and highways (at high speed), with the city emission ratio 43% higher than on the highway. Direct measurement of many vehicles across a wide area may help to reduce the uncertainties of model-based projections of vehicle fleet emissions.

Berges et al. (1993) calculated that if the entire fleet of existing automobiles were equipped with present day catalysts the nitrous oxide emissions from cars could reach 6–32% of the atmospheric growth rate of this species. A similar analysis based on our measurements implies that the above scenario would produce a less alarming result, with N_2O emission rates reaching between 4% and 7% of the atmospheric growth rate, using our cross road and mobile emission rates, respectively. More work is needed to understand the large differences between the existing studies.

Acknowledgements

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