Remote Sensing of NO and NO_2 Emissions from Heavy-Duty Diesel Trucks Using Tunable Diode Lasers

JOSE L. JIMENEZ,*,† GREGORY J. MCRAE,‡ DAVID D. NELSON,§ MARK S. ZAHNISER,§ AND CHARLES E. KOLB§

Departments of Mechanical Engineering and Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Aerodyne Research, Inc., Billerica, Massachusetts 01821

On-road remote sensors can measure the emissions of motor vehicles under real-world conditions. The most sensitive remote sensing technique reported to date is tunable infrared laser differential absorption spectroscopy (TILDAS). A TILDAS remote sensor was used in this study to measure the NO_x emissions of heavy-duty diesel trucks (HDDTs). The remote sensor could operate with an optical path length of 88 m or more than five times that of NDIR-UV instruments. Good agreement was obtained when comparing the TILDAS measurements with the on-board measurements of an instrumented HDDT. The distribution of NO emissions from HDDTs was found to be close to normal. Remote sensing of NO_2 emissions was demonstrated for the first time. The NO_x emission factor determined in this study is consistent with other recent measurements. These emissions are underestimated in the EPA inventory, although part of the discrepancy can be explained by the effect of a "defeat device" that increases NO_x emissions.

Introduction

Emissions of oxides of nitrogen (NO and NO_2, collectively referred to as NO_x) contribute to a variety of environmental problems, including photochemical smog, acid deposition, and visibility impairment through particulate nitrates (*1*). As the NO_x emissions of passenger cars and light-duty trucks (LDTs) have become more tightly controlled, the relative importance of heavy-duty diesel trucks (HDDTs) as a NO_x source has increased. EPA estimates that HDDTs emitted 8% of the NO_x emissions in the U.S. in 1997 vs 20% for cars and LDTs. In contrast, a recent assessment of on-road emissions estimated that HDDTs contribute as much NO_x as cars and LDTs; it also indicated that large uncertainties remain about the magnitude and distribution of these emissions (*2*). A recent study found that California's emission inventory model may underestimate NO_x emissions from heavy-duty diesel trucks (HDDTs) by up to a factor of 2.3 (*3*).

* Corresponding author phone: (978)663-9500; fax: (978)663-4918; e-mail: jlj@alum.mit.edu.

† Department of Mechanical Engineering, M.I.T. Currently at Aerodyne Research, Inc. and Department of Chemical Engineering, M.I.T.

‡ Department of Chemical Engineering, M.I.T.

§ Aerodyne Research, Inc.

Recent developments highlight the increasing attention being given to HDDT NO_x emissions. The composition of U.S. on-road diesel fuel was changed to reduce emissions in 1993 (*4*). More stringent U.S. emission standards for heavy-duty diesel engines, which seek to reduce NO_x emissions by about 50% (from 4 to 2 grams per brake horsepower hour or g/bhp-h) were enacted in 1997 (*5*). In addition, in 1998 EPA accused seven major diesel engine manufacturers of using a "defeat device" in order to improve fuel economy. The use of this device resulted in large increases in NO_x emissions (*6*). This claim was settled with a total cost for the manufacturers in excess of $1 billion, including a faster introduction of the new emission standards, a rebuild program for in-use engines, and the largest civil penalty ever for violation of environmental law ($83 million) (*6*). Standards requiring further reductions to about 0.5 g/bhp-h starting in 2007 are now being planned (*7*).

Achieving low-NO_x emissions from heavy-duty diesel engines is a significant challenge. Two fundamental approaches can be taken: lowering in-cylinder NO_x formation or removing NO_x from the exhaust gases. The latter is problematic for on-road diesel engines. The three-way catalysts used for highly efficient NO_x reduction to N_2 in light-duty vehicles perform very poorly when the exhaust O_2 concentration is high (*8*). Other postcombustion NO_x removal concepts, such as lean-NO_x catalysts, NO_x-trap catalysts, selective catalytic reduction systems, and plasma treatment technologies, are under very active research but still face significant issues for commercial application in heavy-duty vehicles (*9, 10*). EPA sees the 2007 standards now under planning as forcing exhaust gas aftertreatment and ultralow sulfur diesel fuel (*7*). Until now, lowering in-cylinder NO_x formation has been the main strategy used to reduce emissions. This approach is difficult due to the nature of the diesel combustion process. In diesel engines NO_x formation is due mainly to the thermal (Zeldovich) mechanism (*11*). NO appears first; smaller amounts of NO_2 may result from NO oxidation reactions (see below). NO production by the thermal mechanism increases exponentially with temperature. The other important variable is oxygen concentration, with NO formation peaking at slightly lean of stoichiometric and decreasing rapidly for rich and lean conditions. In diesel engines the average cylinder composition is always fuel-lean. Fuel injection into the air-containing cylinder begins toward the end of the compression stroke just before the start of combustion and continues after combustion initiation. Combustion starts with spontaneous ignition of a small part of the fuel which has vaporized and mixed with the hot air in the combustion chamber and continues in a mixing-limited, near stoichiometric regime as additional fuel is injected. The flame region and post-flame gases are inevitably at high-temperature and near stoichiometric conditions, which produces high NO levels (*11*). An observed tradeoff between reducing in-cylinder NO_x formation and increasing undesirable particulate emissions further complicates NO_x reduction (*12*). However, substantial NO_x reductions have been and continue to be achieved by fine-tuning the mixing and combustion processes, mainly through electronic engine control, followed by changes in diesel fuel injection systems, air intake improvements, combustion chamber modifications, and exhaust gas recirculation. Some of these strategies may cause a fuel economy penalty.

The "defeat device" that EPA claimed that manufacturers have used since 1988 was a series of engine electronic control

10.1021/es9911622 CCC: $19.00
Published on Web 05/04/2000

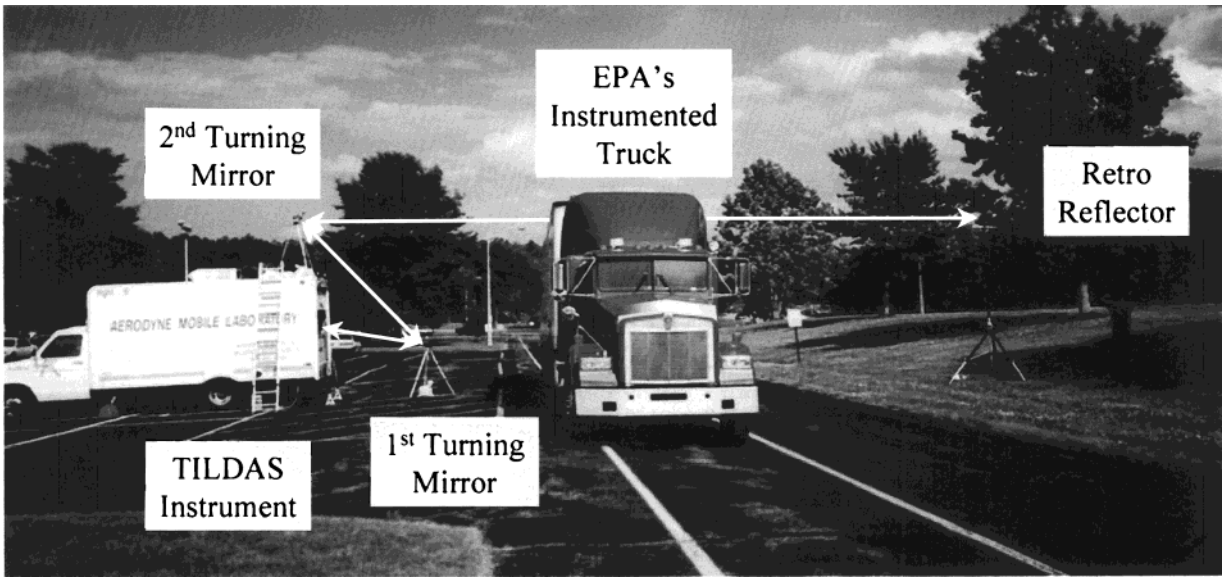

FIGURE 1. Optical setup for the remote sensing of emissions from heavy-duty diesel trucks.

system strategies, different for each engine manufacturer. The details of each system have not been released by EPA since they are considered proprietary information; however, the general strategy was to lean out engine operation during extended steady cruise conditions to achieve improved fuel economy (*13*). Since the resulting increases in NO_x emissions were undetected during the U.S. on-road heavy-duty diesel engine test procedure which includes transients on time scales of 6 min (*14*), it is safe to assume that the "defeat device" control strategies did not come into effect before 6 min of steady-state operation. NO_x emissions increases with the "defeat device" were of the order of a factor of 2 (*15*).

The measurement of real-world NO_x emissions from HDDTs is important for evaluating the implementation and durability of emission controls and for the design and evaluation of air pollution abatement strategies. There are three basic approaches for on-road emission quantification: measurements of the emissions of individual vehicles as they are driven in a chassis dynamometer or on-road (*16*−*20*), tunnel studies where the concentration of a pollutant in the air leaving the tunnel and a tunnel airflow estimate are used to determine emission factors (*4, 21, 22*), and on-road remote sensing (*23*−*25*).

Remote sensing instruments can determine the emissions of passing vehicles with optical absorption measurements. Remote sensing of passenger car emissions was pioneered by Donald Stedman and Gary Bishop of the University of Denver using nondispersive infrared and ultraviolet (NDIR-NDUV) techniques (*26*). This group has recently developed a dispersive UV instrument for improved NO measurement (*27*). An instrument based in near-infrared tunable diode lasers has recently been commercialized (*28*). Remote sensing of emissions from heavy duty diesel trucks were first reported by Bishop et al. (*29*). A high precision remote sensor based on tunable (mid-)infrared laser differential absorption spectroscopy (TILDAS, also known as tunable diode laser spectroscopy) has been developed and applied to the measurement of NO and N_2O emissions from passenger cars and light-duty trucks (*30*−*32*). This is the most sensitive on-road remote sensing technique reported to date. This paper presents the results of a study in which the TILDAS technique was adapted to remote sensing of heavy-duty diesel truck emissions. The goals of this study were to demonstrate the application of this technique to HDDTs and to clarify some of the outstanding questions about their NO_x emissions.

Experimental Section

In this study a TILDAS remote sensor was used to measure the emissions of heavy-duty diesel trucks. The details of this technique have been described elsewhere (*32*). Briefly, a TILDAS instrument measures pollutant emissions from vehicles by sending beams of infrared laser light across the road and back while measuring the transmitted light with an infrared detector. The column density of a given species is determined by fitting the spectral dependence of the transmitted light to a Lorentzian line shape. In this study, two spatially overlapped, temporally multiplexed lead-salt mid-infrared lasers were used to determine the column density of NO and CO_2 (or NO and NO_2) in the exhaust plume of a given vehicle. The NO emission index of a vehicle is determined from the ratio of the column density of NO to that of CO_2. A correction is necessary if the amounts of CO and hydrocarbons in the exhaust are significant, which is generally not the case for HDDTs (*11, 23, 25*).

Some modifications of the optical setup used for automobiles were necessary in order to adapt the TILDAS technique to the remote sensing of emissions from heavy-duty diesel trucks. The exhaust pipe of most heavy-duty trucks in the U.S. terminates as a vertical stack located immediately behind the tractor cab discharging exhaust gas to the atmosphere at a height of about 3.3−3.6 m above the roadway. The trailer height may exceed the exhaust discharge height and can be as high as 4.3 m. The TILDAS laser beam was therefore elevated to a height of about 4.4 m in order to traverse the exhaust gases while avoiding blockage by the truck's trailer. Another difference between the experimental configurations used with HDDTs and light duty vehicles is that the light duty vehicle emissions measurements are automatically triggered by the signal interruption associated with the passing of the vehicle. A spectrum acquired before the interruption is used as a reference spectrum to reduce noise and to account for background absorption. Since the HDDTs do not block the laser beam, triggering was accomplished manually. This approach worked well, and background corrections were accomplished in the usual manner. The alignment of the optical system is facilitated by a visible HeNe laser which is coaligned with the infrared laser beam. The experimental setup is shown in Figure 1.

We carried out a measurement campaign in the Raleigh−Durham area of North Carolina on June 16−19, 1997. This work was carried out in collaboration with the heavy-duty

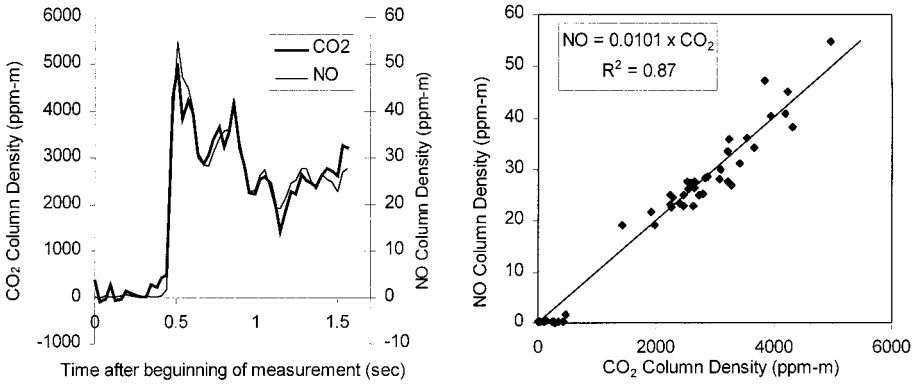

FIGURE 2. Single remote sensing measurement of the EPA instrumented truck: (left) NO and CO_2 column densities vs time and (right) NO vs CO_2 regression. This measurement was made across a four-lane highway (NC-54) with a total optical path length of 88 m.

diesel research group from the EPA Emissions Characterization and Prevention Branch based at Research Triangle Park, NC. This group has instrumented a heavy-duty trailer with a system to measure and record the gas composition and several other parameters (*33*). The tractor used during the measurements described in this paper was a 1990 Kenworth equipped with a 60 Series Detroit Diesel Engine (with a displacement of 12.7 L). This engine was certified at about 6.5 gr/bhp-h NO_x or about 0.010 NO_x/CO_2 (using the conversion factor in ref *15* and the fuel properties and fuel economy in ref *4*).

Four experiments were performed in four consecutive days and are described in the next section. This comprised measurements (1) across a four-lane highway to demonstrate the long optical path length of the TILDAS remote sensor; (2) of the EPA instrumented heavy-duty truck exhaust to verify the accuracy of the remote sensor; (3) across a two-lane interstate highway to obtain a distribution of the emissions from random trucks at high-speed cruise; and (4) of the EPA instrumented HDDT to demonstrate the capability of measuring the NO_2/NO emission ratio.

Results and Discussion

Demonstration of Long Optical Path Length. NDIR-based instruments can operate with very limited cross-road path lengths due to the angular dispersion of their nonlaser light, and because the absorption due to relatively large background CO_2 levels decreases the signal-to-noise ratio of their CO_2 measurement (*34*). The longest path lengths reported with this type of instrument are 12−15 m (*34, 35*). Bishop and Stedman (*26*) report in a recent description of their NDIR-NDUV instrument that "the system is designed to operate on a single lane road... Multiple lane operation has been reported but is not recommended". Near-infrared TILDAS systems specify total path lengths of up to 36 m; however, they are about 50 times less sensitive for NO_x than the mid-infrared TILDAS system used here (*28, 32*).

A long path length is of interest since it allows greater flexibility in the placement of the sensors. One example is sampling across multilane highways, although for heavy traffic conditions this introduces the need to detect and discard the measurements for which several vehicles are driving by the sensor simultaneously in different lanes. Some studies also suggest that drivers change their behavior while driving in front of a remote sensor. Walsh and Gertler (*36*) found that for those light-duty vehicles with one high and one low remote sensing measurement, the first measurement was the high one in 60% of the cases. They suggest that motorists may have become aware of the remote sensing device after the first pass and may have altered their driving in response. A longer path length could avoid this problem since the instrument could be moved farther off the road and made less visible. It would also diminish associated concerns of motorist and operator safety, which greatly limit the selection of remote sensing sites (*36*), and of vandalism of unmanned remote sensors.

To demonstrate the long path capabilities of the TILDAS technique, measurements were made across a four-lane highway (NC-54) with a total optical path length of 88 m. Figure 2 shows the NO and CO_2 column densities vs time and a regression plot from such a measurement. The NO and CO_2 signals are highly correlated. Only a minor degradation in signal-to-noise is observed compared to shorter path lengths. This is the longest path length which has been demonstrated with any on-road remote sensor.

During this experimental campaign we observed systematic deviations in the first one or two data points of some measurements. We believe that this deviation was caused by the measurement of unmixed relatively hot plumes very near the exhaust outlet. The deviation was always in the same direction and consistent with the relative variation of the line strenghts of NO and CO_2 with source gas temperature. High gas temperature also induces small variations in the widths of the absorption lines, which were also observed in these cases, providing additional evidence for this explanation. A more sophisticated analysis than we used in this work is required to account for these temperature effects and will be implemented in future measurements. In this case we simply rejected those data points at the beginning of the plume which were clear outliers. Such effects could also complicate the interpretation of the results of other remote sensing techniques. This effect was rare in our previous measurements of light duty vehicle emissions (*30*).

Comparison with On-Board Instrumentation. A series of emissions measurements were performed in the parking lot of the EPA facility with the intention of comparing the results from the NO remote sensor and the on-board instrumentation of the EPA heavy-duty diesel truck under low speed (20 mph) conditions. The parameter chosen for the comparison is the NO_x/CO_2 ratio. Expressing the emission index in this way avoids the problem of determining the air-to-fuel ratio in the diesel engine which, unlike gasoline engines, can vary by more than a factor of 2 (*11*). The TILDAS remote sensor measures NO/CO_2 directly, but the EPA instrumented truck measured NO_x/CO_2 during this intercomparison. The NO/CO_2 ratio produced by the TILDAS instrument was converted to NO_x/CO_2 using the average of the NO_2/NO ratios measured with the TILDAS instrument for this same truck (described below).

The comparison of both sets of measurements is shown in Figure 3. Although a wider range of emission ratios would have been desirable for this test, the available HDDT

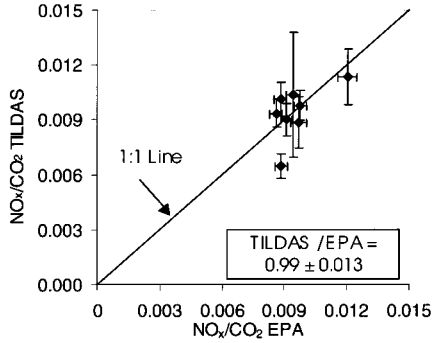

FIGURE 3. Comparison of the EPA and TILDAS NO_x/CO_2 ratios for eight measurements of the emissions of the EPA instrumented heavy-duty diesel truck.

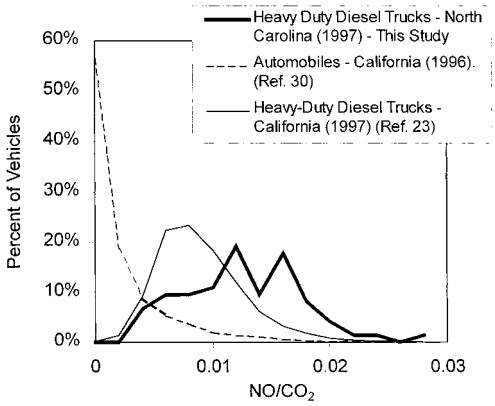

FIGURE 4. Comparison of the distribution of the NO/CO_2 emission ratios measured with the TILDAS instrument for automobiles and light-duty trucks (*30*) and heavy-duty diesel trucks (this study), and also for HDDTs with a NDIR−NDUV instrument (*23*).

produced a very constant emission level. Seven out of 8 measurements are within the 95% confidence interval of the 1:1 line (which would represent perfect agreement between both instruments). The one anomalous measurement is probably due to delays in the EPA truck's sampling system and analyzers during transients in speed and acceleration at the remote sensing site, which were observed in the record of the on-board analyzers. Most of the measurements are close to the certification level estimated for this vehicle of 0.010 NO_x/CO_2. Note that the uncertainty of each TILDAS measurement is different, varying with the overlap between the exhaust plume and the laser beams during a given pass, as described previously (*32*).

Distribution of Emissions from Random Diesel Trucks. We measured the NO/CO_2 ratios of random heavy-duty diesel trucks driving along interstate highway I-40 near Research Triangle Park, NC. The TILDAS instrument was located inside the Aerodyne Mobile Laboratory parked on the grass beyond the breakdown lane. The retroreflector was located in the median strip. All of the trucks were driving at undisturbed interstate speeds in low-density traffic. The estimated speeds were in the range 55−70 mph. The grade at the measurement site was +2.1%. Only the largest trucks ("heavy-heavy duty" or "18-wheelers") were measured, smaller trucks were excluded. At this site the optical system was subject to strong cross winds and radiation loading which caused drifts in the alignment of the open path portion of the optical system. A more robust mounting arrangement will be used in the future. We attempted to compensate for these drifts with frequent realignment, but this problem still caused a number of distinctly noisy measurements. These measurements were identified by their poor correlation between NO and CO_2 column density and were rejected.

Measurements of NO/CO_2 for 73 HDDTs were obtained at this location. The distribution of NO/CO_2 emissions for these measurements is presented graphically in Figure 4, together with the distribution measured for cars and light-duty trucks (LDTs) in California in 1996 using the same TILDAS instrument (*30*). Some statistics of both distributions are presented in Table 1. The distribution of NO emissions from HDDTs resembles a normal distribution, while the car and LDT distribution is very skewed, with most of the readings clustered at very low NO/CO_2 values. Differences between individual HDDTs are small as indicated by a ratio of maximum to minimum emission of 6.5, as compared to about 750 for cars and LDTs. The HDDT distribution has a much larger average value; however, the maximum values of both sets of measurements are very similar. The dirtiest 10% of cars and LDTs contributed 50% of the NO emissions for these vehicles, while the dirtiest 10% of the HDDTs only contributed 17% of the total HDDT emissions. From the other side, the cleanest 50% of cars and LDTs were responsible for only 4% of the NO emissions, while the cleanest 50% of HDDTs contributed 32% of the total emissions. These differences are very important since they imply that the concepts of "super-emitters" and "clean vehicles" that are applicable for catalyst-equipped vehicle emissions are not appropriate for heavy-duty diesel truck NO_x emissions. This is in qualitative agreement with the results of chassis dynamometer studies (*18*, *20*). A consequence of this result is that inspection and maintenance programs for HDDT NO_x cannot be designed to exclude a large fraction of the fleet ("clean-screening") or to repair broken "super-emitters", as is often done for light-duty vehicles. Strategies that deal with the whole fleet such as stricter emission standards and reformulated diesel fuel are necessary for reducing these emissions.

Figure 4 also shows the distribution of NO/CO_2 emissions from HDDTs measured in another 1997 study in California using an NDIR-NDUV remote sensor by Countess et al. (*23*). The distribution measured by the TILDAS remote sensor has a larger average and is less skewed than the one from the California HDDT study. However, the two distributions have a similar shape, span the same range of values, and are very different from the automobile distribution in the ways described above. The difference between the two HDDT remote sensing distributions may be partially due to differences in driving conditions. The nearest entrance into the highway in our HDDT study was about 6 miles before the measurement location or about 5−7 min of high speed steady state driving. It is likely that most vehicles had been driving considerably longer. Under these conditions the "defeat device" described above would have been activated in those vehicles that had it, resulting in higher emissions. The HDDTs in the California study were leaving a weighing station after a low speed transient, and the enabling of the "defeat device" is highly unlikely to have occurred there. Another possible reason is differences in the HDDT fleets. For example, Countess et al. report that trucks with in-state registration and dump trucks had higher NO emissions than out-of state trucks, indicating an effect of fleet composition, age, and/or maintenance on emissions.

The differences between the automobile and the HDDT distributions in Figure 4 are traceable to the differences in NO_x production and control between light-duty gasoline vehicles and heavy-duty diesel trucks. The flame region in diesel engines inherently combines near-stoichiometric and high-temperature conditions, which result in significant NO_x formation. This, together with a lack of a catalyst explains why there are no measurements near zero and the relatively large emissions of all vehicles. The chemical mechanism of NO formation for gasoline (or "spark ignition") engines is the same as for diesel engines described above. However, the combustion process in a traditional gasoline engine is

TABLE 1: Summary of Statistics for the Distributions of NO/CO_2 Ratios Measured for Heavy-Duty Trucks and Automobiles and Light-Duty Trucks[a]

	heavy-duty diesel trucks	automobiles and light-duty trucks	HDDT/ autos
number of vehicles	73	1473	
average	12.5×10^{-3}	2.4×10^{-3}	5.2
standard deviation	4.9×10^{-3}	4.0×10^{-3}	1.2
median	12.4×10^{-3}	0.7×10^{-3}	18
maximum	27.2×10^{-3}	28.6×10^{-3}	0.95
minimum	4.2×10^{-3}	0.037×10^{-3} [b]	113
max/min	6.5	751[c]	0.009
skewness	0.33	2.80	0.1
% of emissions due to the 10% dirtiest vehicles	17%	50%	0.34
% of emissions due to the 50% cleanest vehicles	32%	4%	8.0

[a] For both gasoline and diesel vehicles the exhaust concentration of NO in the exhaust gases (including water vapor) can be approximated as NO (ppmv) $\cong NO/CO_2 \times 135\,000$ (multiply by 154 000 for concentration in the dry gases). These concentrations have been corrected to the amount of air present at stoichiometric conditions; actual concentrations will be significantly lower for diesel vehicles. [b] TILDAS precision of ~5 ppm NO, which is of the order of the emisssions of the cleanest light-duty vehicles (*27, 30, 32*). [c] Estimated as (maximum value)/(TILDAS detection limit).

very different than that of a diesel engine (*11*). In a gasoline engine, air and fuel are premixed and combustion is started by a spark. The composition is close to stoichiometric and homogeneous across different locations in the cylinder. NO forms in the high-temperature burned gases during combustion and is "frozen" by the cooling brought about by the expansion of the cylinder. This type of engine can generate from very low to about 3000 ppm NO_x (22.4×10^{-3} NO_x/CO_2) depending mainly on power demand, since flame temperature scales with this parameter (*11*). The main control technology for gasoline engine NO_x emissions is the three-way catalyst (*8, 10, 11, 37*), which when warmed-up reduces engine-out emissions by about 90%, to levels below about 300 ppm (2.2×10^{-3} NO_x/CO_2). For this reason the emission distribution for cars and light-duty trucks is clustered at low emission values. Higher emission levels, unlikely but possible in properly functioning vehicles (*38*) and common for the small fraction of vehicles with malfunctioning emission control systems, result in the long tail of higher emissions and a very skewed distribution. Additional support for this explanation comes from remote sensing data showing that the emission distributions of catalyst cars were much more skewed than those of noncatalyst cars (*39*) and from dynamometer data that show the same difference between the distributions of catalyzed and engine-out emissions (*38*).

Remote Sensing of the NO_2/NO Ratio. Although most of the NO_x emitted by heavy-duty diesel trucks is in the form of NO, a nonnegligible fraction may be present as NO_2 (*11, 40*). The NO_2 fraction is much smaller for gasoline engines (*11*). NO_2 is primarily formed in hot gases by the reaction of NO with the HO_2 radical and is subsequently converted back to NO very quickly via reactions with the O or H radicals (*11, 41*). NO_2 can persist if the decomposition reactions are quenched by mixing with cooler gases. This situation is expected to occur in diesel engines due to the large amount of excess air present in the cylinder but not in spark-ignition engines (*11*), consistent with observations.

During this project the TILDAS instrument was adapted to the simultaneous measurement of NO and NO_2 emissions from HDDTs. A diode laser was used to detect NO_2 by scanning across a group of 24 transitions at a frequency of 1605 cm^{-1} (6.2 μm). NO was measured by scanning the same group of transitions used for the NO/CO_2 measurements at a frequency of 1900 cm^{-1} (5.3 μm). Figure 5 shows both absorption features as detected in a HDDT plume. The shape of the absorption features detected for NO and NO_2 was the same for a reference cell containing both gases and for HDDT exhaust, indicating that no detectable interfering species were present.

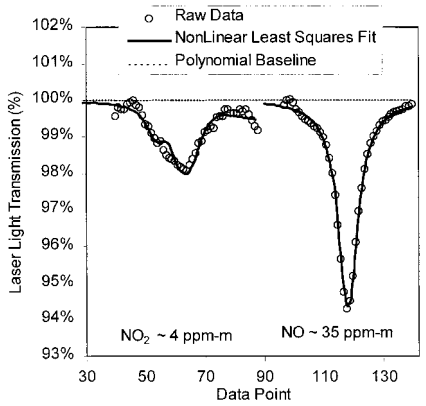

FIGURE 5. Simultaneous NO_2 and NO spectra recorded by remote sensing of the exhaust of the EPA instrumented truck. Also shown is a nonlinear least-squares fit that takes into account the known spectral parameters of the absorption lines.

The time-domain and NO_2 vs NO regression plot of a remote sensing measurement of the EPA instrumented truck are presented in Figure 6. The close correlation of the two signals is a demonstration of the capacity of the TILDAS technique to measure the NO_2/NO ratio in heavy-duty truck exhaust. To our knowledge, this is the first time that on-road remote sensing of NO_2 has been accomplished. Note that in the time domain plot, the signal-to-noise ratio (SNR) is worse for NO_2 than for NO. This is due to the lower column density of NO_2. Since to a first approximation the absolute noise level is similar for both species (of the order of 0.5 ppm-m for this particular measurement) and the signal is about 10 times stronger for NO, the SNR is also about 10 times larger for this species. Temperature effects such as those observed for some NO/CO_2 measurements are of minor importance in the NO/NO_2 measurement since the NO and NO_2 absorption transitions used have very similar temperature dependence. No deviation was observed in any of the time domain or regression plots.

The measured NO_2/NO_x volume (molar) ratios range from 5.6% to 10.9 vol %. The average ratio for the five measurements performed for the EPA instrumented truck was 7.8% ± 2.2%. No comparison can be made with the on-board instrumentation of the EPA truck in this case since the on-board system is not appropriate for NO_2 quantification (*42*). Hilliard and Wheeler (*40*) reported NO_2/NO_x volume ratios

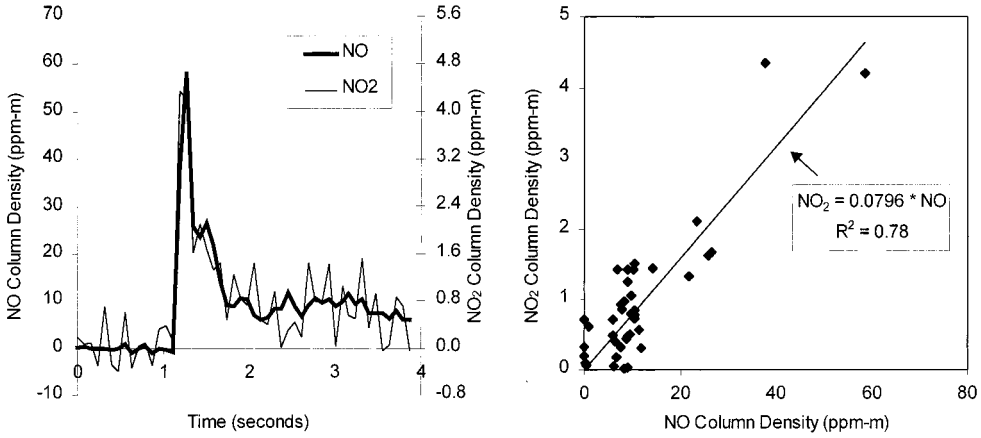

FIGURE 6. Single remote sensing measurement of the EPA instrumented truck: (left) NO and NO_2 column densities vs time and (right) NO_2 vs NO regression.

TABLE 2: Comparison of the Heavy-Duty Diesel Truck NO_x Emission Factor Obtained in This Study with Those of Other Studies[a]

location/reference	year	method	NO_x emission factor (g of NO_x as NO_2/kg of diesel fuel)
U.S.A. (*18*)	1976−1997	review of chassis dynamometer data	35−38
West Virginia (*20*)	1995	chassis dynamometer	46
Colorado (*19*)	1999	chassis dynamometer	39 ± 2
Pennsylvania (*21*)	1992	tunnel study	39 ± 3
Maryland (*21*)	1992	tunnel study	uphill: 37 ± 4 downhill: 34 ± 2
Canada (*22*)	1995	tunnel study	48 ± 17
California (*4*)	1997	tunnel study	42 ± 5
North Carolina (this study)	1997	remote sensing	45 ± 2
California (*23*)	1997	remote sensing	31 ± 0.2
Colorado (*24*)	1998	remote sensing	53
Texas (*25*)	1998	remote sensing	21 ± 2

[a] The diesel fuel properties and HDDT fuel economy reported in ref *4* were used to convert the emission rates reported in the different studies into g/kg fuel.

of 2−30% for diesel engine exhaust. Higher NO_2 fractions were measured at low engine loads and speeds, which can be explained by the higher likelihood of NO_2 quenching due to the larger fraction of air in the cylinder (*11*). Harris et al. (*43*) measured NO_2 concentrations in the range of 0.4−33 ppmv of diesel exhaust with a low-pressure sampling TILDAS system but did not report NO_2/NO_x ratios. They do report higher NO_2 concentrations at low loads, in agreement with the results of Hilliard and Wheeler. Clark et al. (*17*) operated several diesel engines in steady-state conditions on an engine dynamometer and found NO_2/NO_x mass ratios which correspond to volume ratios of 1.5%−12.5%. The same authors also reported some results from testing diesel buses on a chassis dynamometer on the Central Business District cycle and found NO_2/NO_x volume ratios of up to 2.7%. The trends with speed and load were consistent with those of Hilliard and Wheeler. The 5.6−10.9% range that we measured with the TILDAS instrument while the EPA instrumented truck was operated at about 20 mph under mild acceleration is consistent with these literature studies.

Estimation of the NO_x Emission Factor for Heavy-Duty Diesel Trucks. The on-highway NO and NO_x emission factors for heavy-duty diesel trucks can be estimated from the average of the measurements taken on interstate highway I-40. Although this study has a small sample size of 73 vehicles and a single operating condition, a reasonable emission factor can still be determined since heavy-duty truck NO_x emissions (per unit fuel) have been shown to be relatively insensitive to vehicle power demand under high-speed cruise conditions (*21*), and the normality of the distribution allows the determination of an approximate average from a smaller sample than with a skewed distribution. The quantity determined directly from our measurements is the NO emission factor. To estimate the NO_x emission factor we assumed that the average NO_2/NO_x ratio of the fleet was equal to the average of the EPA instrumented truck that we measured by remote sensing. Since there could be some variability in the NO_2/NO_x ratio for different trucks this assumption introduces some additional uncertainty. The average NO_x/CO_2 ratio was found to be 0.0136 ± 0.008, while the emission factor is estimated at 45 ± 2 g of NO_x (as NO_2) per kg of diesel fuel.

This value has been compared in Table 2 to the values obtained in other studies in North America. There is no clear trend of emissions with the year, location of the study, or speed and/or roadway grade of the measurements. The average of all the studies is 39.3 ± 2.4 g NO_x/kg fuel (40.6 ± 3.6 if only studies since 1995 are included in the average). The value reported in this study is 15% higher than the average of all studies. As explained above the location of our study is likely to have selected for higher NO_x emissions due to the operation of the "defeat devices". The other three remote sensing experiments reported the two lowest and the one highest emission factors of all 12 studies. Those studies were conducted at two HDDT highway weigh stations (*23*, *25*) and at the exit of an industrial distribution center (*24*) respectively. At these locations vehicles were operated under relatively low speed transient driving conditions, and the "defeat devices" were most likely disabled. This should have resulted in lower emissions consistent with two of the studies. The

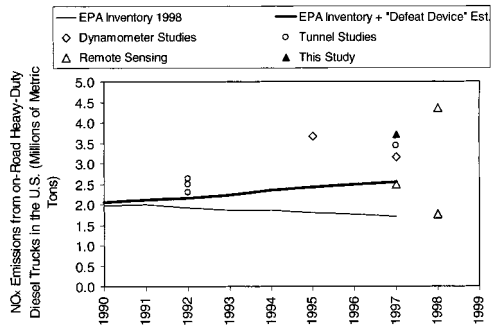

FIGURE 7. Total NO_x emissions in the U.S. from on-road heavy-duty diesel trucks for the period 1990−1998, showing the EPA inventory and the estimates from the on-road emission factors in Table 2 (except the Canadian study).

reason for the very high emissions in the remote sensing study performed in Golden, CO (*24*) is not clear. Some possible reasons include the high altitude of the site (1800 m), differences in engine load and speed with respect to the other sites, and the particular vehicle fleet. Further research is needed to clarify the origin of the differences between the recent studies.

Contribution to the NO_x Inventory in the U.S. Figure 7 shows the EPA HDDT NO_x inventory for the U.S. between 1990 and 1997 (*44*) and the total inventory including the increase estimated by EPA due to the effects of the "defeat device" (*15*). Also shown are the inventories derived from the emission factors in Table 2 using the annual U.S. fuel consumption for diesel trucks (*45*), the fraction of heavy-duty trucks among diesel trucks (*44*), and the fuel properties (*4*). The figure shows a consistent underestimation of these emissions by EPA, which is only partially explained by the "defeat device" correction. It also highlights the variation in the most recent measurements.

Acknowledgments

The authors are grateful to Larry Jones, Bruce Harris, and Foy King of EPA and Edward Brown of Acurex Environmental Corp. for their collaboration with the EPA instrumented heavy-duty diesel truck and for useful discussions during data analysis. We also thank Dr. Robert Slott of the M.I.T. Energy Laboratory, Professors John Heywood and Ahmed Ghoniem of the M.I.T. Mechanical Engineering Department, and Dr. Brett Singer of Lawrence Berkeley National Laboratory for their comments on this work. The financial support of the EPA Office of Research and Development (STAR program; grant number R824794-01-0) is gratefully acknowledged

Literature Cited

(1) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; John Wiley and Sons: New York, 1998.
(2) Sawyer, R. F.; Harley, R. A.; Cadle, S. H.; Norbeck, J. M.; Slott, R.; Bravo, H. A. *Atmos. Environ.*, in press.
(3) Dreher, D. B.; Harley, R. A. *J. Air Waste Manage. Assoc.* **1998**, *48*, 352−358.
(4) Kirchstteter, T. W.; Harley, R. A.; Kreisberg, N. M.; Stolzenburg, M. R.; Hering, S. V. *Atmos. Environ.* **1999**, *33*, 2955−2968.
(5) Control of Emissions of Air Pollution From Highway Heavy-Duty Engines; Final Rule. *40 Code of Federal Regulations*, Parts 9 and 86, *Fed. Regist.* **1997**, *62*(203).
(6) Control of Emissions of Air Pollution From 2004 and Later Model Year Heavy-Duty Highway Engines and Vehicles; Revision of Light-Duty Truck Definition; Proposed Rule. *40 Code of Federal Regulations*, Parts 85 and 86, *Fed. Regist.* **1999**, *64*(209).
(7) U.S. EPA. *Regulatory Announcement: Proposed Strategy to Reduce Emissions from Heavy-Duty Vehicles*; Report EPA 420-F-99-034, U.S. EPA: Ann Arbor, MI, 1999.
(8) Kummer, J. T. *Prog. Energy Combust. Sci.* **1980**, *6*, 177−199.
(9) Heimrich, M. J. *J. Eng. Gas Turb. Power.* **1996**, *118*, 668−672.
(10) Bhattacharyya, S.; Das, R. K. *Intl. J. Energy Res.* **1999**, *23*, 351−369.
(11) Heywood, J. B. *Internal Combustion Engine Fundamentals*; McGraw-Hill: New York, 1988.
(12) Herzog, P. L.; Burgler, L.; Winklhofer, E.; Zelenka, P.; Cartellieri, W. *Soc. Automot. Eng. Technol.* **1992**, Paper 920470.
(13) Glover, E. Personal Communication. U.S. EPA.: Ann Arbor, MI, 2000.
(14) Diesel Engine Test Cycle. *40 Code of Federal Regulations,* Part 86, Section 336−79, **1999**.
(15) Glover, E. L. *Development and Use of Heavy-Duty NOx Defeat Device Emission Effects for MOBILE5 and MOBILE6*; Report EPA 420-P-99-030; U.S. Environmental Protection Agency: Washington DC, 1999.
(16) Whitfield, J. K.; Harris, D. B. Comparison of Heavy-Duty Diesel Emissions from Engine and Chassis Dynamometers and On-Road Testing. In *Eighth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1998; Coordinating Research Council: Atlanta, GA.
(17) Clark, N. N.; Nine, R. D.; Daley, J. J.; Atkinson, C. M.; Peerenboom, W. H.; Suski, V. A. Heavy-Duty Truck Emissions: Vehicle Activity, Driving Routes, and NO_2/NO Ratios. In *Eighth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1998; Coordinating Research Council: Atlanta, GA.
(18) Yanowitz, J.; McCormick, R. L.; Graboski, M. S. Emissions from On-Road Heavy-Duty Diesel Vehicles: a Review of Data from Dynamometer, Tunnel, Remote Sensing, and Idling Studies. In *Ninth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1999; Coordinating Research Council: Atlanta, GA.
(19) Yanowitz, J.; Graboski, M. S.; Ryan, L. B. A.; Alleman, T. L.; McCormick, R. L. *Environ. Sci. Technol.* **1999**, *33*, 209−216.
(20) Atkinson, C. M.; Clark, N. N.; Lyons, D. W. An Estimation of the Comparative Contribution of Heavy-Duty Diesel Buses and Trucks to Mobile Source Emissions. In *Sixth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1996; Coordinating Research Council: Atlanta, GA.
(21) Pierson, W. R.; Gertler, A. W.; Robinson, N. F.; Sagebiel, J. C.; Zielinska, B.; Bishop, G. A.; Stedman, D. H.; Zweidinger, R. B.; Ray, W. D. *Atmos. Environ.* **1996**, *30*(12), 2233−56.
(22) Rogak, S. N.; Pott, U.; Dann, T.; Wang, D. *J. Air Waste Manage. Assoc.* **1997**, *48*, 604−615.
(23) Countess, R.; Cohen, L.; Countess, S. J.; Bishop, G. A.; Stedman, D. H. Remote Sensing of Heavy-Duty Diesel Truck Exhaust. In *Eighth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1998; Coordinating Research Council: Atlanta, GA.
(24) Countess, R.; Countess, S. J.; Cohen, L. Remote Sensing of Heavy-Duty Diesel Trucks Revisited. In *Ninth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1999; Coordinating Research Council: Atlanta, GA.
(25) Morris, J. A.; Bishop, G. A.; Stedman, D. H.; Maly, P.; Scherer, S.; Countess, R. J.; Cohen, L. H.; Countess, S. J.; Romon, R. Remote Sensing and Comparison of Emissions from Heavy-Duty Diesel Trucks. In *Ninth CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1999; Coordinating Research Council: Atlanta, GA.
(26) Bishop, G. A.; Stedman, D. H. *Acc. Chem. Res.* **1996**, *29*, 9(10), 489.
(27) Popp, P. J.; Bishop, G. A.; Stedman, D. H. *J. Air Waste Manage. Assoc.* **1999**, *49*(12), 1463−1468.
(28) MD Lasertech World Wide Web Site. http://www.md-lasertech.com, Accessed Feb 15, 2000.
(29) Bishop, G. A.; McLaren, S. E.; Stedman, D. H.; Pierson, W. R.; Zweidinger, R. B.; Ray, W. D. *Atmos. Environ.* **1996**, *30*(12), 2307−16.
(30) Jiménez, J. L.; Nelson, D. D.; Zahniser, M. S.; Koplow, M. D.; Schmidt, S. E. *J. Air Waste Manage. Assoc.* **1999**, *49*, 463−470.
(31) Jiménez, J. L.; McManus, J. B.; Nelson, D. D.; Zahniser, M. S.; Koplow, M. D.; McRae, G. J.; Kolb, C. E. *Chemosphere: Global Change Sci.*, in press.
(32) Nelson, D. D.; Zahniser, M. S.; McManus, J. B.; Kolb, C. E.; Jiménez, J. L. *App. Phy. B: Lasers Optics* **1998**, *67*(4), 433−441.
(33) Harris, D. B.; King, F. G. Development of On-Road Emission Factors for Heavy-Duty Diesel Vehicles Using a Continuous Sampling System. In *AWMA-EPA Conference: The Emission Inventory, Program and Progress*; Research Triangle Park, NC, 1995; Air and Waste Management Association: Pittsburgh, PA.
(34) *Feasibility Study for the Use of Remote Sensors to Detect High Emitting Vehicles*; Technical Report; Hughes Environmental Systems, Inc.: Manhattan Beach, CA, 1992.
(35) Stedman, D. H.; Bishop, G. A.; Beaton, S. P.; Peterson, J. E.; Guenther, P. L.; McVey, I. F.; Zhang, Y. *On-Road Remote Sensing*

of CO and HC in California; Technical Report; Chemistry Department, University of Denver: Denver, CO, 1994.
(36) Walsh, P. A.; Gertler, A. W. *Texas 1996 Remote Sensing Feasibility Study*; Technical Report; Desert Research Institute, Reno, NV, 1997.
(37) Koltsakis, G. C.; Stamatelos, A. M. *Prog. Energy Combust. Sci.* **1997**, *23*, 1−39.
(38) Jimenez, J. L. Ph.D. Thesis, Mechanical Engineering Department, Massachusetts Institute of Technology, 1999.
(39) Mercer, A.; McArragher, S. Remote Sensing Measurements of On-Road Emissions in Five European Cities. In *Seventh CRC On-Road Vehicle Emissions Workshop*, San Diego, CA, 1997; Coordinating Research Council, Atlanta, GA.
(40) Hilliard, J. C.; Wheeler, R. W. *Soc. Automot. Eng. Technol.* **1979**, Paper 790691.
(41) Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287−338.
(42) Brown, J. E. Personal Communication. Acurex, Inc.: Research Triangle Park, NC, 1997.
(43) Harris, G. W.; Mackay, G. I.; Iguchi, T.; Schiff, H. I.; Schuetzle, D. *Environ. Sci. Technol.* **1987**, *21*(3), 299−304.
(44) U.S. EPA. *National Air Pollutant Emission Trends Update, 1900−1997*; Report EPA 454/E-98-007; U.S. EPA: Research Triangle Park, NC, 1998.
(45) Davis, S. C. *Transportation Energy Data Book: Edition 17*; Report ORNL-6919; Oak Ridge National Laboratory: Oak Ridge, TN, 1997.

Received for review October 11, 1999. Revised manuscript received February 17, 2000. Accepted March 21, 2000.

ES9911622