

Emissions of nitrogen dioxide from modern diesel vehicles

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Abstract

The traditional on-road emissions remote sensing technique has been enhanced with the ability to monitor not only CO, CO₂, HC and NO, but also SO₂, NH₃ and NO₂. Modern diesel powered vehicles, particularly in Japan and Europe are equipped with diesel particle filters (DPFs). These traps are frequently designed to be self regenerating by means of a prior catalytic oxidation of the exhaust NO to NO₂. Because of this intentional conversion to NO₂, the ratio of NO₂ to NO in modern diesel vehicles is very different from older vehicles. The detailed results of measurements from several thousand vehicles measured in Japan, Austria and Sweden in 2006 and 2007 will be compared to results from the USA where there are very few vehicles equipped with DPFs. The overall picture is vehicles without DPFs in the USA emit between 5 and 10% NO₂ while vehicles with DPFs are often observed at 50% NO₂ by moles. This, together with the overall NO_x reductions has strong negative implications for local photochemical ozone production.

Keywords: nitrogen dioxide, automobile emissions, on-road remote sensing.

1 Introduction

In his review of diesel exhaust emissions control strategies, Lemaire [1] suggests that nitrogen dioxide (NO₂) was forgotten as a separate component of the NO_x emissions from diesel vehicles. He further suggests that this omission has caused the observed increases in NO₂ and ozone in a number of cities in Europe. For instance, he shows a very strong correlation between the imposition of diesel particle filters (DPFs) on London buses with the increase in the NO₂/NO_x ratio in London. Carslaw *et al.* [2] draw the same conclusion.



The DPF is an extremely effective means to achieve particle reduction goals. However, these traps are bound to become clogged with carbon particles in normal use and must be regenerated in order to maintain a useful in-service lifetime. The most economical method of regeneration makes use of the fact that NO_2 can oxidize carbon (soot) to gaseous products (CO and CO_2) at typical diesel exhaust system temperatures. This regeneration is however not adequate with the normal NO_2/NO_x ratio in diesel exhaust (between 6% and 9% [3]). As a result, an intentional catalytic conversion of NO to NO_2 , using the excess oxygen from the engine, is carried out in the exhaust system of these DPF equipped vehicles in order to enhance the NO_2/NO_x ratio. Some diesel vehicles not equipped with DPF, nevertheless are equipped with an oxidation catalyst which also has the effect of increasing the NO_2/NO_x ratio.

The reasons for concern about nitrogen dioxide emissions arise in part from observations of ambient air concentrations in urban core areas [2]. These observations generally show decreasing concentrations of total NO_x ($\text{NO} + \text{NO}_2$) but increasing concentrations of NO_2 . Both of these observations, but particularly the NO_2 increase, are of concern to air pollution photochemistry because NO_2 leads directly, through solar photolysis, to ozone formation while NO initially removes ozone in the process of becoming NO_2 . Lowering NO_x concentrations enhances urban ozone [4] while directly emitting NO_x as NO_2 further enhances ozone and many other manifestations of photochemical smog. An attempt to simplify the complexity of these photochemical processes was published by Stedman [5] and in a poster [6]. The two preceding references are available from the web site www.feat.biochem.du.edu and click on "Publications List". Our work and others suggests that modern gasoline powered vehicles emit less than 1% of their NO_x as NO_2 . For instance, Heeb *et al.* measured emissions of twenty Euro III and Euro IV gasoline powered vehicles in a dynamometer based study [7]. Using high-speed sampling and a mass spectrometric analytical method, they arrived at the same conclusion.

1.1 On road remote sensing

On road remote sensing enables fuel-based emission measurements to be made from a very large number of vehicles driving in a real on-road situation. Typically the systems can monitor the emissions of between 3000 and 10000 vehicles per day. The system measures emissions in ratio to fuel burned. Results are frequently reported in gm of pollutant per kg of fuel. The recent development of on-road emission remote sensing for SO_2 , NH_3 and NO_2 is described by Burgard *et al.* [8]. The first two gases are measured in the deep ultraviolet (200-220 nm) using the same diode array spectrometer used for NO at 230 nm. Nitrogen dioxide is monitored by means of its visible absorption at 430 nm using an identical spectrometer but set to monitor at these longer wavelengths. The spectroscopic matrix deconvolution process by means of which these analyses are carried out has been described by Bishop and Stedman [9]. In order to monitor heavy duty diesel vehicles in the USA, the same system which is normally used to monitor passing light duty vehicles in under one second each is



placed upon scaffolding with the optical beam approximately three meters above the ground. A lower level optical trigger is added to initiate plume measurement.

The instrumentation with this new capability has been used on-road in the U.S.A., Japan, Austria and Sweden. In the USA very few diesel vehicles are equipped with either DPF or oxidation catalysts. The comparison study, also reported herein, [10] was carried out on a relatively small fleet of diesel school buses some of which had recently been retrofitted with either DPF or diesel oxygenation catalysts (DOC). Japan, Austria and Sweden, where some of these reported remote sensing observations have been made, have required new model year diesel vehicles to significantly lower their particle emissions using DPF technology.

2 Experimental methods

More than 40,000 measurements were made in Japan in May and June of 2006. We did not obtain vehicle model year (MY), but did obtain a vehicle classification number from the license plate. Vehicles classified in the 100 series are mostly more or less heavy duty diesel vehicles. Vehicles in the 500 series are mostly gasoline fuelled automobiles.

More than 15,000 Measurements were made in Sweden in June 2007 [11] while a similar number of measurements were made in Austria shortly afterwards.



Figure 1: Photograph from Colorado showing the necessary scaffolding and the three calibration cylinders.

Figure 1 shows the instrumentation as set up to monitor truck tractor emissions in Colorado. The three gas cylinders contain the necessary calibration gas mixtures. The main calibration gas cylinder contains CO, CO₂, NO, Propane and SO₂ with the balance nitrogen. The two secondary cylinders contain in one, a known mixture of NO₂, and CO₂ balance air (stored NO₂ is incompatible with both propane and NO) and, in the second, a known mixture of NH₃ and propane in nitrogen because NH₃ and CO₂ are incompatible. All calibration gases are supplied by Scott Specialty Gases of Longmont CO.

3 Results and discussion

Figure 2 shows, in histogram form, the data from the 2006 study in Japan. It is quite noticeable that the gasoline powered vehicles (class 5, mean NO₂ 0.1 and median 0.05 g/kg) have lower NO₂ as well as lower total NO_x than the diesel (class 1, mean NO₂ 1.9 and median 1.4 g/kg) and a very much lower NO₂/NO_x ratio. Several of the diesel trucks emit more than 50% by mass of their NO_x as NO₂. For these comparisons NO_x is given the mass of NO₂ although the majority gas emitted is most often NO.

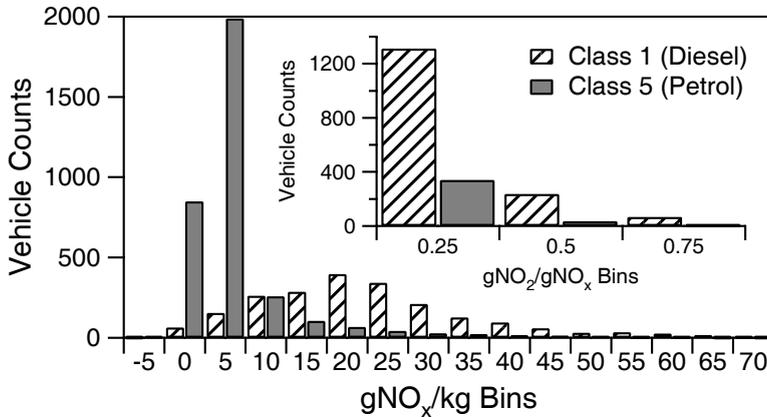


Figure 2: Histogram plots from Japan showing that the class 5 vehicles (cars) have very significantly less NO₂ and NO_x emissions than the class 1 (trucks).

Figure 3 shows a comparison between NO_x emissions from light duty gasoline powered vehicles measured in Sweden [11] and NO_x emissions measured in Denver in the same year [12] and using approximately the same model year groupings. The measured NO₂ emissions (not shown) from both fleets are not statistically distinguishable from zero. A conservative error analysis suggests less than 2%. The other phenomenon, very noticeable from this Figure, is the amazingly successful reduction of NO_x emissions over the about 20 year period shown. This observation is cause for congratulations all round,

because the results not only point to the success of the European and U.S. regulations in reducing automobile emissions, but also to the success of on-road remote sensing in quantitatively demonstrating these phenomena. If the on-road data were significantly contaminated with noise, then these very significant differences would not be observed. The reductions in the U.S., although also dramatic, seem to be somewhat less successful than in Europe over the same time period.

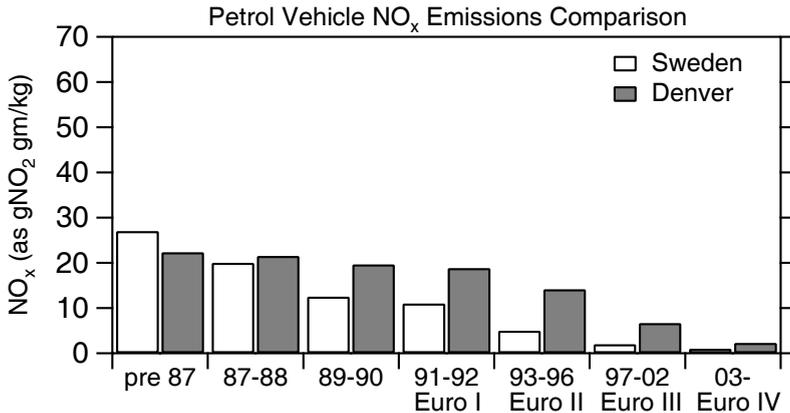


Figure 3: NO_x emissions from petrol (gasoline) light duty vehicles in 2007.

Figure 4 shows NO_x and % of NO_x as NO₂ from medium duty diesel bus vehicles in Sweden compared to a recently reported study from Washington State on retrofitted School Buses [10]. It is very noticeable that the highest NO_x

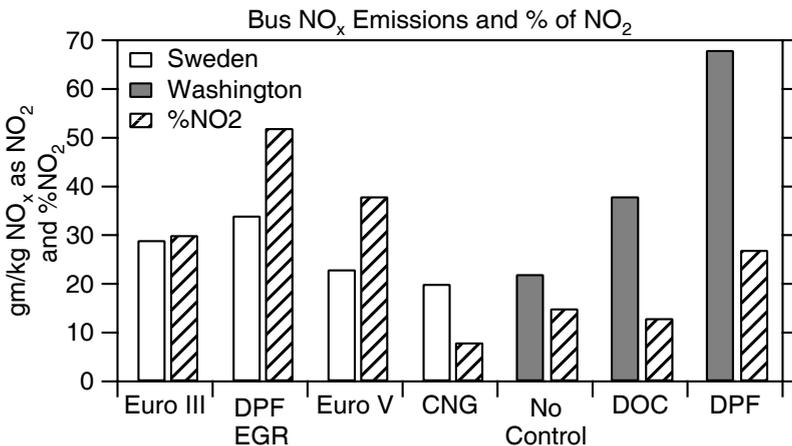


Figure 4: The 2007 NO_x emissions and NO₂ % for buses in the USA and Sweden.



emissions in this entire manuscript (by almost a factor of two) is the DPF equipped school buses in Washington State. It was reported that while the retrofits on these school buses were underway, there were several cases of filter clogging and this caused many of the DPFs to be removed (as worthless) and replaced with DOC on several fleets. This problem may have arisen because the duty cycle on school buses is relatively light load and frequent stops. The system may rarely become hot enough even for NO₂ to regenerate. We speculate that the retrofit contractor, becoming aware of this problem chose to solve it by increasing the NO_x emissions (and possibly the vehicle power) and thus generating enough excess NO₂ that adequate regeneration could take place despite the light duty cycle.

The last Figure 5 shows heavy duty diesel truck NO_x emissions and %NO₂ compared to a U.S. study [3] and shows NO_x and % of NO_x as NO₂ from light duty diesel vehicles in Sweden. Comparing Figures 3 and the last three bars in Figure 5, it is apparent that the modern fleet of light duty diesel vehicles in Europe emit very significantly more NO_x than their gasoline (petrol) fuelled counterparts. Furthermore, a very significant percentage of their emissions is observed to be in the form of NO₂. This is presumably the result of DPF or DOC exhaust aftertreatment equipment on these cars.

It is also apparent from Figures 4 and 5 that, per kg of fuel, the trucks and buses in Sweden do not have very different NO_x emissions although the % of NO₂ is quite different. The Euro 2,3 and 4 standards for the trucks do not seem to have resulted in significant on-road NO_x reductions.

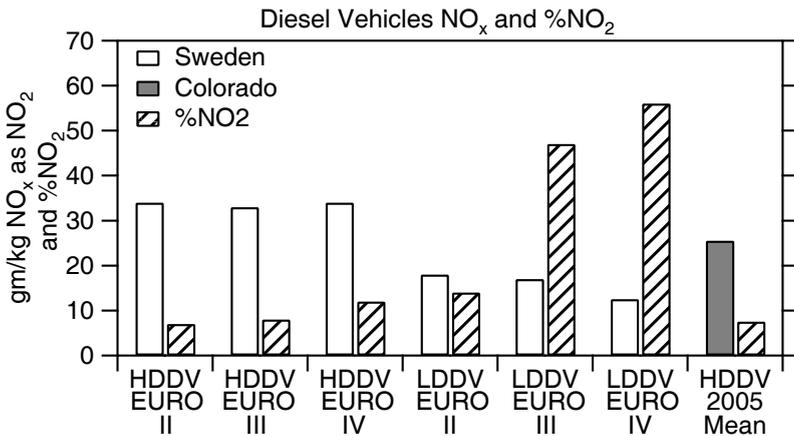


Figure 5: NO_x emissions and % of NO₂ for diesel HDDV and LDDV in Sweden and HDDV in the USA.

The fact that DPF equipped diesel vehicles show evidence of very large NO₂/NO ratios compared to pre-control on-road vehicles is apparent from these data. Our expectation was that the U.S.A. retrofit systems would also have shown evidence of reduced total NO_x emissions. At least in the case of the

Washington State school buses, it seems that the DPF fleet have higher overall NO_x emissions as well as a much larger NO_2/NO ratio.

NO and NO_2 emissions were monitored at three sites in Austria in the summer of 2007. The truck fleet showed relatively low NO_2/NO_x ratios, for instance 50% of the fleet showed a ratio lower than 0.1. Only at the highest load site was the highest 5% of the vehicles measured with $\text{NO}_2/\text{NO}_x > 0.5$. By contrast, and not unlike the situation in Sweden, the 85% diesel car fleet showed very high NO_2/NO_x ratios. At all three sites the top ten percent of the vehicles were all measured with a NO_2/NO_x ratio of above 0.7 and at the highest load site 50% of the whole fleet (gasoline included) were measured above a ratio of 0.5.

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