

# THE IMPORTANCE OF DIRECTLY EMITTED NITROGEN DIOXIDE FROM ROAD VEHICLES TO URBAN AIR QUALITY IN THE UK

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## ABSTRACT

Recent analyses of comprehensive ambient air pollution measurements in London have quantified the proportion of nitrogen oxides (NO<sub>x</sub>) in vehicle exhausts that is emitted as nitrogen dioxide (NO<sub>2</sub>). The analyses show that a greater proportion of NO<sub>x</sub> is emitted directly as NO<sub>2</sub> than previously thought. For the 43 monitoring sites considered, the mean primary NO<sub>2</sub> volume fraction was calculated to be 11.2 %. Emissions of primary NO<sub>2</sub> of this magnitude appear to explain approximately 21 % of measured NO<sub>2</sub> concentrations on average. However, at many congested locations with a high proportion of diesel vehicles, primary NO<sub>2</sub> emissions are thought to explain over 30 % of observed concentrations. For high percentile values of NO<sub>2</sub>, the primary NO<sub>2</sub> contribution can dominate ambient concentrations. These results have implications for the management of air quality in urban areas since it is likely that directly emitted NO<sub>2</sub> would respond differently to NO<sub>x</sub> control measures compared with that chemically produced in the atmosphere. In particular, the source apportionment of NO<sub>2</sub> concentrations can be very different to NO<sub>x</sub> close to roads in London. The results also have implications for dispersion modelling studies of NO<sub>2</sub>, where it is generally assumed that a fixed 5.0 % of the NO<sub>x</sub> emitted by vehicles is in the form of NO<sub>2</sub>. The implications of the increased use of particle traps on the London bus fleet that produce NO<sub>2</sub> to assist in the oxidation of particles is also assessed, together with the potential effects of the London Congestion Charging Scheme.

## INTRODUCTION

In the UK it is projected that many areas will not meet the EU Daughter Directive limit for an annual mean NO<sub>2</sub> concentration of 40 µg m<sup>-3</sup> by 2010. Although there is uncertainty regarding the extent to which areas of London will meet the NO<sub>2</sub> limit, all assessments show that the annual limit for NO<sub>2</sub> will be exceeded at both background and roadside locations [1]. As the area of exceedence reduces there will be an increased interest in the assessment of concentrations close to roads. In the environment close to roads, the characteristics of the emissions source become more important since there is less time available for the NO-O<sub>3</sub> (ozone) reaction to take place and often NO<sub>2</sub> formation is limited by the availability of O<sub>3</sub>. It therefore also becomes important to understand the relative contributions made by primary and secondary NO<sub>2</sub>.

Even though the chemical formation of NO<sub>2</sub> close to NO<sub>x</sub> emission sources follows straightforward and well understood chemistry, the actual amount of NO converted to NO<sub>2</sub> in the ambient environment is difficult to determine in practice. The reaction rate of Equation 1 assumes that NO is fully mixed instantaneously with O<sub>3</sub>, bringing both gases in molecular

contact with one another so that the reactions can take place. However, plumes do not mix instantaneously in ambient air and the efficiency with which they do so is determined by both mechanical and thermal atmospheric turbulence. The timescales of turbulence and NO<sub>2</sub> formation from chemistry through the NO-O<sub>3</sub> reaction are similar and it therefore cannot be assumed that the reaction rate of Equation (1) is relevant to near-field dispersion in an urban area. The reaction rate indicated by Equation 1 maybe erroneous for air masses close to the source where mixing is incomplete. It can be difficult to determine therefore the contribution that NO-O<sub>3</sub> chemistry makes to NO<sub>2</sub> concentrations close to the source.



Given the potential significance of NO<sub>2</sub> for the urban environment, comparatively little work has been carried out to quantify directly emitted i.e. primary emissions of NO<sub>2</sub>. Vehicle emissions legislation in the EU and US set limits for total NO<sub>x</sub>, although a non-negligible proportion is in the form of NO<sub>2</sub>. Several studies have quantified the fraction of NO<sub>x</sub> in the form of NO<sub>2</sub> in vehicle exhausts. Recently the Transport Research Laboratory (TRL) in the UK has conducted several experiments on the primary NO<sub>2</sub> emissions from a small sample of different vehicle types [2]. The TRL work also confirmed that diesel engines have higher NO<sub>2</sub>:NO<sub>x</sub> ratios compared with petrol-engined vehicles. Furthermore, the TRL study showed that higher NO<sub>2</sub>:NO<sub>x</sub> mixing ratios were observed at low vehicle speeds for diesel vehicles.

## **METHOD**

Estimations of the primary NO<sub>2</sub> fraction at 43 different locations in London have been made by Carslaw and Beevers [3]. These estimates were made by considering roadside and background monitoring site pairs and apportioning the observed NO<sub>2</sub> between that generated locally through the NO-O<sub>3</sub> reaction and that derived through the direct emissions from road vehicles. This was achieved by constraining a simple chemical model to describe the difference in NO<sub>2</sub> between a background and roadside location. The approach sought to vary both the primary NO<sub>2</sub> fraction and the time available for the NO-O<sub>3</sub> reaction such that the least error was produced for calculated hourly mean NO<sub>2</sub> concentrations. Fig. 1 shows the error surface based on simulations that vary both the time available for the NO-O<sub>3</sub> reaction to take place and the primary NO<sub>2</sub> fraction for a sub-set of data for Marylebone Road. The minimum error calculated for this data set corresponds to a primary NO<sub>2</sub> fraction of 10.0 % by vol.

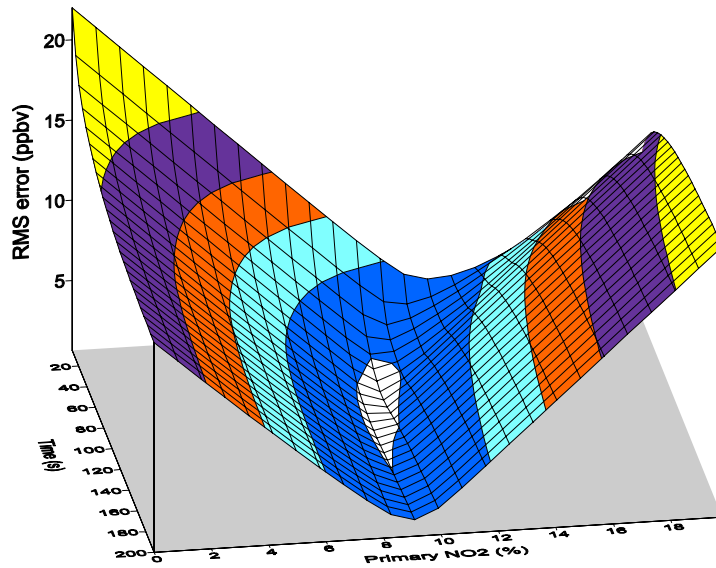


Fig.1 The dependence of the calculated error from fitting measured and fitted  $\text{NO}_x\text{-NO}_2$  relationships on the assumed primary  $\text{NO}_2$  fraction and the time available for chemistry. The error surface related to measurements from Marylebone Road at 9.00am using data between 1998-2002.

## RESULTS AND IMPLICATIONS FOR AMBIENT CONCENTRATIONS OF $\text{NO}_2$

Fig. 2 shows the results from the analysis at 43 roadside locations in London, summarised as a frequency distribution. The mean primary  $\text{NO}_2$  fraction calculated was 11.2 % (range 3.8-22.8 %). The distribution shown by Fig. 2 is close to a Normal distribution (shown by the best-fit line) with an  $r^2 = 0.95$ . The mean primary  $\text{NO}_2$  fraction of 11.2 % by vol. is considerably higher than the 5.0 % commonly used in dispersion modelling studies [1]. Based on these results it is clear that the accuracy of current  $\text{NO}_2$  predictions in the UK could be limited by the current lack of knowledge concerning the temporal and spatial variations in primary  $\text{NO}_2$  from road vehicles in urban areas in the UK. Consequently, there is currently no atmospheric emissions inventory available for primary  $\text{NO}_2$  emissions from road vehicles in the UK.

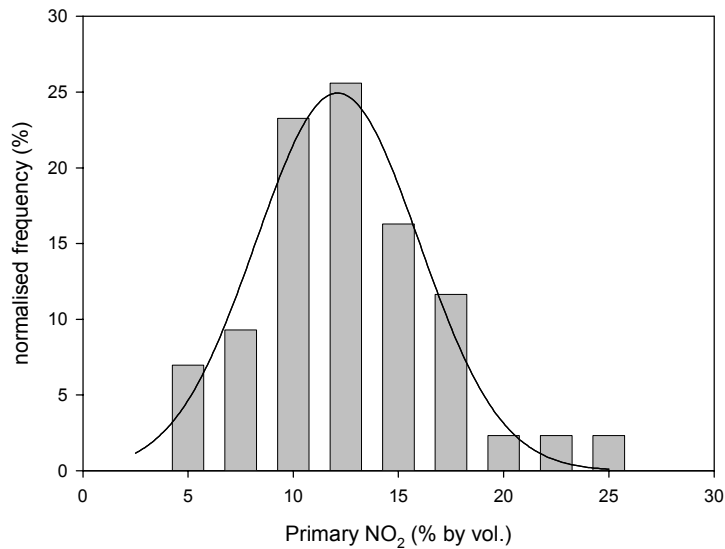


Fig. 2 Histogram of primary NO<sub>2</sub> emission fractions calculated from ambient measurements of NO<sub>x</sub> and NO<sub>2</sub> based on [3]. Also shown is a best-fit curve based on the Normal distribution.

The results from these analyses suggest that primary NO<sub>2</sub> emissions account for a different proportion of total NO<sub>2</sub> concentrations close to roads across the range of NO<sub>x</sub> concentrations. Fig. 3 shows the likely contribution made by NO<sub>2</sub> from three principal origins: a background contribution, a contribution from primary NO<sub>2</sub> emissions and that from the NO-O<sub>3</sub> reaction in the vicinity of the street. Analysis of the results shown in Fig.3 shows that at the Marylebone Road site the mean contribution to measured NO<sub>2</sub> concentrations made by primary NO<sub>2</sub> emissions is 31 %. However, at higher concentrations of NO<sub>x</sub>, the contribution made by primary NO<sub>2</sub> emissions increases. These results therefore suggest that under pollution episode conditions, the contribution made by primary NO<sub>2</sub> emissions becomes more important. For example, if only hourly NO<sub>2</sub> concentrations greater than 200 µg m<sup>-3</sup> are considered, the primary NO<sub>2</sub> contribution increases to 48 %. Clearly, at locations where the primary NO<sub>2</sub> fraction is calculated to be higher than that at Marylebone Road, the contribution could be higher for both the mean concentration and under episode conditions.

In 2001, 31 % of buses operated by Transport for London, which account for an estimated 90 % of total bus vehicle km in London, had been fitted with particle filters including catalysed diesel particulate filters (CDPF) [4]. These filters operate by converting NO to NO<sub>2</sub> in the exhaust and use the NO<sub>2</sub> to assist in the oxidation of particles. The limited amount of emissions data available for vehicles fitted with CDPF suggests that emissions of primary NO<sub>2</sub> can increase. Currently it is not known what effect this could have on atmospheric concentrations of NO<sub>2</sub> close to roads. It is possible however, in some central London locations where bus flows are high that reducing NO<sub>x</sub> emissions over the coming years could be off-set to some extent by increasing emissions of primary NO<sub>2</sub> from such pollution control equipment.

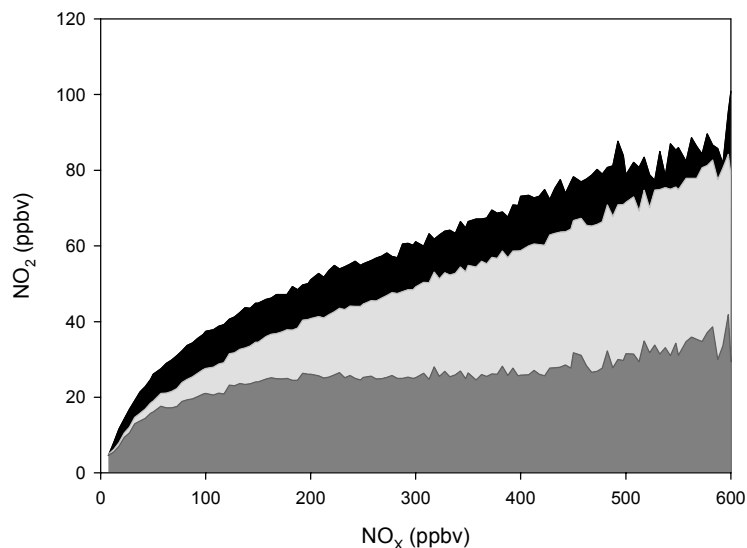


Fig.3  $\text{NO}_x$ - $\text{NO}_2$  relationship for Marylebone Road highlighting the principal contributors to the  $\text{NO}_2$  concentration. The black shading, light grey and dark grey show the estimated contribution from local  $\text{NO}$ - $\text{O}_3$  chemistry, primary  $\text{NO}_2$  emissions and background air (1998-2002).

## CONCLUSIONS

Annual mean concentrations of  $\text{NO}_2$  in excess of EU limit values in London will increasingly be limited to the direct vicinity of roads in London towards 2010. In this environment the characteristics of the emission source can have a large influence on ambient concentrations. In particular, the level of primary  $\text{NO}_2$  emissions is of importance since they can have a direct, significant effect on concentrations of  $\text{NO}_2$  close to roads. The method developed in this study and the results generated from it suggest that the mean primary  $\text{NO}_2$  fraction from vehicle emissions varies widely from 3.2 % to 23.5 % by vol. for different roads in London, with a median value of 10.6 %. Under pollution episodes where the hourly mean concentration is high i.e.  $> 200 \mu\text{g m}^{-3}$ , the contribution made by primary  $\text{NO}_2$  close to roads is much higher than that for an annual mean concentration (ca. 50 % at Marylebone Road for example). Primary  $\text{NO}_2$  emission fractions of this magnitude are much higher than the frequently assumed 5.0 % by vol. used in the prediction of urban  $\text{NO}_2$  concentrations. Consequently, around one third of the measured  $\text{NO}_2$  concentration at many roadside sites in London can be identified as comprising directly emitted  $\text{NO}_2$  from road vehicles. These results have implications for studies of  $\text{NO}_2$  concentrations in London and elsewhere that have assumed a constant 5.0 % by vol. primary  $\text{NO}_2$  fraction since their accuracy will be limited by the current lack of information concerning directly emitted  $\text{NO}_2$  levels. The limited data available on measured  $\text{NO}_2$  emissions from single vehicles also confirms a wide range of primary  $\text{NO}_2$  emission rates. It is clear therefore that primary  $\text{NO}_2$  emissions from road vehicles in an urban area are likely to be highly variable depending on fuel type, vehicle technology and vehicle operating conditions.

These results are likely to be of importance to traffic management options either adopted or being considered in London and elsewhere that potentially affect urban concentrations of NO<sub>2</sub>. In London, for example, the congestion-charging scheme (CCS) started in February 2003. The CCS operates by charging certain vehicle types to enter a small area (22 km<sup>2</sup>) of central London at certain periods during weekdays. The CCS area includes many major roads in central London where EU limit values for annual mean NO<sub>2</sub> are not expected to be met by 2010. Overall, there has been a reduction in passenger car, light goods and heavy goods vehicle flows within the zone, but an increase in taxi and Transport for London bus flows [5]. As previously mentioned all TfL buses will be fitted with particle filters by 2005, which might lead to increased emissions of primary NO<sub>2</sub>. It is not known therefore, whether the reductions in NO<sub>x</sub> and primary NO<sub>2</sub> brought about by the reduced flows of some vehicle types might be offset by increases due to taxi and bus NO<sub>x</sub> and primary NO<sub>2</sub> emissions.

UK projections of urban NO<sub>x</sub> emissions suggest that petrol vehicles emissions of NO<sub>x</sub> will decline at a faster rate than diesel vehicle emissions of NO<sub>x</sub> because of the continued increased penetration of cars equipped with catalysts [1]. Furthermore, diesel car numbers are projected to increase from 14 % of the UK car fleet in 2000 to 42 % of the fleet by 2010. By 2010 therefore, it is likely that the NO<sub>2</sub>:NO<sub>x</sub> ratio of road vehicle emissions will also increase, which should be detectable in datasets of hourly NO<sub>x</sub> and NO<sub>2</sub> concentrations. It is clear from this study that the emissions of primary NO<sub>2</sub> from road vehicles is only partially understood because of the lack of comprehensive measurements of NO<sub>2</sub> from road vehicle emissions tests relevant to the current stock of vehicles in the UK and the rest of Europe. Further detailed emissions testing is therefore required to develop urban NO<sub>2</sub> emissions inventories. This testing should also aim to quantify the effects (if any) of modern emissions control devices fitted to vehicles such as oxidation catalysts fitted to diesel passenger cars and vans and continuous diesel particle filters fitted to heavy-duty vehicles.

## REFERENCES

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