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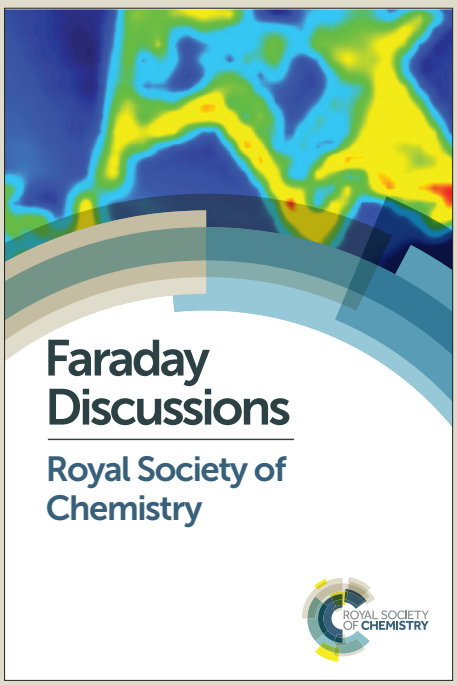

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Have vehicle emissions of primary NO_2 peaked?†

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Reducing ambient concentrations of nitrogen dioxide (NO_2) remains a key challenge across many European urban areas; particularly close to roads. This challenge mostly relates to the lack of reduction in emissions of oxides of nitrogen (NO_x) from diesel road vehicles relative to the reductions expected through increasingly stringent vehicle emissions legislation. However, a key component of near-road concentrations of NO_2 derives from directly emitted (primary) NO_2 from diesel vehicles. It is well-established that the proportion of NO_2 (i.e. the NO_2/NO_x ratio) in vehicle exhaust has increased over the past decade as a result of vehicle after-treatment technologies that oxidise carbon monoxide and hydrocarbons and generate NO_2 to aid the emissions control of diesel particulate. In this work we bring together an analysis of ambient NO_x and NO_2 measurements with comprehensive vehicle emission remote sensing data in London to better understand recent trends in the NO_2/NO_x ratio from road vehicles. We show that there is evidence that NO_2 concentrations have decreased since around 2010 despite less evidence of a reduction in total NO_x. The decrease is shown to be driven by relatively large reductions in the amount of NO_2 directly emitted by vehicles; from around 25 vol. % in 2010 to 15 vol. % in 2014 in inner London for example. The analysis of NO_x and NO_2 vehicle emission remote sensing data shows that these reductions have been mostly driven by reduced NO_2/NO_x emission ratios from heavy duty vehicles and buses rather than light duty vehicles. However, there is also evidence from the analysis of Euro 4 and 5 diesel passenger cars that as vehicles age the NO_2/NO_x ratio decreases. For example the NO_2/NO_x ratio decreased from 29.5±2.0% in Euro 5 diesel cars up to one year old to 22.7±2.5% for four-year old vehicles. At some roadside locations the reductions in primary NO_2 have had a large effect on reducing both the annual mean and number of hourly exceedances of NO_2 for the European Limit Values.

1 Introduction

1.1 Background and aims

Despite several decades of vehicle emissions control, atmospheric concentrations of nitrogen dioxide (NO_2) remain important across many urban areas of Europe. Ambient NO_2 concentrations in Europe are regulated by the Ambient Air Quality Directive (Directive 2008/50/EC), which sets an annual average Limit Value of 40 μg m^{-3} and an hourly Limit Value of 200 μg m^{-3} not to be exceeded more than 18 times a year, both to be attained by 2010 with the possibility of a time extension to 2015 in certain circumstances. The annual average Limit Value is the more stringent and a large fraction of EU Member States, including the UK, are not achieving it.[1] Vehicle emissions legislation has set increasingly stringent limits for the mass of emissions that can be emitted by both light and heavy duty vehicles.[2,3]. The expectation has been therefore that considerable reductions in ambient concentrations of NO_x and NO_2 would have been achieved over the past decade or so.

Historically there has been little interest in the proportion of NO_x that is in the form of NO_2 in vehicle exhaust. In part this lack of interest is because NO is rapidly oxidised to NO_2 in the atmosphere through its reaction with O_3. Additionally, vehicle emissions legislation considers only total NO_x and does not speciate between NO and NO_2.[4] However, in 2003 at a major roadside monitoring site in central London NO_2 concentrations of NO_2 were shown to increase considerably compared with 2002 levels.[5] The increase in NO_2 concentration was particularly important for the hourly Limit Value where the number of hours exceeding 200 μg m^{-3} increased from 2 in 2002 to 463 in 2003.

The reason for the increased NO_2 concentration was found to be largely related to the introduction of retrofit buses fitted with continuously regenerating particle traps (CRTs). These particle filters work by using a diesel oxidation catalyst (DOC) to oxidise NO to NO_2, using the excess NO_2 to further oxidise particle emissions. However, the CRTs fitted to London buses could not on their own explain all the NO_2 observed.[5] Since that time many emission and atmospheric measurement studies have shown that the use of DOC and particle filters in both light and heavy duty vehicles have led to increased NO_2/NO_x ratios in vehicle exhaust.[6–9]

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The increase in the proportion of NO_x emitted as NO_2 has had an important effect of roadside concentrations of NO_2 across Europe. However, UK projections of NO_x emissions from 2000 to 2015 and 2005 and 2015 suggested approximately 60 and 50% reduction in urban road vehicle emissions of NO_x, respectively, as a result of progressively tighter limits on vehicle NO_x emissions resulting due to vehicle emissions legislation (so-called Euro limits).[10] Since that time it has become clear that emissions of NO_x have not deceased as expected.[11–14] The discrepancy between inventory-based NO_x emission estimates and actual emissions has also been revealed by Lee *et al.*[15] using an eddy covariance technique. These measurements were made in London and provide estimates of total surface NO_x emissions also suggest the largest discrepancy between emission inventory and the flux estimates were for wind sectors dominated by road vehicle emissions. The increase in NO_2/NO_x ratios in diesel vehicle exhaust combined with a lack of reduction in total NO_x emissions from road vehicles has led to the situation across Europe where many urban locations exceed EU limits for NO_2 concentration.

This paper considers the recent evidence concerning directly emitted NO_2 from road vehicles. We focus on London (UK) where there are a large number of ambient monitoring sites — and in particular sites located at roadside locations. These sites provide robust information of long term trends and also provide a way in which directly emitted NO_2 emissions can be quantified. Consideration is also given to the recent data from vehicle emission remote sensing measurements also made in London to help understand the observed trends in ambient concentrations and the changes in the NO_2/NO_x emissions ratio from vehicles. Because NO_2 plays an important role in modern emissions control technologies, we consider how these technologies have changed over time and how they have affected the emission of NO_2.

1.2 Changes in vehicle emissions control technology affecting NO_2 emissions

Over the past 15 years or so there have been many developments in vehicle emission after-treatment technology that have affected the emission of NO_2— and in particular the NO_2/NO_x ratio. These developments are directly linked to observed changes in atmospheric composition. In gasoline and diesel vehicles most of the engine-out emission of NO_x is in the form of NO. However, as vehicle emission control technology has developed, NO_2 has become an important aspect of after-treatment technologies. NO_2 plays an important role in helping to burn soot (PM) from diesel vehicles and is also key to the efficient application of Selective Catalytic Reduction (SCR) technologies. The NO_x control in diesel vehicles is significantly

more challenging than for gasoline vehicles.

Stoichiometric operating gasoline vehicles use a three way catalyst (TWC) for emissions control. The role of the TWC is to oxidise hydrocarbons (HC) and carbon monoxide (CO) and simultaneously reduce NO_x. The reduction of NO_x to N_2 uses CO as the reductant. Gasoline vehicles operating under stoichiometric conditions produce NO engine-out and very little if any tailpipe NO_2, as there is no excess oxygen in the exhaust to oxidise NO to NO_2 over the TWC. Gasoline vehicles have used the TWC very effectively over the past 20 years for exhaust emissions control, as also shown by vehicle emission measurements.[11,16]

For Euro 3 diesel vehicles (introduced in 2000), DOC were used to control HC and CO. The DOC can oxidise NO to NO_2 in excess oxygen over active precious metal catalysts containing a mixture of Platinum (Pt) and Palladium (Pd), which provide highly efficient oxidation reactions. This oxidation can lead to increased NO_2 at the tailpipe for DOC-only applications.

For Euro 5 diesel vehicles (introduced in 2009), the PM limits required the use of a Diesel Particulate Filter (DPF) to physically trap the PM. The stored PM needs to be oxidised in order not to completely block the filter, which could impact vehicle operation. There are two mechanisms for soot oxidation: high temperature oxidation at approximately 600°C with oxygen and lower temperature oxidation (250 – 450°C) using NO_2 as the oxidant. Hence, the NO_2 formed over the DOC can be used for soot control, also leading to an increase in the amount of NO_2 emitted.

The tighter limits for Euro 6 diesel emissions (introduced in 2014) has led the the development and introduction of after-treatment technologies to specifically reduce emissions of NO_x. Excess oxygen in lean operating diesel engines impacts NO_x reduction considerably requiring the use of additional reductants and dedicated NO_x control catalysts. The catalysts for lean NO_x control are the Lean NO_x Trap (LNT) which requires reductants that are formed by the engine ($HC/CO/H_2$) and SCR, which requires the injection of urea into the vehicle exhaust to form ammonia, which is used as the reductant. LNT and SCR catalyst technologies remove both NO and NO_2 and hence reduce the tailpipe NO_2 emissions. For good low temperature NO_x control from SCR, NO_2 is required and hence has a positive benefit on NO_x control.

Fig. 1 provides an indication of how emissions of NO_2 have changed through pre-Euro to Euro 6 i.e. from pre 1993 to post 2014, for diesel cars. The most significant change in NO_2 emissions occurred when Euro 3 DOCs were introduced, resulting in a step-change increase in NO_2 emissions. Further increases in the emissions of NO_2 occurred when DPFs were introduced with late Euro 4 and Euro 5 vehicles. The reduction in

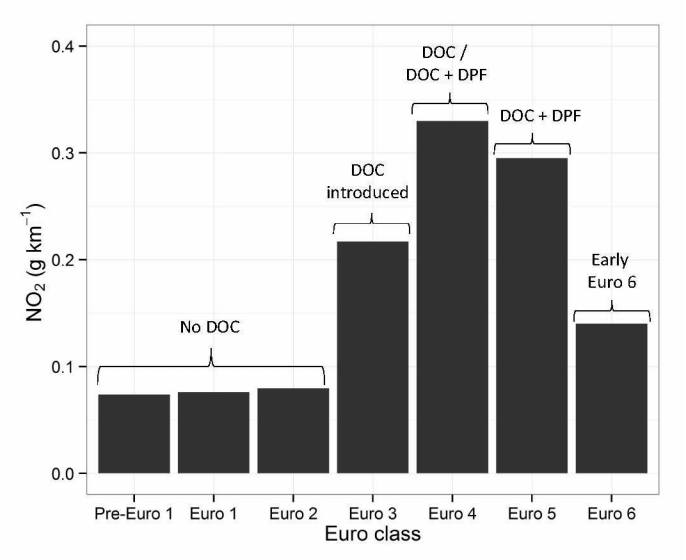


Fig. 1 Evolution of NO_2 emissions from diesel passenger cars based on emission factors used in the UK National Atmospheric Emissions Inventory.

Euro 6 NO_2 emissions is a result of the introduction of LNT and SCR technologies, which reduce absolute emissions of NO_x and not necessarily the ratio of NO_2/NO_x.

For heavy duty vehicles, exhaust NO_x control via SCR has been implemented since Euro IV in 2005 and has been continued to be used for Euro V in 2008, hence controlling both NO and NO_2 tailpipe emissions. Euro VI from 2014 has required the addition of a particulate filter for PM control. Where the PM can be controlled via the direct oxidation with NO_2 and/or oxygen. Furthermore, local air quality requirements led to a significant amount of retrofit applications targeting soot control, for example buses — including buses in London. These applications rely on the direct oxidation of PM with NO_2 and do not use the high temperature reaction with oxygen. Hence the role of the retrofitted DOC is to produce NO_2 to control the PM, which led to an increase in the tailpipe NO_2 emissions compared to a non-retrofit application.

There are other factors that will affect the NO_2/NO_x ratio in vehicle exhausts related to the catalysts used. For example, 'catalyst thrifting', where catalyst developers and Original Equipment Manufacturers (OEMs) reduce the amount of platinum group metal (PGM) used, will potentially affect the amount of NO_2 formed. Second, catalyst deactivation over time might also have an effect on the conversion of NO to NO_2 on the DOC. Thus, aged catalyst technologies may have substantially reduced oxidative capacity through thermal deactivation or poisoning. For these reasons,

the exhaust from diesel vehicles when first introduced may have higher NO_2/NO_x ratios compared with vehicles introduced at a later time through catalyst thrifting. Similarly, the exhaust from older vehicles may also have lower NO_2/NO_x ratios than newly introduced vehicles. These effects are difficult to quantify in real vehicle fleets but are likely to play an important role in affecting the emission of NO_2.

2 Experimental

2.1 Ambient measurement sites

The analysis in the current work focuses on ambient monitoring sites in Greater London. London provides a useful case study for several reasons. First, it has a large number of ambient monitoring sites that form part of the Defra Automatic Urban and Rural Network (AURN) or the London Air Quality Network (LAQN). Second, as described in Section 2.3, there is a large data set of vehicle emission remote sensing data available from two campaigns. The two networks provide more than 70 ambient monitoring sites at urban background and roadside locations. In particular, there are a relatively large number of 'traffic-influenced' measurements sites that can be analysed for both trends and to estimate the NO_2/NO_x ratio from vehicle emissions. In this work we have used data from 35 long-term measurement roadside sites where there has been at least 10 years of measurements over the period 1996 to 2014.

2.2 Deriving NO_2/NO_x emission ratios

Techniques are available to estimate the NO_2/NO_x ratio from vehicle emissions through the analysis of ambient monitoring data.[17–19] Jenkin[18] showed that by considering the 'total oxidant' gradient, $(NO_2 + O_3)/NO_x$, estimates could be made of the primary (direct) NO_2/NO_x ratio from vehicle emissions. One of the limitations of the total oxidant approach for estimating the NO_2/NO_x ratio from vehicles is that roadside measurements of O_3 are also required. However, there are very few roadside measurement sites in London (and the UK) that measure O_3, making it difficult to build a comprehensive view of typical NO_2/NO_x ratios along different roads. To overcome this problem, Carslaw and Beevers[20] developed an approach that did not require roadside measurements of O_3.

Briefly, the increment in NO_2 concentration at a roadside monitoring site above an urban background site (at North Kensington) is partitioned into NO_2 that is chemically derived through the reaction between NO and O_3 and that which is emitted directly by road vehicles. The technique uses a constrained chemistry model that is based on a simple set of chemical

reactions used to describe the time-dependent change in NO, NO_2 and O_3 concentrations as vehicle plumes are mixed with background air. By considering different values of the assumed NO_2/NO_x emissions ratio from road traffic and the time available for the NO-O_3 reaction to take place (τ), the best agreement between modelled and measured roadside concentrations of hourly NO_2 concentrations is sought. In practice, several hundred combinations of the NO_2/NO_x emissions ratio from road traffic sources and the time available, τ for the NO-O_3 reaction to take place are considered before the best single combination, resulting in the minimum error, as determined by the residual sum of squares, between modelled and measured NO_2 concentrations, is identified.

The technique assumes that the increment in NO_2 concentration above a local background site is controlled by the availability of O_3 and directly emitted NO_2 only. The formation of NO_2 through other routes (e.g., through reactions involving VOCs) is assumed to be negligible. To further minimise the potential influence of other photochemically-driven reactions, data are only considered from October through to March. Another source of uncertainty is the use of chemiluminescent NO_x analysers with molybdenum catalysts used in UK national networks. These instruments are affected by interferences due to NO_y species and will detect them as NO_2. However, at roadside locations — and for increments above local background concentrations, the influence of NO_y species is expected to be small. However, it is known that vehicle emissions are a direct source of nitrous acid (HONO), which would also be detected as NO_2 in these instruments. Measurements of HONO in vehicle exhausts does suggest that only low amounts are emitted. For example, Kirchstetter *et al.*[21] measured a HONO/NO_x ratio of $2.9\pm0.5 \times 10^{-3}$. Nevertheless, the direct emission of HONO is a potential interferent. The approach yields estimates of hourly NO_2 and O_3 at roadside sites, as well as an estimate of the road transport NO_2/NO_x emissions ratio for vehicles using the road adjacent to each roadside monitoring site. The analysis provides a monthly mean estimate of the NO_2/NO_x ratio for the vehicle emissions at the roadside site being analysed.

2.3 Vehicle emission remote sensing

Comprehensive vehicle emission measurements have been used from two vehicle emission campaigns carried out in London in 2012 and 2013. A comprehensive description of the instrument set up and locations used for roadside sampling is given in Carslaw and Rhys-Tyler[16] and is not repeated here. The 2013 measurements were mostly focused on understanding the in-use emissions from Transport for London (TfL) Euro III buses retrofitted with a 'low NO_2' SCRT system described later in Section 3.3.[22] Never-

theless, the 2013 measurements also included a considerable number of measurements from the wider vehicle fleet. In total, there were approximately 105,000 valid measurements made of individual vehicles from the combined 2012 and 2013 campaigns.

The remote vehicle exhaust sensor was developed at the University of Denver named Fuel Efficiency Automobile Test (FEAT) was used to collect all of the emission measurements over two six week campaigns (one each in June-July 2012/2013). The instrument consists of a light source and detector unit separated by a single lane of road. The detector is composed of four non- dispersive infrared (NDIR) detectors, including a reference channel (3.9 μm), CO (3.6 μm), CO_2 (4.3 μm), and hydrocarbons (HC, 3.3 μm), and two dispersive ultraviolet spectrometers. The first spectrometer measures NO, sulphur dioxide, and ammonia (NH_3) between 198 and 227 nm, while the second records NO_2 spectra between 430 and 450 nm. All of the detectors sample at 100 Hz and have been extensively described in the literature.[23–25] The measurements from the remote sensing detector provide fuel based emission factors (e.g. g NO_x kg^{-1} fuel) and a direct measure of the NO_2/NO_x ratio from individual vehicles.

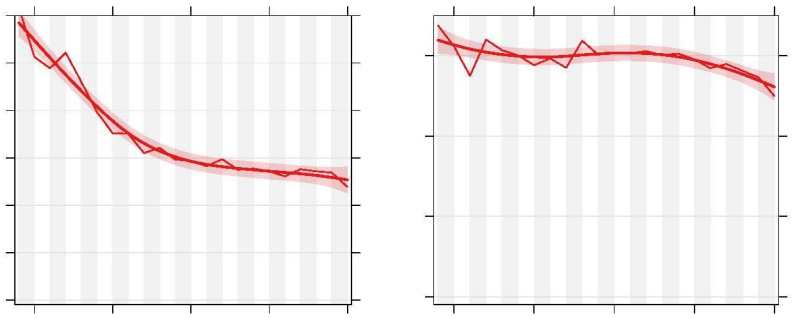
3 Results and discussion

3.1 Trends in ambient concentrations of NO_x and NO_2

Trends have been calculated for ambient NO_x and NO_2 concentrations across 35 roadside monitoring sites in London that have at least 10 years of data capture. A summary of the trends from 1996 to 2014 is shown in Fig. 2. Over the full period from 1996 to 2014 concentrations of NO_x at roadside locations in Londion have decreased by 2.4±1.5% yr^{-1}. The corresponding change in NO_2 was 0.4±0.4% yr^{-1}. The trend analysis shows that on average across all roadside sites there has been little evidence of a decrease in concentrations of NO_2. The trends over the period 1996 to 2014 have however not been linear. For example, from around 2002 to 2014 the reduction in NO_x has been weakly downward at about 1.4±0.5% yr^{-1}. Similarly, for NO_2 Fig. 2(b) shows that there is evidence of a decrease in concentrations from around 2010. Clearly, the trends in NO_x and NO_2 at individual sites spans a range of behaviours but are not considered in detail here.

3.2 Trends in primary NO_2 emissions

The trend in estimated NO_2/NO_x emission ratios from ambient roadside data is shown in Fig. 3. The results are shown separately for inner and outer London, as defined in Fig. 3. When considering the data in this way



(a) (b)

Fig. 2 a) Trends in the mean concentration of NO_x across 35 roadside sites in Greater London with at least 10 years of data capture b) same for NO_2. Trend estimates were made using the *openair* package.[26]

it is clear that there are differences between these two regions of London. In the mid-1990s both inner and outer London had similar values for the NO_2/NO_x ratio of about 5 vol. %. However, after this time, inner London is shown to have a higher NO_2/NO_x ratio than outer London. The patterns of change over the 19 years are revealing. From around 2003 inner London is shown to diverge from outer London and has a much higher NO_2/NO_x ratio than outer London. The likely reason for the divergence is related to the increased use of CRT after-treatment devices fitted to Transport for London (TfL) buses, which were retrofitted from 1999 onwards. The use of these filters increased from 60 to 90% over the period 2003 to 2005.

Also apparent in Fig. 3 for outer London sites is the increase in NO_2/NO_x ratio from 2008 to 2009, which is less apparent for the inner London data. It is difficult to reconcile this increase with known changes in Euro standards for vehicles. One explanation is that the increase is related to the introduction of the London Low Emission Zone (LEZ).[27,28] The LEZ came into operation on 4 February 2008 with a phased introduction targeting vehicles more than 12 tonnes gross weight. From the 4 February 2008 only Euro III compliant (for PM_{10}) vehicles were permitted into Greater London. From July 2008 more vehicles were restricted including HDVs from 3.5 to 12 tonnes, buses and coaches. These additional vehicle types were also required to be Euro III compliant. The TfL baseline monitoring report does show that the number of vehicles fitted with a particle filter through the 'Reduced Pollution Certificate' scheme increased when the LEZ was introduced in 2008.[29] It is likely therefore that the increased use of catalytic particle filters would have led to an overall increase in the NO_2/NO_x emission ratio from these vehicles. Specific information

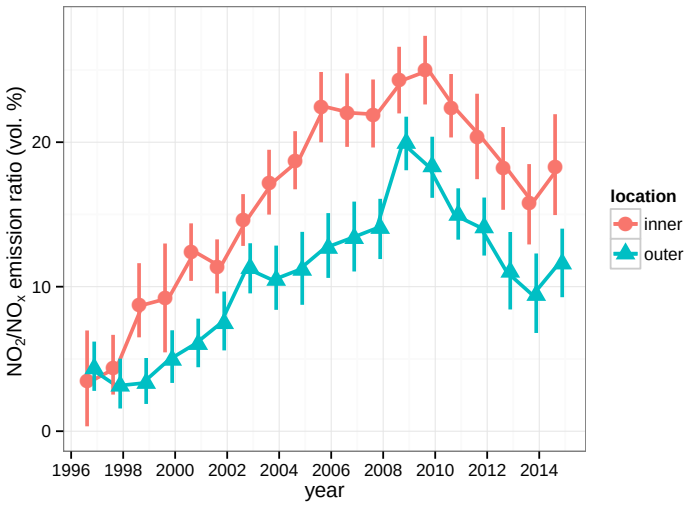


Fig. 3 Estimates of the NO_2/NO_x emission ratio calculated from ambient monitoring sites in London. The ratio has been calculated separately for inner and outer London. Inner London is assumed to include the following local authorities: Camden, City of London, Hackney, Hammersmith and Fulham, Islington, Kensington and Chelsea, Lambeth Southwark, Tower Hamlets and Wandsworth Westminster. The error bars represent the 95% confidence in the mean estimates. Note that data for 2015 only include the first three months of the year.

on the types of filter used are not available but given the proportionately greater number of these types of vehicle in outer London compared with inner London it would be expected that outer London roads would be more strongly affected. Neither Kelly *et al.* [28] nor Ellison *et al.* [27] specifically quantify the potentially important effect of increased particle filter use on primary NO_2 emissions.

Table 1 summarises the vehicle flows for the roads adjacent to the roadside monitoring sites based on Department for Transport manual count data from 2005 to 2013. On average the flow of vehicles is similar for inner and outer London — 34,274 and 36,285 respectively. The principal differences between the inner and outer London sites related to the vehicle flows of buses and taxis. Buses are much more important in inner London, with flows being approximately double those in outer London. Similarly, taxis are also more important in inner London with flows three times those in outer London. Buses and taxis are all diesel vehicles and therefore inner London has a much greater influence due to diesel vehicles than outer London.

Table 1 Annual average daily flows of different vehicle types grouped by location in London. The data represent mean flows based on Department of Transport data from 2005 to 2013. Inner London is defined in Fig. 2. HDV are heavy duty vehicles and LGV light goods vehicles.

location	car	taxi	bus	LGV	HDV rigid	HDV articulated	motorcycle	All
inner	21201	2463	1603	4894	1146	133	2042	34274
outer	27522	834	837	4650	1271	454	709	36285

Table 2 shows the relative contribution to total emissions of NO_x along the same roads as considered in Fig. 2. These emission total estimates reveal some important differences by vehicle type between inner and outer London. In inner London, buses and taxis account for a large amount of the total NO_x emitted (31.8 and 7.1%, respectively) i.e. almost 40% of the total NO_x. By contrast, buses and taxis in outer London contribute a total of only 17% of the total NO_x. Consequently, the contributions of other vehicle types are also different — in particular there is a more significant contribution from passenger cars and articulated HDVs in outer London.

Table 2 Mean percentage contribution to total NO_x emissions split by inner and outer London. The emissions are based on NAEI estimates for the roadside sites considered in the trend analysis (see Section 2.1). Inner London is defined in Fig. 2.

location	car	taxi	bus	LGV	HDV rigid	HDV articulated	motorcycle	All
inner	23.7	7.1	31.8	13.6	20.3	3.0	0.6	100.0
outer	36.1	3.0	13.7	16.5	20.2	10.1	0.3	100.0

The changes in ambient concentrations of NO_x and NO_2 and primary NO_2 emissions have had important influences at specific monitoring sites. For example, at Marylebone Road in central London annual mean NO_x concentrations were very similar in 2008 (312 µg m^{-3}) and 2014 (316 µg m^{-3}). Despite the close similarity in concentrations of NO_x, concentrations of NO_2 differ markedly. The annual mean NO_2 concentration in 2008 was 115 µg m^{-3}, where was in 2014 it was 79 µg m^{-3} i.e. over 30% less. However, the hourly Limit Value is much more sensitive to these changes. In 2008 there were 812 hours above 200 µg m^{-3} compared with only 60 exceedances in 2014. Such a dramatic difference in NO_2 concentrations despite the similarity in NO_x concentration is driven by directly emitted NO_2 emissions. In 2008 the NO_2/NO_x ratio was about 23% compared with about 13% in 2014 at the Marylebone Road site. The results for Marylebone Road illustrate how important primary NO_2 emissions can be in controlling ambient concentrations of NO_2 close to roads.

3.3 Changes in primary NO_2 emissions based on vehicle emission remote sensing

The preceeding analysis has shown that at London roadside monitoring sites the concentration of NO_x has changed little over the past decade. However, there is evidence that ambient NO_2 concentrations are decreasing at many sites. The analysis of ambient measurements also shows that from around 2010 the mean NO_2/NO_x emissions ratio has shown clear decreases in both inner and outer London. It is important that the underlying causes of these decreases in the NO_2/NO_x ratio are understood.

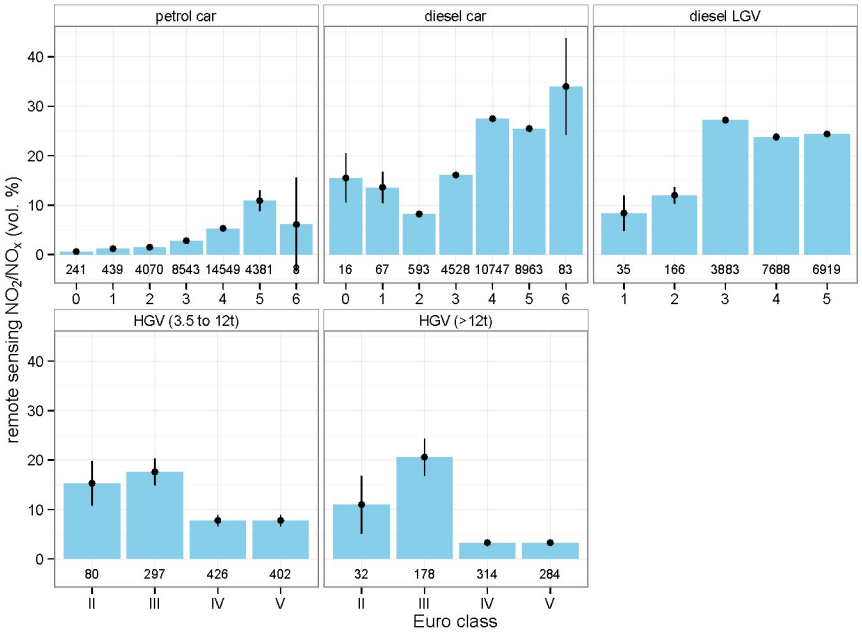


Fig. 4 Trend in NO_2/NO_x ratio by major vehicle and Euro class based on vehicle emission remote sensing data from the 2012 and 2103 London campaigns. The uncertainties show the 95% confidence interval in the mean. The numbers at the bottom of the plot show the sample size. Note that these ratios have not been weighted by vehicle numbers.

Fig. 4 shows how the NO_2/NO_x ratio has changed through the Euro classes for the main types of vehicle. The ratios of petrol vehicles are low — and for Euro 4 to 6 unimportant because the absolute emissions of NO_x are very low. Diesel passenger car ratios of NO_2/NO_x were around 10 to 15% for pre-Euro to Euro 2 vehicles but increased to 16.1±0.6% with the introduction of Euro 3 vehicles. The NO_2/NO_x ratio increased again with Euro 4 (27.6±0.6%) and Euro 5 (25.5±0.7%). LGVs have a similar pattern to diesel passenger cars. For both classes of HDV vehicle weights, the NO_2/NO_x ratio was around 10 to 20% for Euro II and Euro III vehicles

(there were insufficient measurements of Euro I and pre-Euro vehicles). However, the data clearly show that the NO_2/NO_x ratio decreased sharply for Euro IV and V vehicles in both weight categories. For vehicles 3.5 to 12 t, the NO_2/NO_x ratio for Euro IV/V vehicles is 7.8±1.2%. However, for the heavier Euro IV/V vehicles >12 t the NO_2/NO_x ratio is only about 3.3±0.7%.

The reasons for the sharp reductions in the NO_2/NO_x ratio from HDVs are unclear, although there are several factors that could affect the emission of NO_2. First, the requirement for a tailpipe NO_x sensor at Euro V for On-board Diagnostic (OBD) purposes may have reduced the number of vehicles with poor calibration. Second, as previously mentioned, reduced PGM levels through catalyst thrifting of the DOC, so as not to over-produce NO_2 for DOC + SCR vehicles and retrofitted DOC + DPF vehicles. Finally, the improved SCR efficiency moving from Euro IV to Euro V where the SCR system is efficient at removing a 1:1 ratio of NO_2:NO via the fast reaction ($NO_2 + NO + 2NH_3 \rightarrow 2N_2 + 3H_2O$). Even though there is little evidence of a reduction in NO_x from HDVs in London,[16] the reduction in the emission of NO_2 would likely have had an important effect on atmospheric concentrations of NO_2.

The data split by Euro class consist of a range of vehicle ages. For diesel cars for example (for which the sample sizes are large), Euro 5 vehicles span the years 2009 to 2013 (when the measurements were made). These data allow some consideration of the effect vehicle age has on the NO_2/NO_x ratio. Fig. 5 shows the results for Euro 4 and 5 diesel cars by vehicle age. It is clear that as the age of the vehicle increases the NO_2/NO_x ratio decreases. Four year old Euro 5 diesel cars have a NO_2/NO_x ratio of 22.7±2.5%, whereas those up to one year old have a NO_2/NO_x ratio of 29.5±2.0%. A similar behaviour is also seen for Euro 4 diesel cars, which are older overall than Euro 5 diesel cars.

These results show that older vehicles tend to have a lower NO_2/NO_x ratio than newer vehicles for the same Euro class. This is a potentially important finding suggesting that as vehicles age the amount of NO_2 emitted decreases. One reason for such a decrease is that the catalysts become less active over time, as indicated in Fig. 5. Such degradation effects are not currently considered in emission factors for the NO_2/NO_x ratio but could nevertheless be important. Another influence could be 'catalyst thrifting' as discussed in Section 1.2. Four year old Euro 5 cars for example, tend to have lower NO_2/NO_x ratios than four year old Euro 4 cars — which could indicate a change in the catalyst PGM composition between these two classes of vehicle.

Within the TfL bus fleet there have also been changes to the emissions control technology that affects the emissions of NO_x and NO_2. In particular,

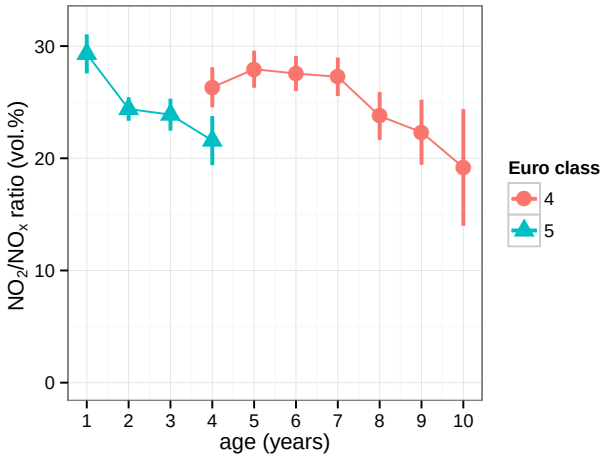


Fig. 5 Trend in NO_2/NO_x ratio for Euro 4 and 5 diesel cars by vehicle age based on a total sample of 25,721 vehicles from the 2012 and 2013 remote sensing data. The uncertainties show the 95% confidence interval in the mean.

since 2012 approximately 2000 Euro III buses have been retrofitted to SCRT technology. The 'low-NO_2' SCRT technology used by TfL consists of a CRT (Continuously Regenerating Trap, to reduce particle emissions) and SCR system (to reduce NO_x emissions). The system consists of several closely coupled stages: a diesel oxidation catalyst (DOC), followed by a diesel particulate filter, urea/water injection, SCR catalysts and finally an ammonia slip catalyst. The performance of the TfL SCRT retrofit buses was measured by Carslaw *et al.* [22] where over 700 measurements were made using vehicle emission remote sensing. The SCRT on-road measurements showed that emissions of NO_x were reduced by 45% compared with similar vehicles using only a CRT. There was however a greater reduction in emissions of NO_2 of 61%.

By March 2014 there were 1479 TfL buses fitted with the SCRT system out of a total fleet of 8958 (Finn Coyle, personal communication). Furthermore, these bus conversions are not evenly spread across London but focused on certain bus routes. For this reason it would be expected that certain air pollution monitoring sites could be affected by the SCRT retrofits more than others. Such a change would also have the effect of potentially increasing the variation of NO_x and NO_2 emissions between monitoring sites and hence also atmospheric concentrations. Conversely, any changes to the majority of the rest of the vehicle fleet would be expected to be more consistent across the road network because the types of vehicle involved would tend to be uniformly mixed. The variation in the trends in NO_2 at individual roadside monitoring sites will likely be influenced by the variation in the bus fleet after-treatment technologies;

although there is insufficient information available to verify whether this is the case.

3.4 Comparison with the COPERT emissions model

The comprehensive nature of the remote sensing measurements allows useful comparisons to be made with commonly used emissions models in Europe. The NO_2/NO_x ratio from the 2012 and 2013 remote sensing surveys can usefully be compared with those in the COPERT emission factor model and the emission factor advice considered in the EMEP/EEA air pollutant emission inventory guidebook.[30] COPERT is widely used throughout the world and forms the basis of vehicle emission factors used in most European national emissions inventories, including the UK. The comparison between the remote sensing-derived NO_2/NO_x ratios and COPERT is shown in Fig. 6, split by light and heavy duty vehicles. The comparison between the COPERT and remote sensing NO_2/NO_x ratios is a direct one and not dependent on the absolute e.g. g km^{-1}, emission estimates of NO_x and NO_2.

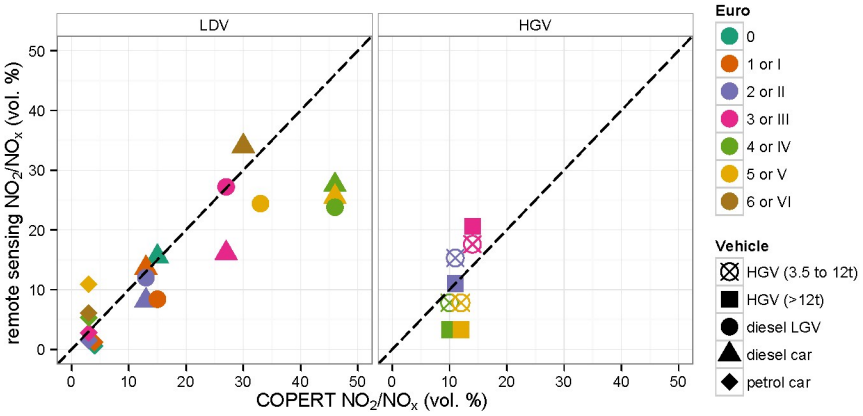


Fig. 6 Comparison of COPERT NO_2/NO_x ratios with those from vehicle emission remote sensing in London in 2012 and 2013. The data are shown by Euro class and major vehicle type and are split by light and heavy duty vehicles (LDV and HDV).

The petrol vehicle NO_2/NO_x ratios for both data sources are low (typically below 5%). Furthermore, petrol vehicle NO_x emissions from post Euro 4 vehicles are very low and consequently the ratio of NO_2/NO_x will have little importance with respect to atmospheric concentrations of NO_x and NO_2.[16] For diesel cars pre-Euro 3 vehicles agree well, where the NO_2/NO_x ratio is around 15%. Where the estimates deviate is for Euro 3 to 5 vehicles. The remote sensing data suggests Euro 3 vehicles have a NO_2/NO_x ratio of 16.1±0.6%, whereas the ratio for COPERT is 27%.

There are however larger discrepancies for Euro 4 and 5 vehicles, where the remote sensing data NO_2/NO_x ratio is 27.5±0.6% and 25.5±0.7% and COPERT is 46% in both cases. There is less certainty for diesel Euro 6 passenger cars because there were only 83 measurements from the remote sensing. Nevertheless the remote sensing NO_2/NO_x ratio of 34.0±9.8% is similar to the COPERT value of 30%. The situation is also similar for diesel LGVs i.e. Euro 3 to Euro 4 NO_2/NO_x ratios from remote sensing are considerably lower than those assumed in COPERT.

In general the HDV NO_2/NO_x ratios are less than those observed for light duty vehicles. However, the remote sensing data does show that the NO_2/NO_x ratios for larger Euro IV and V HDVs (>12 tonnes) is much lower than that reported by COPERT (about 3.3±0.7% and 10 to 12%, respectively). As discussed in section 3.3, there are several reasons why the remote sensing NO_2/NO_x ratios are low. The COPERT NO_2/NO_x ratios for HDVs also show very little variation, as shown in Fig. 6. It is known from previous work that HDV NO_2/NO_x ratios can be highly variable, depending on both the emissions technology used and the vehicle manufacturer.[16] The small variation in COPERT NO_2/NO_x ratios might reflect the relatively few HDVs that are tested as part of emission factor development. Additionally, the emission factor data for NO_2/NO_x at least, also reflect a mean of all driving conditions and not necessarily the urban conditions of the remote sensing data. The comparisons made in the current work therefore suggest that some refinement of the NO_2/NO_x ratios used in COPERT for HDVs is required.

Overall, the comparison between the remote sensing and the COPERT NO_2/NO_x ratios suggests that the ratios assumed by COPERT are higher than those observed from on-road measurements. As discussed in Section 3.3, there is evidence that the NO_2/NO_x ratio decreases with vehicle age and such effects might explain some of the discrepancies observed. Similar to vehicle emission factors accounting for vehicle emissions deterioration — usually resulting in increased emissions with vehicle age, it is also important to specifically consider the effect of deterioration on the NO_2/NO_x ratio.

4 Conclusions

Exceedances of EU Limit Values for NO_2 remain important in many urban locations throughout Europe. Despite the introduction of increasingly stringent emissions legislation to reduce emissions of NO_x from vehicles, ambient concentrations of NO_x have not decreased as expected close to roads. Over the past 10 to 15 years directly emitted NO_2 from vehicles has become an important contributory factor affecting the near-road environ-

ment of NO_2 concentrations. The current work shows that in London, the NO_2/NO_x emissions ratio increased substantially from around 5 vol. % in 1996 to around 20 to 25 vol. % in 2010. Such a large increase has had an important effect on ambient NO_2 concentrations, especially close to roads. These increases have not been uniform along different roads due to the variation in vehicle fleet compositions. However, it is clear that the most significant increases in the NO_2/NO_x ratio have been in central and inner London where the proportion of diesel vehicles is high, and in particular, where there is a large number of buses fitted with CRTs. In outer London, the mean NO_2/NO_x ratio has been consistently lower that inner London by about 5% (absolute).

This work shows for the first time that directly emitted NO_2 emissions have started to decline in London when expressed as a NO_2/NO_x ratio. The decreases have been substantial since around 2009/2010 e.g. reducing from a peak of around 25 vol. % in 2010 to about 15 vol. % at the end of 2014 in inner London. Furthermore, these decreases are similar in both inner and outer London. The recent decreases in the NO_2/NO_x emission ratio has led to a decrease in roadside NO_2 concentrations despite concentrations of NO_x remaining almost constant. The reasons for the decrease are likely related to considerable reductions in the NO_2/NO_x ratio for HDVs for Euro IV/V vehicles, confirmed by the comprehensive vehicle emission remote sensing emission measurements. Additionally, this work shows that for Euro 4 and 5 diesel passenger cars there is evidence that the NO_2/NO_x ratio decreases as vehicles age. Reductions in the NO_2/NO_x ratio are also seen in the TfL bus fleet. In particular, the increased use of 'low-NO_2' SCRT systems on TfL buses is also of note, as these systems have been shown under real-world conditions to reduce the NO_2/NO_x ratio by around 60% compared with that measured on buses before they were converted.

The analysis of the vehicle emission remote sensing data reveals that the NO_2/NO_x ratios assumed for many important classes of diesel vehicles used in European emission factors are likely too high. In particular, Euro 4 and 5 diesel passenger cars and vans have measured NO_2/NO_x ratios of around 25 to 27 % on average compared with 46% assumed in the emission factors. Given the large numbers of these types of vehicle currently in service it is also likely that emission inventories also overestimate the amount of directly emitted NO_2 being emitted. This situation represents a reversal of that in the early 2000s where no consideration was given to NO_2 emissions and a default 5 to 10% value was assumed, which would have led to an underestimate of emissions of NO_2.

The future impact of Euro 6/VI technologies on the NO_2/NO_x ratio is currently unclear due to a lack of NO_x *and* NO_2 emission measurements from different vehicle technologies. However, if these vehicles deliver

the expected substantial NO_x reduction, then the proportion of NO_2 in the exhausts of these vehicles will become less important because of the reduction in absolute emissions of NO_x and NO_2. For the existing diesel vehicle parc, this work shows that for diesel cars at least, there is evidence that the NO_2/NO_x ratio decreases as vehicles age. This decrease will have a potentially important effect on further reducing real-world NO_2/NO_x ratios from vehicles in the future, particularly if a similar behaviour is seen for other types of diesel vehicle.

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