Atmospheric Environment 81 (2013) 339–347

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

New insights from comprehensive on-road measurements of NO_x, NO_2 and NH_3 from vehicle emission remote sensing in London, UK

David C. Carslaw [a,*], Glyn Rhys-Tyler [b,1]

[a] King's College London, Environmental Research Group, Franklin Wilkins Building, 150 Stamford Street, London SE1 9NH, UK

[b] Transport Operations Research Group, School of Civil Engineering and Geosciences, Newcastle University, Newcastle-upon-Tyne NE1 7RU, UK

HIGHLIGHTS

- First direct measurements of NO_2 and NH_3 using remote sensing in the UK.
- Selective catalytic reduction no better than non-SCR technology in reducing NO_x.
- Variations in NO_2 by vehicle technology, engine size and vehicle manufacturer.
- Comprehensive emission factor for NO_x, NO_2 and NH_3 for others to use.
- Important implications at a European level for meeting NO_2 limits.

ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form
9 September 2013
Accepted 14 September 2013

Keywords:
Vehicle emissions
Remote sensing
Primary NO_2
Emissions inventory
Selective catalytic reduction
Hybrid vehicle

ABSTRACT

In this paper we report the first direct measurements of nitrogen dioxide (NO_2) in the UK using a vehicle emission remote sensing technique. Measurements of NO, NO_2 and ammonia (NH_3) from almost 70,000 vehicles were made spanning vehicle model years from 1985 to 2012. These measurements were carefully matched with detailed vehicle information data to understand the emission characteristics of a wide range of vehicles in a detailed way. Overall it is found that only petrol fuelled vehicles have shown an appreciable reduction in total NO_x emissions over the past 15–20 years. Emissions of NO_x from diesel vehicles, including those with after-treatment systems designed to reduce emissions of NO_x, have not reduced over the same period of time. It is also evident that the vehicle manufacturer has a strong influence on emissions of NO_2 for Euro 4/5 diesel cars and urban buses. Smaller-engined Euro 4/5 diesel cars are also shown to emit less NO_2 than larger-engined vehicles. It is shown that NO_x emissions from urban buses fitted with Selective Catalytic Reduction (SCR) are comparable to those using Exhaust Gas Recirculation for Euro V vehicles, while reductions in NO_x of about 30% are observed for Euro IV and EEV vehicles. However, the emissions of NO_2 vary widely dependent on the bus technology used. Almost all the NO_x emission from Euro IV buses with SCR is in the form of NO, whereas EEV vehicles (Enhanced Environmentally friendly Vehicle) emit about 30% of the NO_x as NO_2. We find similarly low amounts of NO_2 from trucks (3.5–12t and >12t). Finally, we show that NH_3 emissions are most important for older generation catalyst-equipped petrol vehicles and SCR-equipped buses. The NH_3 emissions from petrol cars have decreased by over a factor of three from the vehicles manufactured in the late 1990s compared with those manufactured in 2012. Tables of emission factors are presented for NO_x, NO_2 and NH_3 together with uncertainties to assist the development of new emission inventories.

1. Introduction

1.1. Background

Emissions of NO_x and NO_2 from road vehicles are of key importance to urban air quality, as well as contributing to regional and global scale air pollution. It is now over 20 years since vehicle emissions legislation was introduced in Europe to control carbon monoxide (CO), hydrocarbons (HC), NO_x (= NO + NO_2) and

* Corresponding author.
E-mail address: david.carslaw@kcl.ac.uk (D.C. Carslaw).
[1] Present address: Department of Mechanical Engineering and Mathematical Sciences, Faculty of Technology, Design and Environment, Oxford Brookes University, Wheatley Campus, Oxford OX33 1HX, UK.

1352-2310 © 2013 The Authors. Published by Elsevier Ltd. Open access under CC BY-NC-ND license.
http://dx.doi.org/10.1016/j.atmosenv.2013.09.026

particulate matter. Since that time emissions legislation has become increasingly stringent by setting progressively lower emission limits for these species (EC, 2009, 2007). Ambient measurements show that concentrations of CO and HC have decreased by around an order of magnitude over the past 20 years, providing clear evidence of the effectiveness in both the legislation and emissions control technology (EEA, 2012). However, the same has not been true of NO_x and in particular NO_2. Of principal concern is the concentration of NO_2 because in Europe legislation exists to set limits on the maximum annual and hourly concentrations of NO_2. The Framework Directive (96/62/EC, 1996) and First Daughter Directive (1999/30/EC, 1999) aim to control the concentrations of NO_2 in ambient air to which the public is exposed. Two limit values have been specified for NO_2 in the First Daughter Directive: an annual mean value of 40 $\mu g\ m^{-3}$ and an hourly value of 200 $\mu g\ m^{-3}$ with 18 permitted exceedances each year. Both limit values entered into force on 01/01/2010 but exceedances (particularly of the annual mean Limit Value) are widespread throughout Europe (EEA, 2012).

In recent years two issues have emerged as being important for urban concentrations of NO_x and NO_2. First, the proportion of NO_x that is NO_2 in the exhausts of vehicles was shown to be increasing (Carslaw, 2005; Anttila et al., 2011; Anttila and Tuovinen, 2010; Hueglin et al., 2006). An increasing ratio of NO_2/NO_x is important for concentrations of NO_2 close to roads and can have a large effect on exceedances of both the annual and hourly mean EU Limit Value for NO_2. Second and more recently, it has emerged that emissions of total NO_x from diesel vehicles have not decreased as expected. For example, Weiss et al. (2011) using a Portable Emission Monitoring System (PEMS) fitted to diesel passenger cars showed that their emissions in use were considerably higher than those over legislated test cycles. Additionally, Carslaw et al. (2011) and Beevers et al. (2012) showed that urban concentrations of NO_x close to roads have stabilised. Moreover, in the UK and many other European countries the proportion of diesel cars in the passenger car fleet has increased.

Previous work by Grice et al. (2009) reviewed the information on the NO_2/NO_x ratios for a wide range of vehicle types based mostly on dynamometer measurements and assumptions concerning the likely future levels. For Euro 3 diesel passenger cars a NO_2/NO_x ratio of 30% was assumed, whereas Euro 4–6 were assumed to emit 55% of the total NO_x as NO_2. Grice et al. (2009) further assumed that heavy duty vehicles (trucks and buses) typically emit 10–15% NO_2/NO_x ratio for all Euro classifications, with the exception of vehicles fitted with continuously regenerating particle filters, which were assumed to emit 35% of their NO_x as NO_2. Importantly, vehicles using selective catalytic reduction (SCR) were assumed to emit a low amount of primary NO_2 (10%), although it was acknowledged that these assumptions were based on very little experimental data.

The use of SCR on vehicles is an important development as far as NO_x emissions are concerned because the technology specifically aims to reduce total NO_x emissions. Velders et al. (2011) reported results from a PEMS for seven trucks (six meeting Euro V and one an EEV — Enhanced Environmentally friendly Vehicle). The EEV vehicle is equivalent to a Euro standard somewhere between Euro V and Euro VI i.e. it has the same NO_x limit as the Euro V emission standard, but with a lower PM_{10} limit. SCR systems were used on six trucks, whereas one truck was equipped with an Exhaust Gas Recirculation (EGR) system. Both SCR and EGR are systems used for reducing NO_x emissions to comply with the Euro V emission standard. Velders et al. (2011) found that these vehicles tended to emit about a factor of three more NO_x along city streets, and 10–40% more NO_x along motorways compared with the Euro standards for these vehicles. Velders et al. (2011) suggested that these high NO_x emissions might have been caused by a relatively low engine load, causing the exhaust gas temperature to be too low for proper functioning of the SCR system. The single truck equipped with an EGR system performed better at low average speeds. No information was available on the speciation between NO and NO_2.

Kousoulidou et al. (2008) updated the assumptions of Grice et al. (2009) for certain vehicle types. There seems to be general agreement that for petrol cars with catalytic converters both the level of NO_x and the NO_2/NO_x are very low. As noted by Kousoulidou et al. (2008) in the case of diesel engines, the NO_2/NO_x ratio is in principle determined by the existence or not of SCR as an after-treatment device, where it is expected to minimise tailpipe NO_2 emissions ($NO_2/NO_x = 5\%$). However, deviations from ideal in urea injection over transients may lead to NO_2 slip. Another potentially important issue is the need for high efficiency for cold starts — which may lead manufacturers to place SCR close to the engine outlet, followed by a catalysed DPF (diesel particulate filter). In common with other catalysed DPF this could lead to high NO_2/NO_x ratios of around 60%. Kousoulidou et al. (2008) therefore assumed a value of 55% for Euro 4 to Euro 6 for diesel cars and vans i.e. the same as Grice et al. (2009). For HGVs, the NO_2/NO_x ratio was estimated at 18% and 35% for the Euro V and Euro VI cases. The Euro V value was derived assuming that three quarters of the fleet will be equipped with SCR and one quarter will be equipped with cooled EGR with an oxidation catalyst. The assumption for Euro VI is that 45% of the fleet would be equipped with SCR following a DPF and that 55% will be equipped with cooled EGR and catalysed DPFs.

In more recent work (Keuken et al., 2012), aggregated NO_2/NO_x factors were assumed for different years and driving conditions (urban, non-urban and motorway). For 2010 in urban areas for example, an NO_2/NO_x ratio of 22% was assumed for passenger cars and 6–7% for trucks (5.5–12t and >12t). Based on the assumptions used by Keuken et al. (2012) primary NO_2 emissions from road traffic in the Netherlands is expected to increase from 8 kt in 2000 to 15 kt by 2015 and subsequently to decrease to 9 kt by 2020.

Fu et al. (2013) used a PEMS on two Euro IV SCR-equipped urban buses. To understand the on-road SCR performance, Fu et al. (2013) calculated the amount of time aqueous urea was injected, based on the on-board instantaneous diagnostic (OBD) records. In SCR systems, aqueous urea is injected into the diesel exhaust gas stream when the catalyst light-off temperatures are above approximately 200 °C. Under real driving conditions, the catalyst temperatures are variable due to varying engine load. If catalyst temperatures are below the light-off temperature, the SCR system will stop injecting urea. Under higher speed freeway-type driving Fu et al. (2013) found that the injection ratio (a measure of how much urea is injected) was between 71 and 83%. In contrast, when driving on urban roads, the injection ratios were below 35%, which would be due to lower engine temperatures and therefore reduced injection of urea. These results underline that under urban-type driving conditions the effectiveness of SCR may be limited because the engine temperatures are too low for efficient operation.

What is clear from the previous work discussed is that there are many uncertainties associated with estimating both vehicular NO_x emissions and the level of NO_2/NO_x. Understanding the emissions is an increasingly complex issue because of the many technology options that can be adopted by manufacturers. Currently there is a lack of data concerning the performance of SCR systems under real driving conditions. While it is known these systems can be less effective under urban-type driving conditions, their emissions performance has not been adequately quantified. Additionally, there is further uncertainty over the amount of NO_2 that is emitted by these systems as a ratio to total NO_x — some work suggests very low NO_2/NO_x ratios while others suggest much higher ratios. A further and critical issue is understanding how vehicles emit in-service and whether the few test vehicles used in previous work adequately reflect emissions under actual usage conditions. These issues are of utmost importance to urban air pollution and in particular for exposure to NO_2. Exceedances of the European annual mean Limit Value for NO_2 tend to be restricted to urban areas where populations are highest and also where there is evidence that SCR systems may be ineffective.

The current work uses a comprehensive, dedicated vehicle emission remote sensing campaign in London with the principal aim of developing a better quantitative understanding of these issues. First, highly disaggregated emissions of NO_x, NO_2 and NH_3 are presented that provide new information on these issues. Second, we make use of detailed vehicle information to show how specific vehicle technologies affect emissions of NO_x and the NO_2/NO_x ratio and the effect of vehicle manufacturer. Finally, consideration is given to the NO_2/NO_x ratio estimates derived from the analysis of ambient measurements.

2. Experimental

2.1. Instrument details

Earlier work reported results from a commercial RSD (remote sensing detector) instrument — an AccuScan RSD-4600 instrument supplied by Environmental Systems Products (Carslaw et al., 2011, 2013; Rhys-Tyler and Bell, 2012; Rhys-Tyler et al., 2011). While the commercial instrumentation has proved to be effective, a critical deficiency for the current work is its ability to measure only NO and not NO_2. Given the potentially large contribution NO_2 could make to total NO_x for diesel vehicles the lack of NO_2 measurement is a significant drawback. For this reason the University of Denver FEAT (Fuel Efficiency Automobile Test) system was hired for a duration of 6 weeks during the summer of 2012. This instrument is described at length in other studies e.g. Popp et al. (1999) and Burgard et al. (2006a,b). An important advantage of the University of Denver FEAT is also its ability to measure ammonia (NH_3) in addition to NO_2. The measurement of ammonia is of potential importance for SCR systems where it is used to reduce (in both senses of the word) NO_x to N_2. Currently there are very few NH_3 emission measurements available from in-use vehicles.

The Denver FEAT instrument consists of a dual element light source (silicon carbide gas drier igniter and a xenon arc lamp) and a detector unit with four non-dispersive infrared detectors that provide an infrared (IR) reference (3.9 μm) and measurements of the gases carbon monoxide (CO, 3.6 μm), nitrogen dioxide (NO_2, 4.3 μm), and hydrocarbons (HC, 3.3 μm). The detector unit is connected by fibre optic cable to two, dispersive ultraviolet spectrometers that measure NO, sulphur dioxide (SO_2), NH_3 between 200 and 226 nm, and NO_2 between 430 and 447 nm. In addition to the spectrometers, two parallel light beams are used to measure the vehicle speed and acceleration and a video camera captures the vehicle number plate.

Instrument calibration for quality assurance purposes was performed a minimum of twice per day (morning and afternoon) on site, in accordance with guidance from the instrument developers. Three certified calibration gas cylinders (supplied by Air Products) were used containing known ratios of (a) CO, CO_2, C_3H_8, NO, SO_2, N_2 balance; (b) NH_3, C_3H_8, N_2 balance; and (c) NO_2, CO_2, air balance. A puff of gas is released into the instrument's path, and the measured ratios from the instrument are then compared to those certified by the gas cylinder manufacturer. These calibrations account for possible variations in instrument performance, and variations in ambient CO_2 levels caused by local sources, atmospheric conditions and instrument path length. Since propane (C_3H_8) is used to calibrate the instrument, all hydrocarbon measurements obtained from the remote sensor are reported as propane equivalents.

2.2. Vehicle information

A commercial supplier was used to match the 72,712 extracted licence plates against available vehicle records from the Driver and Vehicle Licensing Agency (DVLA) database, and the Society of Motor Manufacturers and Traders (SMMT) Motor Vehicle Registration Information System (MVRIS). The DVLA and SMMT data provided a reasonably comprehensive description of relevant vehicle parameters for passenger cars such as vehicle type, fuel type, vehicle age, and engine capacity. In addition, the datasets contained partial data (44%) on emissions 'Euro' classification for passenger cars, particularly for newer vehicles.

Where the Euro classification for passenger cars was missing from the DVLA/SMMT datasets, use was made of the light vehicle data published by the Vehicle Certification Agency (VCA), which has published data since 2000. These data include technical parameters for the vehicles such as manufacturer, year of manufacture, fuel type, engine capacity, CO_2 emissions, and emissions Euro standard. By matching these VCA data with the available data from DVLA/SMMT the majority (88%) of Euro classifications for observed passenger cars could be determined. Missing Euro classifications for the remaining passenger cars (12%) manufactured before 2000 (9%), were estimated from the year of manufacture.

Comprehensive vehicle information data were obtained from Transport for London (TfL) regarding the Euro classification of the bus fleet (Finn Coyle, Transport for London, 2012, pers.comm.). These data contained information on over 8500 TfL buses including registration number (allowing an exact match with the RSD measurement), manufacturer, engine size and Euro classification. Of particular value was information on the vehicle emissions technology used, including whether a vehicle used DPF, EGR, SCR and whether the vehicle used hybrid technology. The Euro II and III buses have all been retrofitted with DPF. The EGR vehicles use a partial flow DPF. All SCR-equipped vehicles (Euro IV, V and EEV) do not use a DPF and rely on in-cylinder control to reduce particle emissions e.g. high injection pressures and advanced timing. This emission reduction strategy can result in high engine-out emissions of NO_x, which is controlled by SCR. It should be noted that the SCR systems on the TfL buses were all OEM (Original Equipment Manufacturer) and were not optimised specifically to reduce NO_x emissions for urban driving conditions. Since these surveys were undertaken, TfL has started a bus retrofit programme that will fit 900 Euro III buses with an optimised SCR system designed to work effectively under London traffic conditions.

Euro emission classes for vehicle types other than passenger cars were determined as follows. Taxi (black cabs) Euro class was based on model, engine type, and year of manufacture. LTI TX1 models (Nissan engines) were originally manufactured to Euro 2 emissions standards, whereas later LTI TXII models with Ford engines (introduced around 2002) were manufactured to Euro 3 emissions standards. LTI TX4 models with VM Motori engines (introduced around 2006) were originally built to Euro 4 standards, with a Euro 5 compliant version introduced in 2012. Other taxi types with much smaller sample sizes include the LTI FX, the Carbodies Metrocab, the Mercedes Vito 111 (Euro 4), and the Mercedes Vito 113 (Euro 5). Where Euro classification data were missing for light and heavy goods vehicles, and powered two-wheelers, these were estimated based on year of manufacture. When combined with valid measurements for NO_2 a total of 68,073 observations were available for analysis.

2.3. Measurement surveys

The remote sensing surveys were carried out at four locations in London, from May 21st to July 2nd 2012. Data were collected on

Table 1
Summary characteristics of the four sampling locations in London. The vehicle summaries give the total count by major vehicle type. VSP is the estimated vehicle specific power based on Jimenez-Palacios (1998).

	Aldersgate St.	Queen Victoria St	A40 slip Rd	Greenford Rd
Latitude	51°31′8.21″N	51°30′42.87″N	51°32′39.56″N	51°31′11.03″N
Longitude	0°5′49.44″W	0°5′49.14″W	0°22′56.48″W	0°21′16.75″W
Mean speed ($km\ h^{-1}$)	28.3	29.1	60.2	40.1
Mean VSP ($kW\ t^{-1}$)	3.8	4.6	5.4	2.9
Cars	2844	6423	7105	18139
Vans	2403	5599	1868	3565
Taxi	4246	10796	30	67
Bus	1347	704	40	492
HGV 3.5t–12t	74	294	101	324
HGV >12t	47	98	219	204

weekdays during daylight hours, generally during the period 0800–1800 h, weather permitting. Across the entire survey period, ambient temperatures varied from ≈9–27 °C. The remote sensing instrumentation is not weather proof, so surveys were suspended during periods of rain. A particular focus of these surveys was to measure a large proportion of diesel vehicles; both light and heavy duty. For this reason two of the surveys were carried out in central London where there is a very high proportion of buses and taxis.

Table 1 gives a summary of the main characteristics of the four sampling campaigns. The two sites in central London (Aldersgate Street and Queen Victoria Street) both had very high proportions of buses and London taxis ('black cabs'). In total 15,139 measurements were made of London taxis. The bus measurements were split between those operated by TfL (1805) and non-TfL buses (782). For the passenger car fleet 20,030 petrol cars were measured together with 769 petrol hybrids and 13,582 diesel cars. Diesel cars therefore accounted for 39.5% of the car fleet. Note however, that for the more modern fleet (Euro 4/5) diesel cars accounted for 47% of total numbers, reflecting the recent increased sales of diesel cars in the UK. Together these surveys cover the range of urban-type driving conditions typical of London and many other urban areas.

The data from the four survey locations shown in Table 1 were combined into a single data set. The principal reason for combining the data was maximise overall samples sizes for further analysis while ensuring a good spread of urban driving conditions. It should also be noted that while there were differences in vehicle emissions between the sites, plotting the emission against VSP gave very similar relationships, suggesting that VSP provides a good way in which to account for the effect that vehicle operation has on emissions.

3. Results and discussion

3.1. Overall emission characteristics

The FEAT system provides emission results expressed as ratios to CO_2, which can also be expressed as fuel-based emission factors e.g. $g\ kg^{-1}$ of fuel burned. Expressing emission factors in this way is a very effective method of determining differences in emissions between vehicles and manufacturer model years. To express the emissions in absolute terms e.g. $g\ km^{-1}$ requires an estimate of fuel use at the time of measurement, which is not available but can be estimated (see Carslaw et al., 2011 for an example of such estimates). Clearly, if vehicles have improving fuel economy over time then this would affect the absolute emission estimate and this should be taken into account when considering the emission results.

The main results are summarised in Fig. 1 (for NO_x) and Fig. 2 (for the NO_2/NO_x ratio). These results have also been presented in tabular form to assist those who wish to use these results in emission inventory development (Table 2 for light duty vehicles and Table 3 for heavy duty vehicles). This section provides an overview of emissions by major vehicle category before considering the emissions from passenger cars, taxis and TfL buses in more detail. These latter three categories can be examined in more detail because in the former case the sample size is large and in the latter case due to the availability of detailed vehicle information.

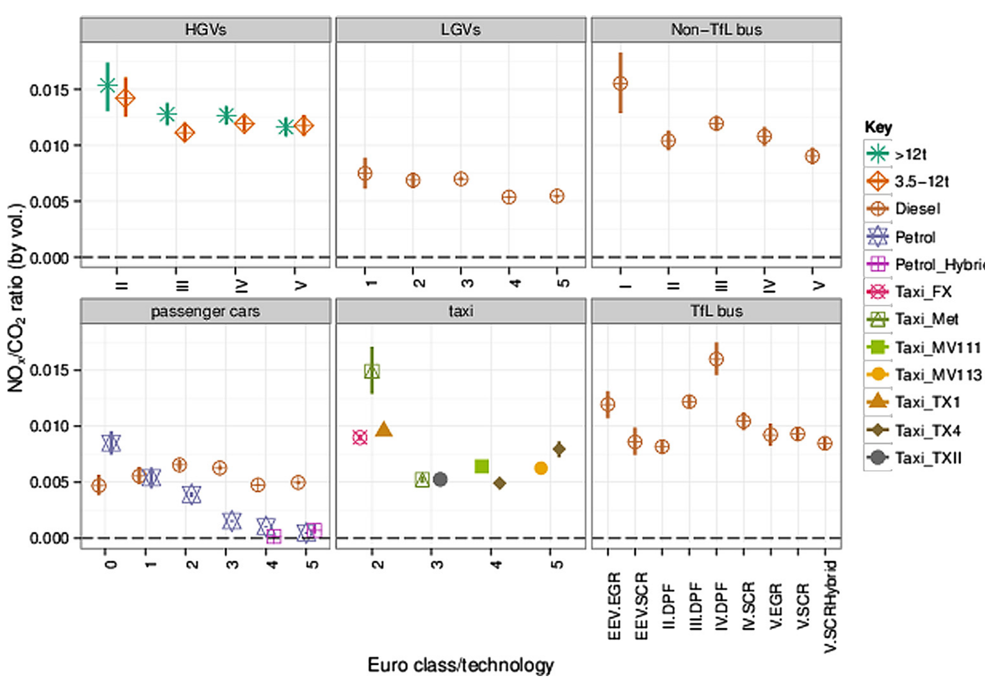

Fig. 1. Summary of NO_x/CO_2 ratios by major vehicle type. The uncertainties refer to the 95% confidence intervals in the mean. Vehicle types are split according to Euro classification, vehicle size, type of vehicle or fuel type.

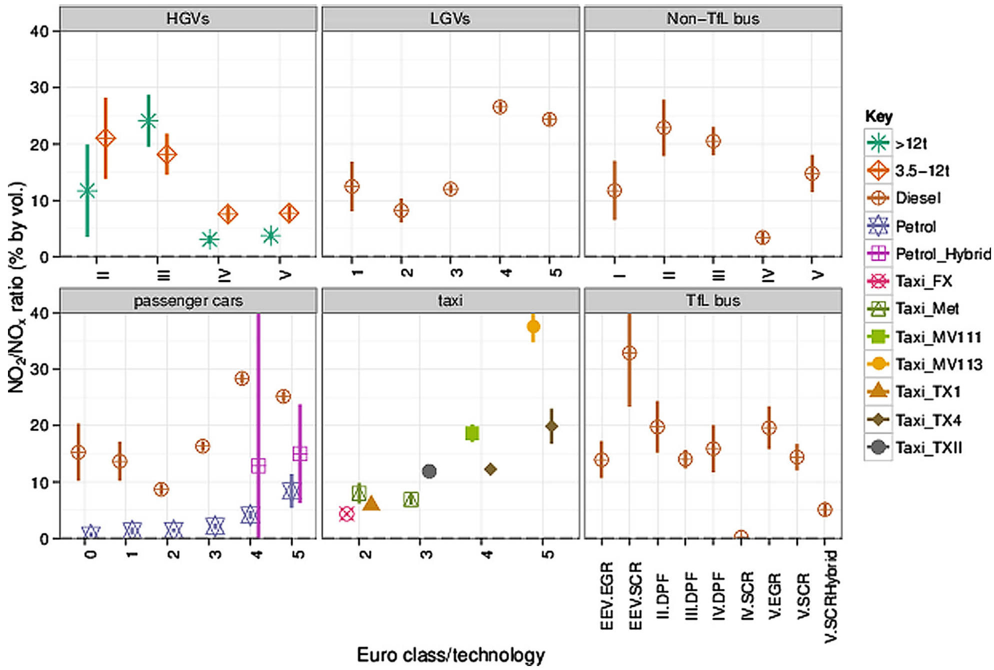

Fig. 2. Summary of NO_2/NO_x ratios by major vehicle type (% by vol.). The uncertainties refer to the 95% confidence intervals in the mean. Vehicle types are split according to Euro classification, vehicle size, type of vehicle or fuel type.

The summary overview of NO_x emissions shown in Fig. 1 reveals that progression through the Euro classes for almost all vehicle types indicates there has not been a significant change in NO_x emission. Unless stated otherwise all vehicles shown in Fig. 1 are diesel. The only vehicle type to have shown considerable reduction in NO_x is the petrol passenger car (including hybrids). Emissions from Euro 5 petrol cars are about a factor of 20 lower than pre-catalyst (pre Euro 1) vehicles. However, it should be noted that pre-catalyst cars are now at least 20 years old and vehicle degradation could be important. Nevertheless, emissions of NO_x from modern (Euro 5) petrol passenger cars are on average a factor of 10 less than equivalent diesel cars. Furthermore, in agreement with previous work the NO_2/NO_x ratio for petrol vehicle NO_x is also very low as shown in Fig. 2 and Table 2 — typically <5% except for Euro 5.

For the NO_2/NO_x ratio there is a much wider range across the different vehicle types, as shown in Fig. 2, Tables 2 and 3. For diesel

Table 2
Emission ratios (species/CO_2) for different light duty vehicles types. The volume ratios have been multiplied by 10,000. The uncertainties are shown as the 95% confidence interval in the mean. n is the sample size. The uncertainties in the NO_2/NO_x ratio were calculated based on the mean uncertainties calculated for NO_2 and NO_x.

Vehicle type	Fuel/type	Euro class	n	NO_x	NO_2	NO_2/NO_x (%)	NH_3
Passenger car	Petrol	0	204	85.1 ± 10.7	0.5 ± 0.4	0.6 ± 0.4	5 ± 1
Passenger car	Petrol	1	392	54.1 ± 6.5	0.7 ± 0.3	1.3 ± 0.6	9.3 ± 1.2
Passenger car	Petrol	2	2848	39.3 ± 2.4	0.5 ± 0.1	1.4 ± 0.4	9.4 ± 0.4
Passenger car	Petrol	3	5593	15.3 ± 1	0.3 ± 0.1	2.1 ± 0.5	7.8 ± 0.3
Passenger car	Petrol	4	8843	10.3 ± 0.7	0.4 ± 0.1	4.1 ± 0.7	5.4 ± 0.2
Passenger car	Petrol	5	1998	4.8 ± 0.7	0.4 ± 0.1	8.4 ± 3	3.4 ± 0.4
Passenger car	Petrol hybrid	4	154	1.6 ± 1	0.2 ± 0.4	12.9 ± 27.8	1.9 ± 0.6
Passenger car	Petrol hybrid	5	605	7 ± 3.2	1.1 ± 0.4	15 ± 8.9	4.5 ± 0.5
Passenger car	Diesel	0	15	47 ± 8.7	7.2 ± 2	15.3 ± 5	0.2 ± 0.2
Passenger car	Diesel	1	62	55.7 ± 7.4	7.6 ± 1.5	13.7 ± 3.3	0.2 ± 0.2
Passenger car	Diesel	2	363	65.5 ± 4.1	5.7 ± 0.5	8.7 ± 0.9	0.4 ± 0.2
Passenger car	Diesel	3	2610	62.9 ± 1.5	10.3 ± 0.4	16.3 ± 0.8	0.4 ± 0
Passenger car	Diesel	4	5836	47.7 ± 0.9	13.5 ± 0.4	28.4 ± 0.9	0.3 ± 0
Passenger car	Diesel	5	4577	49.9 ± 1	12.6 ± 0.4	25.2 ± 0.9	0.3 ± 0
London taxi	FX	2	877	90.1 ± 2.8	3.9 ± 0.3	4.3 ± 0.3	0.4 ± 0.1
London taxi	Met	2	80	149.4 ± 20.3	11.9 ± 2.1	8 ± 1.8	0.1 ± 0.5
London taxi	TX1	2	4148	95.7 ± 1.3	5.6 ± 0.2	5.9 ± 0.2	0.3 ± 0
London taxi	Met	3	148	52.5 ± 3.1	3.6 ± 0.5	6.9 ± 1	0.2 ± 0.1
London taxi	TXII	3	4050	52.7 ± 1	6.3 ± 0.2	11.9 ± 0.4	0.2 ± 0
London taxi	MV111	4	594	64.1 ± 1.3	11.9 ± 0.9	18.6 ± 1.5	0.2 ± 0
London taxi	TX4	4	4719	49.2 ± 0.7	6 ± 0.3	12.3 ± 0.5	0.2 ± 0
London taxi	TX4	5	185	79.7 ± 7.4	15.8 ± 2	19.9 ± 3.2	0.3 ± 0.1
London taxi	MV113	5	329	62.9 ± 3.1	23.6 ± 1.2	37.6 ± 2.7	0.3 ± 0
Van (N1)		1	26	74.8 ± 14.6	9.3 ± 2.8	12.5 ± 4.5	0.3 ± 0.2
Van (N1)		2	93	68.6 ± 7.7	5.6 ± 1.4	8.2 ± 2.2	0.2 ± 0.1
Van (N1)		3	2603	69.8 ± 1.6	8.4 ± 0.4	12 ± 0.7	0.3 ± 0
Van (N1)		4	5347	53.5 ± 1	14.2 ± 0.4	26.6 ± 0.9	0.3 ± 0
Van (N1)		5	4412	54.5 ± 1.2	13.3 ± 0.4	24.4 ± 0.9	0.3 ± 0

Table 3
Emission ratios (species/CO_2) for different heavy duty vehicles types. The volume ratios have been multiplied by 10,000. The uncertainties are shown as the 95% confidence interval in the mean. *n* is the sample size. The uncertainties in the NO_2/NO_x ratio were calculated based on the mean uncertainties calculated for NO_2 and NO_x.

Vehicle type	Technology	Euro class	*n*	NO_x	NO_2	NO_2/NO_x (%)	NH_3
TfL bus	DPF	II	161	81.9 ± 6	16.2 ± 3.6	19.7 ± 4.6	0 ± 0.1
TfL bus	DPF	III	631	122.1 ± 5.1	17.1 ± 1.8	14 ± 1.6	0 ± 0.1
TfL bus	DPF	IV	89	160.2 ± 13.9	25.5 ± 6.1	15.9 ± 4.1	0.1 ± 0.1
TfL bus	EGR	V	106	92.5 ± 10.1	18.1 ± 2.8	19.6 ± 3.8	0.1 ± 0.2
TfL bus	EGR	EEV	63	119.7 ± 12.6	16.7 ± 3.2	13.9 ± 3	−0.1 ± 0.2
TfL bus	SCR	IV	257	104.6 ± 7.8	0.2 ± 0.2	0.2 ± 0.2	1.2 ± 0.8
TfL bus	SCR	V	266	93.3 ± 6.1	13.4 ± 1.9	14.4 ± 2.2	0.6 ± 0.4
TfL bus	SCR	EEV	65	86.1 ± 11.9	28.3 ± 7.5	32.9 ± 9.8	0.4 ± 0.4
TfL bus	SCR hybrid	V	158	84.8 ± 5.4	4.3 ± 0.9	5.1 ± 1.1	0.2 ± 0.1
Non-TfL bus		I	11	155.4 ± 29.4	18.2 ± 7.2	11.7 ± 5.2	0 ± 0.4
Non-TfL bus		II	84	104.1 ± 8.7	23.8 ± 4.9	22.9 ± 5.1	0 ± 0.2
Non-TfL bus		III	318	119.5 ± 6.8	24.5 ± 2.6	20.5 ± 2.5	0.1 ± 0.1
Non-TfL bus		IV	159	108 ± 9.1	3.7 ± 1	3.4 ± 1	0.4 ± 0.5
Non-TfL bus		V	203	90.2 ± 7.7	13.3 ± 2.7	14.8 ± 3.3	0.1 ± 0.1
HGV (3.5–12t)		II	50	142.1 ± 18.2	29.9 ± 9.5	21 ± 7.2	0.8 ± 0.7
HGV (3.5–12t)		III	196	111.4 ± 8.4	20.2 ± 3.7	18.2 ± 3.6	0.3 ± 0.1
HGV (3.5–12t)		IV	307	119.2 ± 6.9	9 ± 1.6	7.5 ± 1.4	0.3 ± 0.1
HGV (3.5–12t)		V	230	117.5 ± 9.2	9.1 ± 1.4	7.7 ± 1.3	1.4 ± 1.8
HGV (>12t)		II	17	153.4 ± 21.6	18 ± 12.4	11.7 ± 8.2	0.4 ± 0.4
HGV (>12t)		III	130	127.7 ± 10.4	30.8 ± 5.4	24.1 ± 4.7	0.2 ± 0.2
HGV (>12t)		IV	223	126.8 ± 7.8	3.9 ± 0.9	3.1 ± 0.7	0.3 ± 0.3
HGV (>12t)		V	191	116.1 ± 8.2	4.4 ± 0.8	3.7 ± 0.7	0.2 ± 0.2

passenger cars the NO_2/NO_x ratio has increased from around 10–15% for pre-Euro 3 vehicles to between 25 and 30% for Euro 4 and Euro 5. These levels of NO_2/NO_x ratios are considerably lower than the estimates contained in Grice et al. (2009) where Euro 4/5 vehicles were assumed to emit 55% of their NO_x as NO_2. Similar findings were found for light goods vehicles. Furthermore, the taxi results also show similarities to the diesel cars and vans i.e. higher NO_2/NO_x ratios for Euro 4/5 vehicles compared with previous generations.

For the heavy duty vehicles there has been a clear reduction in NO_2/NO_x ratio from about 20% for Euro II/III to between 5 and 10% for Euro IV and V. There is also evidence to suggest the smaller HGVs (3.5–12t) tend to emit a higher NO_2/NO_x ratio than larger HGVs (>12t). For TfL and non-TfL buses the most striking result shown in Fig. 2 is that Euro IV NO_2/NO_x ratios can be very low. Indeed the results for Euro IV TfL buses suggest that almost all the NO_x emitted is in the form of NO.

3.2. Emissions from passenger cars

The detailed matching of individual vehicle emission measurements with comprehensive vehicle information allows the emissions from vehicles to be considered in many ways. For diesel passenger cars, for which there are large sample sizes and where it has been shown they are important emitters of NO_x and NO_2, the emissions can be considered in more detail than many other vehicle classes. Table 2, Figs. 1 and 2 show that Euro 4 and 5 diesel cars are both numerous (10,413 observed) and high emitters of NO_x and NO_2. Considering the emissions from Euro 4 and 5 passenger cars in more detail shows that there are several important determinants of emissions that are masked by aggregating to Euro class. In particular, it is found that both engine size and manufacturer are important. Fig. 3 summarises the information by plotting each manufacturer separately and identifying whether a vehicle is <2.0 L or ≥2.0 L engine size and whether the vehicle is Euro 4 or Euro 5.

There are several important findings shown in Fig. 3. The first characteristic to note is that there are clear differences in emissions by manufacturer. The second characteristic to note is that the emissions of NO_x span a relatively narrow range for both Euro 4 and Euro 5 vehicles and for all engine sizes, with the vast majority of emissions between the 0.004 to 0.006 range. There is however more variability in the NO_x emissions for Euro 5 vehicles compared with Euro 4. The third characteristic to note is that there is a much wider range in the NO_2 /NO_x ratio from ≈12% to ≈55%. Within this broad range of NO_2/NO_x there are consistent patterns that emerge. First, vehicles with engines <2.0 L tend to be associated with lower NO_2/NO_x ratios (mean NO_2/NO_x = 27%) compared with vehicles with engines >2.0 L (mean NO_2/NO_x = 43%). While there are broad differences seen in the NO_2/NO_x ratio by engine size it is not clear whether engine size itself is the causal factor controlling the NO_2/NO_x ratio.

It is more likely that the variation seen in Fig. 3 for the NO_2/NO_x ratio is determined by the emission control strategies used by specific manufacturers. Considering just the Euro 5 vehicles, one major manufacturer accounting for 22% of measurements is associated with the lowest NO_2/NO_x ratio of 12.1 ± 0.9%, whereas another major manufacturer accounting for 25% of measurements is associated with a NO_2/NO_x ratio of 37.6 ± 8.5%. Even these differences can be disaggregated further e.g. to particular model cars where more variation can be found — although the sample size reduction can become important. The main point however is that simple representations of emissions by Euro class e.g. as used in emission inventories hide a very large amount of variation in the NO_2/NO_x ratio. It also follows that if manufacturers were to adopt the emissions reduction strategies of the lowest emitters of NO_2 then there would be scope for considerable reduction in NO_2 emissions.

Several studies have reported NH_3 emissions from vehicles can be important (Bishop et al., 2010; Burgard et al., 2006b; Huai et al., 2005). The NH_3 results for passenger cars are shown in Fig. 4. It is clear from Fig. 4 that NH_3 emissions are most important for petrol-fuelled vehicles. It is also clear that NH_3 emissions increased when catalyst-equipped vehicles first entered the UK fleet in 1992. The emissions of NH_3 are highest for the early catalyst vehicles (Euro 1 and Euro II). Since the introduction of Euro 3 vehicles in 2000, NH_3 emissions have monotonically reduced such that emissions in 2012 are about a third of those during the mid and late 1990s. Fig. 4 also confirms that hybrid petrol vehicles behave in the same way as conventional petrol cars.

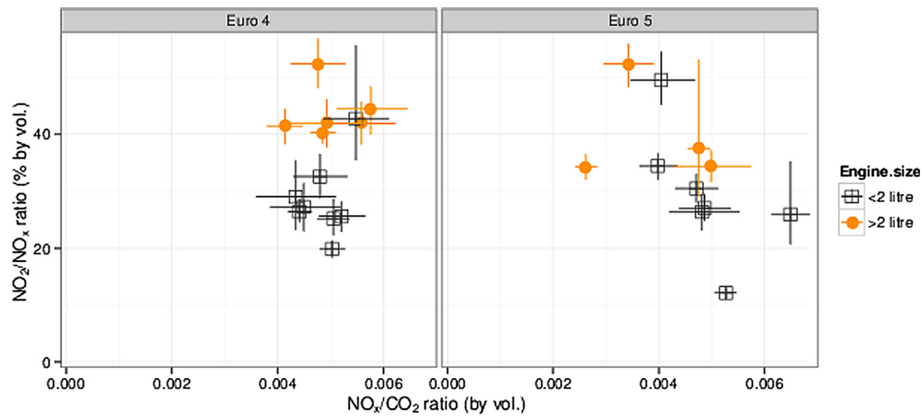

Fig. 3. Summary of NO_x emissions from Euro 4 and 5 diesel passenger cars against NO_2/NO_x ratio split by engine size (<2.0 L and ≥2.0 L). Each point represents a different vehicle manufacturer and data are only shown where more than 100 measurements are available for a particular manufacturer, Euro class, engine size combination. The uncertainties refer to the 95% confidence intervals in the mean.

3.3. Emissions from London taxis

Over 15,000 measurements of taxis were made, the majority being London Taxi International (LTI) TX1, TXII, and TX4 models. As a result of the large sample size, the emissions from taxis can be disaggregated in more detail than most other vehicle types. Current TfL regulations stipulate that annual licences are only issued to taxis that meet Euro 3 emissions standards, which is achieved either by (a) operating a vehicle originally manufactured to Euro 3 standards (or later); (b) retro-fitting approved emissions reduction equipment; or (c) using an LPG conversion.

There is a clear indication that the NO_2/NO_x ratio from taxis manufactured since around 2008 has been increasing. This is true for the LTI TX4, and the Mercedes Vito models. The newest versions of the Mercedes Vito taxis (manufactured in 2011 and 2012) are shown to have the highest absolute emissions of primary NO_2. The NO_2/NO_x ratio from the taxi fleet is observed to increase significantly for taxis manufactured since around 2009, with substantial variation between manufacturers. Whilst NO_2/NO_x ratio was typically below 10–12% prior to 2005, LTI TX4 models manufactured in 2011 and 2012 have NO_2/NO_x ratios of around 27%, whilst the Mercedes Vito models manufactured in 2011 and 2012 have NO_2/NO_x values of around 35–40%. These changes are similar in many ways to those seen for diesel passenger cars in that recent (Euro 4/5) vehicles have not shown an appreciable decrease in NO_x emissions but the NO_2/NO_x ratio has increased considerably.

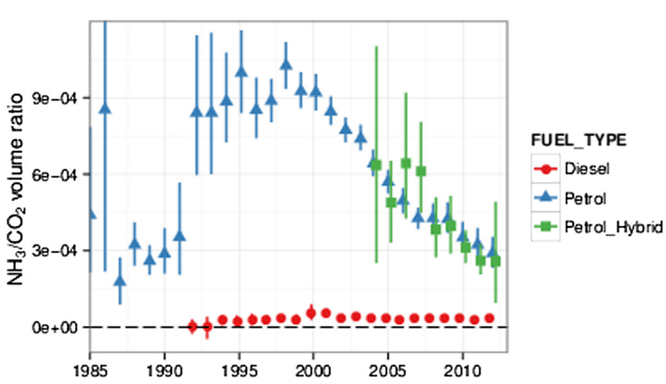

Fig. 4. Summary of NH_3 emissions from passenger cars by year of manufacture. The uncertainties refer to the 95% confidence intervals in the mean. Vehicle types are split according to fuel or technology type.

3.4. Emissions from TfL buses

The comprehensive vehicle information from TfL on their bus fleet allows for a more detailed consideration of emissions. In particular, the identification of individual buses with specific after-treatment technology is very useful. Additionally, because manufacturers can adopt different approaches in their implementation of technologies such as SCR it is also useful to consider the effect of bus manufacturer on emissions. The following results anonymise the manufacturer name but still provide useful information on the differences that can be expected.

The results for NO_x are shown in Fig. 5a, which shows the effect of manufacturer, Euro classification and type of after-treatment technology used. Overall there is a relatively narrow range of NO_x emissions with most technologies and manufacturers being around the 0.01 NO_x/CO_2 ratio. There is little indication in Fig. 5a that emissions of NO_x improve as the Euro classifications advance, which can also be seen in Table 3. Nevertheless, there are differences by Euro class. Euro II vehicles have lower NO_x emissions than Euro III vehicles. It is also clear that within the Euro III vehicles there are some important differences by manufacturer. However, probably the most important result from Fig. 5a is the performance of SCR systems. For Euro V vehicles the SCR results are comparable but not better than EGR. However, for Euro IV and EEV vehicles, SCR does show an improvement over the DPF or EGR-equipped vehicles of approximately 30% for NO_x. The SCR technology offers manufacturers some freedom to increase engine-out NO_x emissions for the benefit of higher fuel efficiency and reduced PM emissions, knowing that the NO_x should be controlled by the SCR. The lack of a reduction in NO_x is consistent with other work reported for SCR systems operating under urban-type driving conditions e.g. Velders et al. (2011) and Fu et al. (2013). However, unlike previously published information, the results shown in Fig. 5a consist of measurements from hundreds of vehicles in use.

In contrast to the NO_x result shown in Fig. 5a the NO_2/NO_x ratio shows far more variability as shown in Fig. 5b. These results span NO_2/NO_x ratios from almost zero to over 40%. The highest NO_2/NO_x ratios are observed for buses fitted with DPF, where NO_2 is deliberately formed to help oxidise particle emissions. Even here, there can be a wide range of NO_2/NO_x ratios, which strongly depend on the bus manufacturer. For example, manufacturer B2 has a very low NO_2/NO_x ratio of about 7%, whereas manufacturer B8 has NO_2/NO_x ratio >40% — for Euro III vehicles. For buses fitted with a DPF it is found that on average the NO_2/NO_x ratio is 15–20%, which is lower

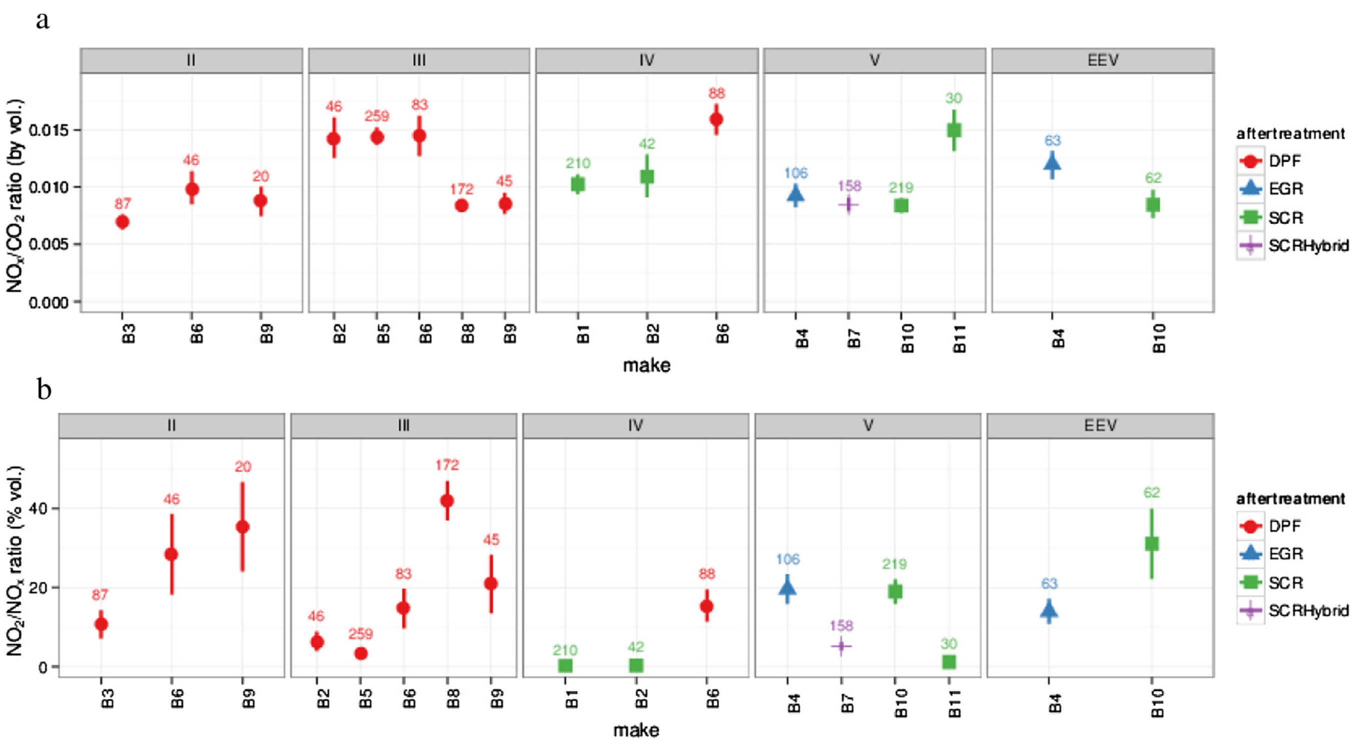

Fig. 5. a) NO_x/CO_2 ratios by bus manufacturer and b) NO_2/NO_x ratios. The results are shown by Euro class in each panel and are split by the type of after-treatment used. The bus manufacturer has been anonymised. The numbers show the sample size.

than previously reported values nearer 40% (AQEG, 2008; Grice et al., 2009).

Perhaps most striking about Fig. 5b is the very wide range in NO_2/NO_x ratios seen for buses fitted with SCR. While these buses show only a small range in NO_x emissions, the range in NO_2/NO_x ratio is very large i.e. from close to zero to about 30%. For bus manufacturers B1 and B2 almost all the NO_x measured is in the form of NO. The SCR-equipped buses with very low NO_2 emissions are Euro IV (two manufacturers) and Euro V (one manufacturer). For Euro IV vehicles only 'mild' reduction appears to be occurring where NO_2 is reduced to NO and not through to N. The low NO_2/NO_x ratios seen for Euro IV SCR buses has also been observed in other work. For example, Fu et al. (2013) used a PEMS on two Euro IV buses and also found low NO_2/NO_x ratios of only 2.8% (Fu et al., 2013, personal communication, 3 May). The two vehicles tested by Fu et al. (2013) only had SCR systems fitted and not other after-treatment devices. However, as already noted by Fu et al. (2013), the injection of urea under low temperature (urban) driving conditions is low, which would tend to suggest the very low NO_2/NO_x ratios are related to the optimisation of the combustion conditions in the engine rather than being related to the SCR system.

The most advanced EEV vehicles tend to have much higher NO_2/NO_x ratios of about 30%. A summary of this variation by Euro classification is better seen in Fig. 2. The higher NO_2/NO_x ratios seen for the newer vehicle types could be due to stronger oxidation being used in these vehicles to reduce PM, CO and HC emissions. A further issue is that for SCR to work efficiently i.e. the reactions are fast, equal amounts of NO and NO_2 are required in the reaction with NH_3. In other words, oxidation of NO to NO_2 is required upstream of the SCR. However, similar to the behaviour of the Euro IV vehicles, the SCR does not appreciably reduce total NO_x but this time results in higher NO_2/NO_x ratios due to the increased oxidation upstream of the SCR.

One concern with the use of SCR on road vehicles is increased emissions of NH_3, which this work has been able to quantify. Emissions of NH_3 are important because of its role in secondary aerosol formation. However, it is found that only small amounts of NH_3 are emitted by TfL buses that are fitted with SCR, as shown in Table 3. There is some evidence that older SCR (Euro IV) emit higher amounts of NH_3 compared with newer (Euro V and EEV) vehicles, but the emissions are still low. Indeed, when expressed as a ratio to CO_2, Euro IV SCR buses emit considerably less NH_3 than older catalyst-equipped petrol cars. For example, Euro IV TfL buses emit 1.2 ± 0.8 and Euro 1 petrol cars emit 9.3 ± 1.2 NH_3/CO_2.

The benefit of the TfL bus information data is that the behaviour of a large number of vehicles can be understood in terms of the vehicle after-treatment used. It is apparent from these results that clear patterns of behaviour emerge. While no similarly detailed information was available for HGVs or non-TfL buses, similar patterns of behaviour emerge. For example, in Fig. 1 it is apparent that neither HGVs (3.5t–12t and >12t) nor non-TfL buses show any clear evidence of a reduction in NO_x emissions from Euro II to Euro V; similar to what is observed for TfL buses. Similarly, NO_2/NO_x ratios for Euro IV HGVs and non-TfL buses are also on average much lower than Euro II and III, as shown in Fig. 2.

4. Conclusions

The main finding from this work is that there is little evidence of NO_x emissions reduction from all types of diesel vehicles over the past 15–20 years. It is only petrol passenger cars (including hybrids) where strong evidence exists for effective NO_x control. The lack of NO_x reduction in diesels is also apparent for vehicles with after-treatment specifically designed to reduce NO_x. The large number of measurements made together with detailed vehicle information reveals that the level of NO_2 in the exhausts of diesel vehicles can be highly variable. For diesel passenger cars there is a strong effect of both engine size and vehicle manufacturer on the level of NO_2 emission, where the NO_2/NO_x ratio varies from $\approx 12\%$ to $>50\%$. These findings suggest that the after-treatment approaches adopted by some manufacturers results in much lower NO_2/NO_x ratios than others and also highlights the considerable variability that exists within simple Euro class-based emission factor approaches.

The detailed vehicle information provided by TfL concerning their bus fleet (e.g. whether a vehicle uses SCR, EGR etc.) provided an opportunity to quantify the emissions from a large number of specific vehicle technologies. It is clear that urban buses fitted with OEM SCR systems are not effective at reducing total NO_x emissions. However, within the range of SCR systems fitted to buses is a very wide behaviour for emissions of NO_2 — from almost all the exhaust being NO (Euro IV) to about 30% of it being in the form of NO_2. For newer bus technologies (EEV) also there is no appreciable reduction in emissions of NO_x compared with non-SCR systems but they have a higher emission of NO_2. The higher emission of NO_2 in EEV vehicles is likely due to the stronger oxidation used, resulting in the more efficient conversion of NO to NO_2.

TfL have recognised the issues with OEM SCR systems under urban (low temperature) conditions and have been developing systems optimised for NO_x reduction under these conditions. Unfortunately these optimised retrofit vehicles only entered the fleet after the measurement campaigns discussed in this paper. For this reason it would be useful to use the RSD technique again when appreciable numbers of these vehicles enter the fleet to understand their in-use emissions performance for NO_x and NO_2. Such measurements will be important because it is now clear that OEM SCR systems fitted to current generation buses are ineffective under these conditions. While it is also important to reduce NO_x for other types of conditions (e.g. motorway driving) the poor performance in urban areas is a particular concern because that is where exposure is most important and where exceedances of European standards for NO_2 are mostly located.

Acknowledgements

We wish to thank the Department for Environment, Food and Rural Affairs (Defra) for funding this work. We would like to thank Professor Donald Stedman and his team at the University of Denver for making available their remote sensing equipment, Enviro Technology Services plc for their experimental support and Colin Oates for his work towards the measurement campaigns. We would like to thank the London boroughs for their help and support in planning and implementing the surveys in London. In particular thanks go to Ruth Calderwood (City of London), Dr John Freeman and Rizwan Yunus (Ealing), and Bill Legassick (Southwark). We are very grateful to Finn Coyle from TfL for providing both the comprehensive bus information used in this report and for comments on aspects of it. We also benefited enormously from the work of Camilla Ghiassee (now at Public Health England) during many of the surveys.

References

1999/30/EC, D., 29.6.1999. Council Directive 1999/30/EC of, 22 April, 1999. Relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air (The First Daughter Directive). Off. J. Eur. Communities L163/41. En Series.

96/62/EC, D., 21.11.1996. Council Directive 96/62/EC of, 27 September, 1996. On ambient air quality assessment and management (The Framework Directive). Off. J. Eur. Communities L296/55. En Series.

Anttila, P., Tuovinen, J.-P., 2010. Trends of primary and secondary pollutant concentrations in Finland in 1994–2007. Atmos Environ. 44 (1), 30–41.

Anttila, P., Tuovinen, J.-P., Niemi, J.V., 2011. Primary NO_2 emissions and their role in the development of NO_2 concentrations in a traffic environment. Atmos. Environ. 45 (4), 986–992.

AQEG, 2008. Trends in Primary Nitrogen Dioxide in the UK. Air Quality Expert Group. Report prepared by the Air Quality Expert Group for the Department for Environment. Food and Rural Affairs; Scottish Executive; Welsh Assembly Government; and Department of the Environment in Northern Ireland.

Beevers, S.D., Westmoreland, E., de Jong, M.C., Williams, M.L., Carslaw, D.C., 2012. Trends in NO_x and NO_2 emissions from road traffic in Great Britain. Atmos. Environ. 54, 107–116.

Bishop, G.A., Peddle, A.M., Stedman, D.H., Zhan, T., MAY 1 2010. On-road emission measurements of reactive nitrogen compounds from three California cities. Environ. Sci. Technol. 44 (9), 3616–3620.

Burgard, D., Dalton, T., Bishop, G., Starkey, J., Stedman, D., 2006a. Nitrogen dioxide, sulfur dioxide, and ammonia detector for remote sensing of vehicle emissions. Rev. Sci. Instrum. 77, 14101-1-5.

Burgard, D.A., Bishop, G.A., Stedman, D.H., 2006b. Remote sensing of ammonia and sulfur dioxide from on-road light duty vehicles. Environ. Sci. Technol. 40 (22), 7018–7022.

Carslaw, D.C., 2005. Evidence of an increasing NO_2/NO_x, emissions ratio from road traffic emissions. Atmos. Environ. 39 (26), 4793–4802.

Carslaw, D.C., Beevers, S.D., Tate, J.E., Westmoreland, E., Williams, M.L., 2011. Recent evidence concerning higher NO_x emissions from passenger cars and light duty vehicles. Atmos. Environ. 45, 7053–7063.

Carslaw, D.C., Williams, M.L., Tate, J.E., Beevers, S.D., 2013. The importance of high vehicle power for passenger car emissions. Atmos. Environ. 68, 8–16.

EC, 2007. Regulation (EC) No 715/2007 of the European Parliament and the Council of 20 June 2007 on Type Approval of Motor Vehicles with Respect to Emissions from Light Passenger and Commercial Vehicles (Euro 5 and Euro 6). European Commission, Brussels, Belgium.

EC, 2009. Regulation (EC) No 595/2009 of the European Parliament and the Council of 18 June 2009 on Type-approval of Motor Vehicles and Engines with Respect to Emissions from Heavy Duty Vehicles (Euro VI). European Commission, Brussels, Belgium.

EEA, 2012. Air Quality in Europe — 2012 Report. European Environment Agency. No. 4/2012, ISSN 1725-9177.

Fu, M., Ge, Y., Wang, X., Tan, J., Yu, L., Liang, B., 2013. NO_x emissions from Euro IV busses with SCR systems associated with urban, suburban and freeway driving patterns. Sci. Total Environ. 452–453 (0), 222–226.

Grice, S., Stedman, J., Kent, A., Hobson, M., Norris, J., Abbott, J., Cooke, S., 2009. Recent trends and projections of primary NO_2 emissions in Europe. Atmos. Environ. 43 (13), 2154–2167.

Huai, T., Durbin, T.D., Younglove, T., Scora, G., Barth, M., Norbeck, J., 2005. Vehicle specific power approach to estimating on-road NH_3 emissions from light-duty vehicles. Environ. Sci. Technol. 39 (24), 9595–9600.

Hueglin, C., Buchmann, B., Weber, R., 2006. Long-term observation of real-world road traffic emission factors on a motorway in Switzerland. Atmos. Environ. 40 (20), 3696–3709.

Jimenez-Palacios, J., 1998. Understanding and Quantifying Motor Vehicle Emissions with Vehicle Specific Power and TILDAS Remote Sensing (Ph.D. thesis). Massachusetts Institute of Technology.

Keuken, M.P., Roemer, M.G.M., Zandveld, P., Verbeek, R.P., Velders, G.J.M., 2012. Trends in primary NO_2 and exhaust PM emissions from road traffic for the period 2000–2020 and implications for air quality and health in the Netherlands. Atmos. Environ. 54 (0), 313–319.

Kousoulidou, M., Ntziachristos, L., Mellios, G., Samaras, Z., 2008. Road-transport emission projections to 2020 in European urban environments. Atmos. Environ. 42 (32), 7465–7475.

Popp, P.J., Bishop, G.A., Stedman, D.H., 1999. Development of a high-speed ultraviolet spectrometer for remote sensing of mobile source nitric oxide emissions. J. Air Waste Manag. Assoc. 49 (12), 1463–1468.

Rhys-Tyler, G.A., Bell, M.C., 2012. Toward reconciling instantaneous roadside measurements of light duty vehicle exhaust emissions with type approval driving cycles. Environ. Sci. Technol. 46 (19), 10532–10538.

Rhys-Tyler, G.A., Legassick, W., Bell, M.C., 2011. The significance of vehicle emissions standards for levels of exhaust pollution from light vehicles in an urban area. Atmos. Environ. 45 (19), 3286–3293.

Velders, G.J.M., Geilenkirchen, G.P., de Lange, R., 2011. Higher than expected NO_x emission from trucks may affect attainability of NO_2 limit values in the Netherlands. Atmos. Environ. 45 (18), 3025–3033.

Weiss, M., Bonnel, P., Hummel, R., Provenza, A., Manfredi, U., 2011. On-road emissions of light-duty vehicles in Europe. Environ. Sci. Technol. 45 (19), 8575–8581.