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The diminishing importance of nitrogen dioxide emissions from road vehicle exhaust

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ABSTRACT

The direct emission of nitrogen dioxide (NO_2) from road vehicle exhaust has been an important contributor to near-road ambient concentrations of NO_2 in many European cities. Diesel vehicles and their use of emission control technologies such as Diesel Oxidation Catalysts, have dominated the emission of NO_2 from road vehicles. In this work, we summarise findings from recent vehicle emission remote sensing measurements in the UK that provide detailed information on the emissions of NO_2 and total NO_x(NO_2 + NO). We show that while new diesel cars and light commercial vehicles are associated with high (typically 30%) proportions of NO_2/NO_x, the amount of absolute NO_x and NO_2 emitted by most Euro 6 vehicles has decreased substantially and that absolute emissions of NO_2 have been reducing since around 2007. Additionally, we find that the amount of NO_2 decreases as the vehicle mileage increases. Taken together, these factors have led to substantial reductions in emissions of NO_2 in recent years from light duty diesel vehicles, which has contributed to reduced roadside NO_2 concentrations. There is a need however for commonly used emission factor models to account for these changes in emissions of NO_2.

1. Introduction

1.1. Background and aims

In Europe there remains considerable concern over the ambient concentrations of NO_2, which in many locations exceed European Directive limit values. In particular, exceedances of the annual mean NO_2 limit value of 40 $\mu g\,m^{-3}$ is the principal concern. Locations where the 40 $\mu g\ m^{-3}$ limit are exceeded tend to be restricted to the near-road environment. It is these locations where directly emitted (primary) NO_2 emissions from vehicles has greatest impact. The extent to which primary NO_2 emissions affect roadside concentrations can vary considerably depending on the nature of the vehicle fleet and the absolute concentrations of NO_x and NO_2.

Over the past 15 years or so, the emission of directly emitted NO_2 emerged as an important issue (Carslaw, 2005) affecting near-road concentrations of NO_2. More recent studies in Europe have also confirmed the importance of directly emitted NO_2 on the ambient NO_2 concentrations close to roads (Degraeuwe et al., 2017; Casquero-Vera et al., 2019). The increased importance of NO_2 emissions has been driven by the adoption of diesel emission control technologies such as Diesel Oxidation Catalysts (DOC), which deliberately oxidise NO to NO_2 and use the NO_2 to enhance the oxidation of CO, hydrocarbons and particulate matter.

Recently, evidence has emerged from the analysis of atmospheric measurements that the proportion of NO_x emitted as NO_2 has levelled-off or decreased at roadside sites (Grange et al., 2017; Carslaw et al., 2016). The corresponding evidence relating to NO_2 emissions from vehicle emission testing is however weaker. In part, this relative lack of evidence is related to vehicle emissions legislation itself, which only considers total NO_x and does not speciate NO_2. However, a wider issue is that it is challenging to undertake measurements under real-world driving conditions from sufficient vehicles to robustly characterise their emissions.

Emissions of NO_x and other pollutants from vehicles are constantly evolving as new technologies enter vehicle fleets and older vehicles leave. Over the past few years there have been major changes in this respect as advanced diesel NO_x control technologies have been adopted. Two major technologies are now in common use: Lean NO_x Traps (LNT) and Selective Catalytic Reduction (SCR). Both these technologies have the potential to reduce the emissions of NO_x and NO_2 significantly. LNT

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and SCR are now the dominant technologies used on light duty vehicles for the control of NO_x and it is important to understand their efficacy under real driving conditions with respect to overall NO_x reduction and their influence on direct NO_2 emissions. With LNT NO_x is adsorbed onto a catalyst during lean engine operation. When the catalyst is saturated, the system is regenerated using short periods of fuel-rich operation during which NO_x is catalytically reduced. In SCR a catalyst reduces NO_x to gaseous nitrogen and water in the presence of ammonia. For light-duty vehicles aqueous urea solution (AdBlue™) is the source of ammonia.

Over the past few years, there has been a considerable increase in the number of laboratory and on-road emission measurements from vehicles. This increase reflects the concern that emissions from vehicles emitted under real driving conditions are many times that measured over laboratory conditions. The widespread adoption of LNT and SCR on light duty Euro 6 vehicles has coincided with an increased amount of emissions data from these vehicles (Ko et al., 2017; O'Driscoll et al., 2018; Bernard et al., 2018). However, while these measurements provide much-needed information on the emissions of NO_x, most studies fail to speciate between NO and NO_2. While such speciation is irrelevant from a Type Approval perspective, it is nevertheless important from an urban air pollution perspective.

This paper aims to better understand the recent evidence from comprehensive vehicle emission remote sensing measurements relating to the emission of NO_x and NO_2. Consideration is given to how the emission of NO_2 has changed through progressively more stringent Euro standards and by the date a vehicle was manufactured. The focus of the current work is on understanding the emissions from light duty vehicles; specifically diesel passenger cars and Light Commercial Vehicles (LCV, N1 Type Approval category). For the first time, we consider the effect of vehicle mileage at the time of measurement to understand potential deterioration effects.

2. Experimental

2.1. Instrumentation

The current work is based on comprehensive measurements from a spectroscopic remote sensing (RS) instrument developed by the University of Denver. The Fuel Efficiency Automobile Test (FEAT) instrument has been used in numerous campaigns around the world and is described extensively elsewhere (Carslaw and Rhys-Tyler, 2013; Bishop and Stedman, 2015; Burgard et al., 2006; Jerksjö et al., 2008).

The instrument consists of a source and detector positioned on either side of a single lane road. The source is a collinear beam of non-dispersive infrared (IR) and dispersive ultraviolet (UV) light, which is focused across the single lane and into the detection unit. Upon entering the detector, the collinear beam is focused onto a dichroic beam splitter, which separates the IR and UV components. The IR component passes onto a spinning polygon mirror, which spreads the beam equally across four infrared detectors, to measure CO, CO_2, hydrocarbons (HCs) and a background reference. The UV component is reflected off the dichroic mirror and passes through a quartz fibre bundle to two separate UV spectrometers. The first measures SO_2, NH_3 and NO, and the second measures NO_2. As a vehicle passes through the FEAT setup, the control computer triggers the assessment of the exhaust plume when it detects the rear of the vehicle blocking the first speed bar laser. At this point, the ratio of CO, HCs, SO_2, NH_3, NO and NO_2 to CO_2 are quantified using the method described above. All species are assessed as a ratio to CO_2, due to a vehicle exhaust plume varying greatly in terms of density, path length and position of emission. The speed bar lasers provide a measurement of the vehicle speed and acceleration. Finally, a video camera is used to photograph the vehicle registration plate, which can then be used to obtain vehicle technical information as described in section 2.3.

As these measurements are spectroscopic, changes in atmospheric conditions can alter the absorbance peaks used to characterise all species. To counter these effects, a two-stage calibration process was undertaken every few hours. First, the absorbance from each respective UV spectrum for SO_2, NH_3, NO and NO_2 is compared to a calibration spectrum, using a classical least squares fitting routine in the same region used to obtain the vehicle emissions. In background conditions, *i.e.* no traffic flow, quartz cells containing the high purity reference gases are inserted into the detector, directly in front of the UV light passing into the optic fibre, giving clear reference spectra. The second step involves using reference calibration gases of each component as a ratio to CO_2. Three audit cylinder were used: (1) 6000 ppm propane, 6% CO and CO_2, 3000 ppm NO in N_2, (2) 1000 ppm NH_3, 6000 ppm propane in N_2, (3) 500 ppm NO_2, 15% CO_2 in synthetic air. A puff of gas from each cylinder is released into the instrument's path, and the measured ratios from the instrument are then compared to those certified by the cylinder manufacturer (BOC). These calibrations account for day-to-day variations in instrument sensitivity due to changes in ambient CO_2 levels caused by local sources, atmospheric pressure and instrument path length. Since propane is used to calibrate the instrument, all hydrocarbon measurements are reported as propane equivalents.

2.2. Site details and measurement conditions

Remote sensing surveys were carried out in two UK cities, York and London in 2017 and early 2018. York and London were chosen as two contrasting locations, with the latter offering the potential for follow-up measurements made in 2012/2013 (Carslaw and Rhys-Tyler, 2013). A total of 7413 vehicle emission measurements were recorded at three locations in York between 12th July and 20th September 2017 over 12 days, and a further 34,055 vehicles were measured at three locations in London between 14th November 2017 and 12th April 2018 over 15 days. The data were combined into a single data set comprised of 41,468 measurements. The surveys were carried out on weekdays during daylight hours (approximately 0900–1700 h) apart from during periods of rain. Tables 1 and 2 provide further details of the measurement campaigns in York and London respectively. Ambient temperatures ranged from approximately 15 to 21 °C during the York survey period, whilst temperatures were considerably lower during the London measurement period (≈ 3–15 °C). Overall, the surveys represented a wide

Table 1
Site information for measurement locations in York.

	University Rd	A59/A1237	Clifton Moor
Latitude	53°56'57.5"N	53°58'21.2"N	53°59'15.0"N
Longitude	1°03'15.0"W	1°08'38.1"W	1°05'36.5"W
Ambient temperature range (°C)	16–22	17–21	15–16
Gradient (%)	0.4	0.0	0.0
Mean speed (km h^{-1})	28.8	36.4	42.1
Mean VSP (kW t^{-1})	6.1	9.0	13.1
Car (M1)	3648	2609	48
Bus (M2 + M3)	161	9	0
LCV (N1)	551	324	6
HGV (N2 + N3)	20	34	0

Table 2
Site information for measurement locations in London.

	Greenford Rd	West End Rd	Putney Hill
Latitude	51°31'11.4"N	51°34'06.7"N	51°27'19.7"N
Longitude	0°21'16.7"W	0°25'20.8"W	0°13'10.1"W
Ambient temperature range (°C)	12–15	3–7	5–14
Gradient (%)	0.7	0.0	3.0
Mean speed (km h^{-1})	35.1	32.7	33.3
Mean VSP (kW t^{-1})	5.3	8.0	8.6
Car (M1)	2506	2519	16659
Bus (M2 + M3)	121	51	1445
LCV (N1)	552	438	5582
HGV (N2 + N3)	24	25	355

spread of urban-type driving conditions; average vehicle speed by site location varied from 26.8 to 39.0 km h^{-1}, whilst average vehicle specific power (VSP) ranged from 5.3 to 13.1 kW t^{-1}. In total, 27,989 measurements were made of passenger cars. The passenger car fleet was comprised of 13,969 petrol cars, 12,700 diesel cars, 1312 petrol hybrids and 8 diesel hybrids. Diesel cars therefore accounted for 45.4% of the passenger car fleet. Furthermore, around 99% of the measured 7453 light commercial and 458 heavy goods vehicles were diesel vehicles, as determined by the matched technical vehicle information.

2.3. *Vehicle technical information*

Individual vehicle information was obtained from a commercial supplier (CDL Vehicle Information Services Limited). CDL provide two main sources of data that include data collected as part of the UK vehicle taxation system (DVLA) and data queried from the Society of Motor Manufacturers and Traders (SMMT) Motor Vehicle Registration Information System (MVRIS). These data provide information on many of the physical characteristics of road vehicles such as engine size, fuel type, kerb weight; information on when a vehicle was manufactured and first registered and the Euro Standard of the vehicle.

Data were also obtained from CDL relating to the mileage of a vehicle at its last annual MOT inspection test. Mileage data were available for passenger cars and LCVs as well as the date of inspection. While the reported mileage is not that at the actual time of measurement because the MOT could have occurred at any time in the previous 12 months, it is considered close enough that any difference owing to a mismatch in MOT date and measurement date will be small. Another limitation of the data is that it provides no mileage information for vehicles less than three years old because these vehicles are not required to undertake an annual MOT inspection. The lack of mileage data for vehicles under three years old affects the analysis of Euro 6 vehicles, as many of these vehicles currently on the road are less than 3 years old.

For diesel Euro 6 passenger cars, the data were partitioned further by splitting them into vehicle models that are known to use LNT or SCR. This differentiation is considered to be important because most studies that consider the emissions from Euro 6 vehicles consider them as one class of vehicle. However, it is very likely that LNT and SCR technologies have important contrasting emission characteristics. The aftertreatment technology used by vehicles was identified for 219 separate vehicle models. In terms of total Euro 6 vehicles sampled, the aftertreatment technology used could be identified in over 93% of vehicles. On average, LNT-equipped passenger cars had lower engine sizes than SCR-equipped passenger cars (1866, range 1120–2993 cc and 2259 cc, range 1499–4367 cc, respectively). It should be noted that none of the Euro 6 diesel cars tested in this work are designed to conform to RDE regulations i.e. are not Euro 6d-temp or Euro 6d.

2.4. *Model fitting*

To establish relationships between emissions and other variables such as date of manufacture or vehicle mileage, Generalised Additive Model (GAMs) were used. GAMs are a highly flexible ‘data-driven’ modelling approach that is suited to the analysis of vehicle emission remote sensing data (Wood, 2004). The principal advantage of the GAM approach in the current context is the ability to consider non-linear relationships between independent and dependent variables and make no *a priori* assumptions about the nature of the relationship. We adopt the thin-plate regression spline method available in the R package mgcv (Wood, 2003). In the simple models used in the current study, the emission is assumed to be a smooth function of either the date of manufacture of a vehicle or the vehicle mileage. The default options of the gam function of the mgcv package were used without modification, which produced interpretable models with smooth relationships between the dependent and independent variables. Rather than year of manufacture, the manufacture date has been represented to the nearest month. An advantage of the GAM for these analyses is that no prior data aggregation e.g. to year of manufacture, is required to establish the relationship between date of manufacture and emission, despite the individual vehicle measurements exhibiting considerable scatter. The uncertainty intervals shown in the plots are the estimated standard errors, which show higher uncertainties where there are fewer data (typically at the start or end of time series where there are fewer vehicle measurements).

3. Results and discussion

3.1. *Emissions by date of manufacture and emissions control technology*

In this section, consideration is given to the effect of Euro 6 aftertreatment technologies used on diesel passenger cars and LCVs on emissions of NO_x and NO_2. It is clear from Fig. 1 that emissions of NO_x decreased from 2000 to around 2007 and then remained approximately stable until about 2014. From 2014, the emissions of NO_x decrease considerably for all vehicles as a group (the black line). However, Fig. 1 shows that there is a large difference in the performance of LNT and SCR-equipped vehicles. It is apparent for example, that vehicles fitted with SCR technology have much lower emissions of NO_x compared with those using LNT i.e. by a factor of about three. The clear change seen in 2014 shown in Fig. 1 corresponds to the introduction of Euro 6 passenger cars, where new model vehicles were required to be Euro 6 by September 2014. In reality, some manufacturers introduced Euro 6 vehicles before September 2014 but the number of vehicles on the road before this time was low.

The trend in emissions of NO_2 differs considerably from that for NO_x, as shown in Fig. 2. Emissions tended to increase from 2000 to around 2007 to a peak and have decreased since that time. There is some evidence of an accelerated decrease from about 2015 for vehicles overall. Considering the separate behaviours of LNT and SCR-equipped vehicles reveals very different behaviour. While emissions of NO_2 from SCR-equipped vehicles have strongly decreased since 2014, the evidence suggests that NO_2 from LNT vehicles have resulted in an increase in emissions of NO_2. However, the net effect is that the introduction of Euro 6 vehicles has led to decreased emissions of NO_2.

The emissions of NO_2 from LCV vehicles have also shown an increasing trend from model year 2000–2007, similar to diesel passenger cars (Fig. 3). However, for LCVs there is much stronger evidence that NO_2 emissions have decreased considerably since vehicles were introduced in 2010–2011, such that emissions of NO_2 in model year 2017/2018 are

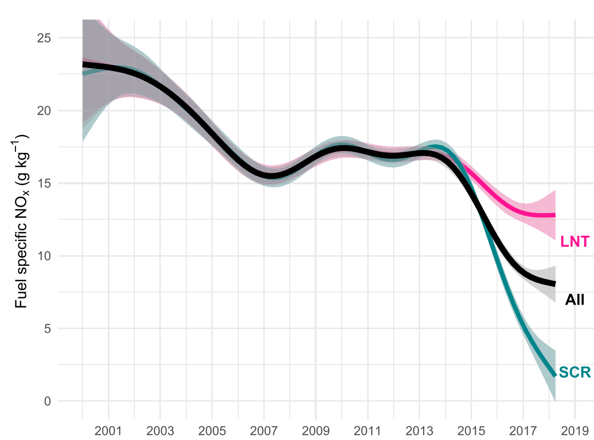

Fig. 1. Emissions of NO_x(g kg^{-1} fuel) as a function of vehicle manufacture date for diesel passenger cars. Where possible, Euro 6 vehicles have been split by their main emissions control technology (LNT or SCR). The black line shows the emissions for all vehicles regardless of the aftertreatment technology used. The relationship between the NO_x emission and manufacture date was derived using a GAM.

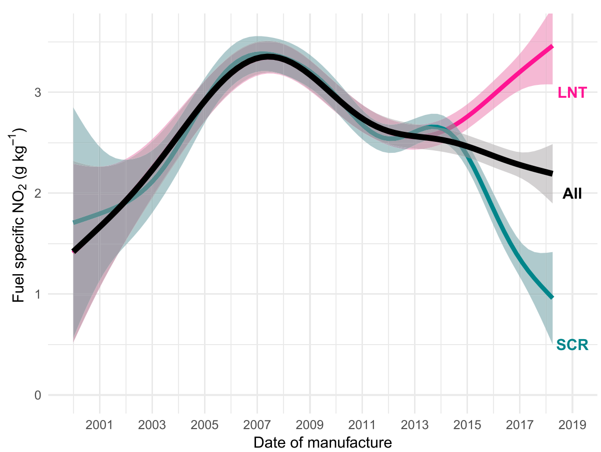

Fig. 2. Emissions of NO_2 (g kg^{-1} fuel) as a function of vehicle manufacture date for diesel passenger cars. Where possible, Euro 6 vehicles have been split by their main emissions control technology (LNT or SCR). The relationship between the NO_2 emission and manufacture date was derived using a GAM.

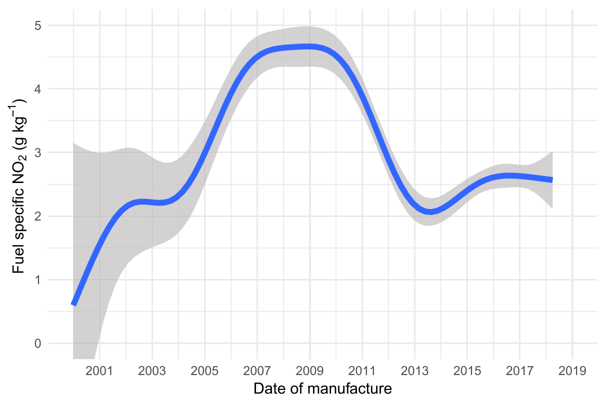

Fig. 3. Emissions of NO_2 (g kg^{-1} fuel) as a function of vehicle manufacture date for diesel LCV. The relationship between the NO_2 emission and manufacture date was derived using a GAM.

approximately half that of vehicles manufactured in 2007. By contrast, NO_2 emissions from diesel passenger cars decrease by approximately one third over the same time period.

A summary of the fuel-specific emission factors is given in Table 3 for passenger cars and LCV. For both vehicle types there is a considerable reduction in emissions of NO_x in going from Euro 5 to Euro 6. The improvement in NO_x reduction is greatest for LCV where there is a 62% reduction, while for PC the reduction is 47%. For both PC and LCV the reduction in NO_2 is modest at ≈10–18%.

Table 3
Emissions of NO_x and NO_2 from diesel vehicles by vehicle type and Euro standard. PC = passenger car, LCV = Light Commercial Vehicle.

Vehicle class	Euro status	NO_x (g kg^{-1})	NO_2 g kg^{-1}	Sample number
PC	2	20.9 ± 3.2	1.5 ± 0.5	42
PC	3	19.8 ± 0.6	2.7 ± 0.2	1028
PC	4	16.1 ± 0.4	3.2 ± 0.1	2639
PC	5	17.2 ± 0.4	2.7 ± 0.1	5255
PC	6	9.1 ± 0.3	2.2 ± 0.1	3735
LCV	0	19.7 ± 3.4	1.5 ± 0.5	53
LCV	2	23.3 ± 2.9	2.0 ± 0.7	66
LCV	3	21.9 ± 1.3	3.1 ± 0.3	462
LCV	4	20.4 ± 0.7	4.6 ± 0.3	1584
LCV	5	24.5 ± 0.5	2.5 ± 0.1	3890
LCV	6	9.3 ± 0.6	2.3 ± 0.2	1306

Fig. 4 shows the NO_2/NO_x ratio for diesel passenger cars and LCVs as a function of date of manufacture.

The relationships shown in Fig. 4 reveal several interesting and important influences. Both diesel passenger cars and LCVs manufactured in the early 2000s have low NO_2/NO_x ratios of ≈ 10%. However, the NO_2/NO_x ratio for passenger cars and LCVs increase to a peak in about 2007 about a year later for LCVs. The lag in the timing of the peak for LCVs is a reflection of the different introduction dates for Euro 4 vehicles. The Type Approval date for passenger cars for new models of vehicle was 1st January 2005 and for LCVs was 1st January 2006. The NO_2/NO_x ratio is then seen to decrease from a peak for passenger cars and LCVs up until around 2014. Finally from 2014, the NO_2/NO_x ratio increases to a maximum of about 30% for both vehicle types for the most recent manufactured date in April 2018.

The interpretation of Fig. 4 is complex because of the number of factors affecting the NO_2/NO_x ratio over the period from 2000 to 2018. First, a wide range of aftertreatment technologies have been used on the vehicles over this period from Exhaust Gas Recirculation (EGR), Diesel Particulate Filters (DPF), LNT and SCR. There is also the effect of vehicle ageing — from effectively new vehicles to vehicles up to about 18 years old. Vehicle ageing (or the effect of increased mileage) will likely affect the ratio of NO_2/NO_x ratio and is considered in more depth later.

The decrease in the NO_2/NO_x ratio seen for PC and LCVs likely has several causes. As discussed by Carslaw et al. (2016), the use of 'catalyst thrifting', where catalyst manufacturers use less platinum group metals would result in less NO_2 being generated. However, it is also likely that the emissions control systems have improved in general and the amount of NO_2 produced more precisely controlled. The more recent increase in the NO_2/NO_x ratio shown Fig. 4 coincides with the introduction of Euro 6 vehicles and shows that for both diesel passenger cars and LCVs, the most recent model vehicles are associated with the highest NO_2/NO_x ratio of about 30%. Such an increase may at first appear concerning from an ambient NO_2 concentration perspective. However, it is also important to consider the absolute emissions of NO_x and NO_2.

3.2. *Emissions by vehicle mileage*

Limited analysis of NO_2 emissions from diesel cars has suggested that as vehicles age, the amount of NO_2 they produce decreases (Carslaw et al., 2016). However, vehicle age is unlikely to be the factor that best describes the deterioration of vehicle aftertreatment systems. A better measure is the mileage a vehicle has driven. The current work makes it possible for the first time to link vehicle emission measurements using remote sensing with the mileage of an individual vehicle. The benefit of linking these two data sets is that the sample sizes and range of mileages

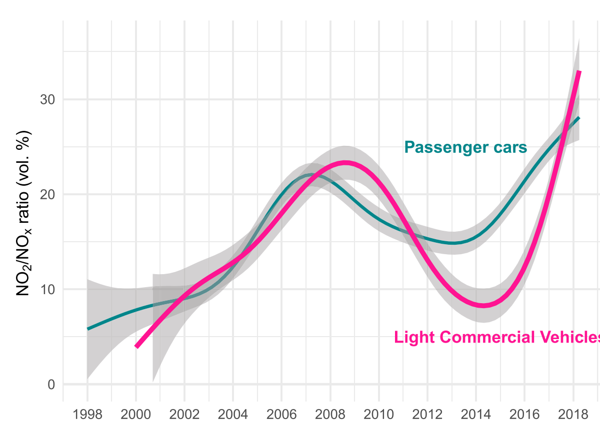

Fig. 4. The NO_2/NO_x ratio as a function of vehicle manufacture date for diesel passenger cars and Light Commercial Vehicles. The relationship between the NO_2/NO_x ratio and manufacture date was derived using a GAM.

is high, which provides detailed information on vehicle deterioration effects.

Mileage information is available for approximately half the diesel car fleet i.e. about 7000 vehicles. The principal reason there is not a higher proportion of vehicles for which mileage is available is that passenger cars in the UK only need undertake an annual MOT inspection once they are over 3-years old. As a result, the mileage information available for Euro 6 cars is more limited. Moreover, because of the relatively recent introduction of Euro 6 vehicles, there is a correspondingly small number that have high mileages.

Fig. 5 shows the relationship between vehicle mileage and NO_2 by Euro Standard for diesel passenger cars. In all cases (from Euro 3 to Euro 6), there is evidence that as the vehicle mileage increases, the amount of NO_2 emitted decreases. The strongest evidence for a decrease in NO_2 is for Euro 5 vehicles, which in part will be due to the larger sample sizes of these vehicles. Overall, the emissions of total NO_x do not change significantly with mileage for diesel cars, which means that the NO_2/NO_x ratio also decreases as the vehicle mileage increases. The results also suggest care is needed when analysing remote sensing data for which only NO measurements are available, which make assumptions about the 'missing' NO_2 (Chen and Borken-Kleefeld, 2016). Where the sample sizes are sufficiently large for Euro 4 and 5 vehicles, the data show that emissions of NO_x remain stable as mileage increases but the balance between NO and NO_2 changes.

The preceding analysis considered measurements made during 2017/2018. However, it is also valuable to compare the NO_2/NO_x ratios with earlier work at the same location in west London on Putney Hill (Carslaw et al., 2015). During the 2013 campaign, 4358 Euro 5 diesel PC were measured during June and July. The NO_2/NO_x ratio for Euro 5 diesel PC in 2013 was 25.5% on average. Five years later, the ratio had decreased to 15.6%. An absolute reduction in the NO_2/NO_x of 10% over ≈5 years is substantial and provides further evidence that as the mileage of a diesel PC increases, the NO_2/NO_x ratio decreases.

For the first time it has also been possible to compare the *same* vehicles sampled in both 2013 and 2017/2018 to consider how emissions of NO_2 have changed over ≈5-year period. These vehicles were identified through their registration plate. While it is not possible to consider individual vehicle emissions because they were typically sampled only once, it is possible to group the vehicles by Euro standard and type. For Euro 5 diesel cars where the same 73 vehicles were measured in 2013 and 2017/8, it can be shown that the emission of NO_2 reduced by 41% since 2013. A similar reduction of 39% was observed for Euro-5 LCV where there were 25 vehicles that were sampled in both time periods. For earlier generation diesel cars (Euro 3 and Euro 4), the reductions in NO_2 were less and typically around 25%. A proportionately lower reduction over this time period for Euro 3 and Euro 4 vehicles relative to Euro 5 vehicles is consistent with a degradation effect i.e. these vehicles would have already degraded to some extent when they were first measured in 2013.

Reductions in the amount of NO_2 emitted with increased mileage may also have consequences for the emission of other species. Specifically, because NO_2 is used as an oxidant in DPFs, lower emissions of NO_2 may have consequences for the efficiency with which particulate matter is reduced in DPF. Unfortunately, remote sensing does not provide a sufficiently specific measure of exhaust particulate to test whether reductions in NO_2 emissions have consequences for particulate matter. It would, however, be worth conducting specific measurements to determine whether reductions in NO_2 emissions do affect the emission of particulate matter from high mileage diesel vehicles.

3.3. Emissions of NO_2 by vehicle manufacturer

The emissions of NO_2 by individual vehicle manufacturer vary considerably. For Euro 6 diesel cars the vehicles have been grouped by manufacturer 'family'. The grouping is based on the approach used by the International Council on Clean Transportation (ICCT) in their analysis of vehicle emission remote sensing data (Bernard et al., 2018). The grouping is considered by fuel type, Euro standard, manufacturer group (for example, the Volkswagen Group includes VW, Audi, SEAT, Skoda, and Porsche) and engine displacement. Within each manufacturer group, the vehicles are grouped further by engine size. The reasoning behind the grouping is that manufacturers would tend to use similar technologies and engine calibrations on ostensibly the same engine. Indeed, this grouping of vehicles is observed in the data itself where emissions from a particular engine for a particular manufacturer are very similar across the vehicle family.

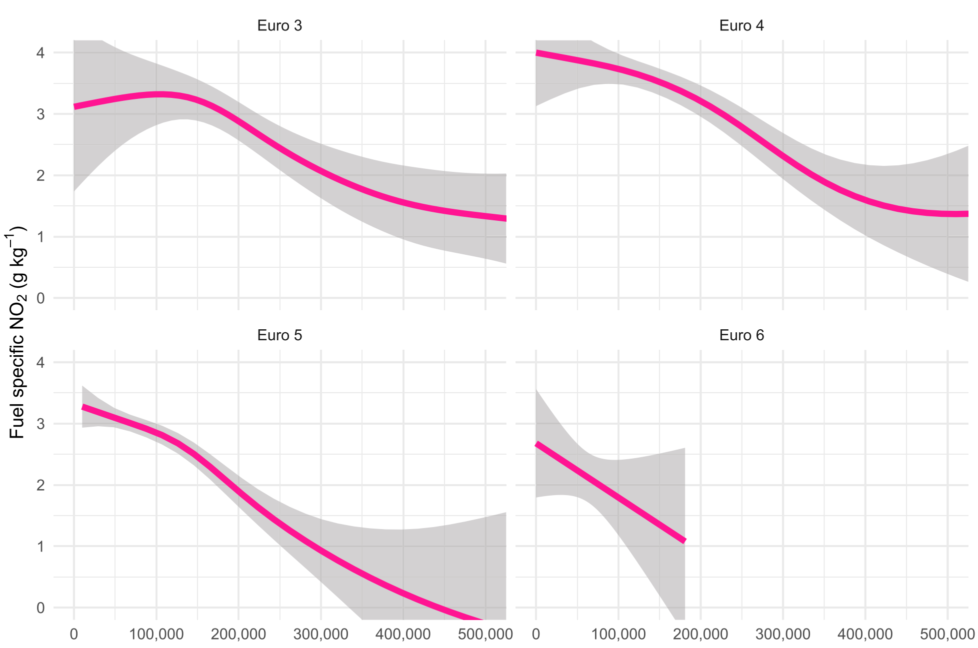

Fig. 5. Emissions of NO_2 (g kg^{-1}fuel) as a function of vehicle mileage for diesel passenger cars, split by Euro standard. The relationship between the NO_2 emission and mileage was derived using a GAM.

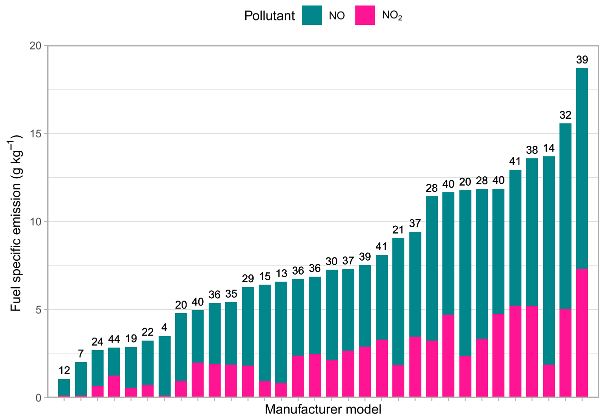

Fig. 6. Emissions of NO_2 and NO (g kg^{-1}fuel) for Euro 6 diesel passenger cars. The results are shown by individual (anonymised) manufacturer family grouping and ranked by their total emission of NO_x. The numbers at the top of each column show the percentage of NO_x that is NO_2. The NO emissions are calculated as NO_2-equivalent.

The emissions by the manufacturer families for Euro 6 diesel cars is shown in Fig. 6. These results show that there is a very wide range in emissions of NO_2 (and total NO_x, where there is a factor of 17 difference between the lowest and highest emitting vehicle) depending on the manufacturer and vehicle engine considered. There is no clear pattern in that the vehicles with the highest emissions of total NO_x are associated with higher and lower emissions of NO_2. Indeed, some of the lowest NO_x-emitters also emit low proportions of NO_2, which demonstrates the potential for manufacturers to produce diesel passenger cars that perform well for NO_x and NO_2. The data also show that the future importance of NO_x and NO_2 emissions will strongly depend on the composition of the fleet. Furthermore, the vehicles measured as part of this work are not RDE-compliant (i.e. Euro 6d-temp or Euro 6d), which indicates that further reductions in emissions can be expected in the coming years.

4. Conclusions

The direct emission of NO_2 from diesel vehicles has been an important factor affecting near-road concentrations of ambient NO_2 across Europe. The future impact of NO_x emissions from road vehicles will depend on both the absolute emissions of NO_x and the amount of the NO_x that is emitted as NO_2. The current work suggests the importance of primary NO_2 from vehicles has been decreasing in recent years.

There are two main factors that act to reduce the importance of direct emissions of NO_2. First, the introduction of Euro 6 vehicles in the past few years has led to a substantial reduction in absolute NO_x emissions from vehicles. Even though the remote sensing measurements show that new vehicles with low mileage have relatively high emissions of NO_2 (with $\approx$ 30% of the NO_x being in the form of NO_2); absolute emissions of NO_2 have still decreased from diesel cars and LCV since around 2007.

Second, the new measurements reported in the current work show that NO_2 emissions tend to decrease with increasing vehicle mileage. This decreasing NO_2 emission with age can be substantial. This is an important finding because current assumptions used in emission factors and inventories do not take account of any change in NO_2 assumptions as vehicles age. Importantly, no evidence is found of a change in total NO_x emissions.

The trend towards decreasing NO_2/NO_x ratios and absolute emissions of NO_2 reported in the current study is consistent with the detailed analysis of ambient measurements at roadside locations in Europe. The study by Grange et al. (2017) shows that from around 2010, the NO_2/NO_x ratio at most roadside locations across Europe started to decrease.

It is clear from remote sensing measurements that there are considerable differences on average between LNT and SCR diesel passenger cars with respect to their emissions of total NO_x. While LNT and SCR NO_2/NO_x ratios are similar on average, in terms of absolute NO_2 emissions, SCR-equipped vehicles emit approximately 60% less NO_2 compared with LNT-equipped vehicles. With the full implementation of RDE Regulations and Euro 6d-temp and Euro 6d vehicles, it is expected that emissions of NO_x and NO_2 will be further reduced with most vehicles adopting SCR or SCR + LNT. Consequently, the importance of emissions of primary NO_2 in the urban atmosphere will continue to diminish.

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