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Roadside NO₂

Reacts with O₂ to form secondary NO₂

NO

Primary NO₂

NOₓ
Investigation of vehicle cold start primary NO\textsubscript{2} emissions from ambient monitoring data in the UK and their implications for urban air quality

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Abstract

Nitrogen oxides (NO and NO\textsubscript{2}, collectively NO\textsubscript{X}) derived from vehicle exhausts are critical pollutants with significant implications for urban air quality and human and environmental health. In this study, we investigate trends in measured ambient nitrogen dioxide (NO\textsubscript{2}) and NO\textsubscript{X} mixing ratios at urban traffic-dominated monitoring sites in the UK for the period 2009-2016. We apply an oxidant analysis approach alongside a number of assumptions to the ambient data to determine trends in the inferred primary NO\textsubscript{2}/NO\textsubscript{X} ratio, and examine evidence for enhanced vehicle “cold start” effects upon these inferred emissions. Ambient NO\textsubscript{2} and NO\textsubscript{X} mixing ratios have experienced an overall decrease of 17.2% and 11.3% respectively for the locations considered over this time period. The inferred primary NO\textsubscript{2}/NO\textsubscript{X} ratio for the majority of the study locations is found to have fallen by 29% (from 0.175 to 0.125) as a monthly mean from 2009 to 2016, with a statistically significant median decrease of 0.32 percentage points per year. However, during cold weather (temperatures less than or equal to 5 °C), the inferred primary NO\textsubscript{2}/NO\textsubscript{X} ratio averaged across all locations, when compared with normal conditions (temperatures higher than 5 °C) increased from 0.062 (±0.004) to 0.102 (±0.001) (64.5% higher) and from 0.056 (±0.004) to 0.098 (±0.001) (75% higher) for cold morning and evening rush hours, with substantially greater increases at some sites. This “cold start” result suggests that the combination of recent vehicle driving history and ambient weather conditions, in conjunction with technological constraints on the operating temperature range of emission control systems in some vehicles, affects NO\textsubscript{X} emissions and hence has a detrimental impact upon air quality in urban environments. Increased cold start emissions imply an increased NO\textsubscript{2} - derived health burden from air pollution, under certain conditions, assessment of which should consider changes in vehicle use as a result of weather, and hence altered personal exposure.
Key words: Urban air quality, Nitrogen oxides - primary NO₂, vehicle cold starts, trend analysis, vehicle emissions, low temperature emissions

1. Introduction

1.1 Background and objectives

Vehicle emissions are a dominant source of air pollution in urban environments in developed nations. Direct emissions include nitrogen oxides (NOₓ, the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO₂)) and particulate matter (PM). NOₓ emissions are of particular importance to urban air quality, since they not only contribute to local and regional scale air pollution, but also to the formation of secondary pollutants such as ozone (O₃) and secondary PM. Vehicular pollutants have been reported to have substantial adverse impacts on human health (Papapostolou et al., 2011), with exposure to NO₂ known to lead to reduced lung function and increased risk of cancer (Adam et al., 2015; Hamra et al., 2015; WHO, 2013), and is responsible for tens of thousands of premature deaths each year across Europe (EEA, 2016; RCP, 2016; COMEAP, 2010). The International Agency for Research on Cancer has recently classified diesel engine exhaust as a Group I carcinogen, based on its association with lung cancer incidence (Attfield et al., 2012; Silverman et al., 2012).

Within the EU, a series of legislative measures have been introduced to address this challenge. The first directive 96/62/EC (EC, 1996), which is commonly referred as the Air Quality Framework Directive, and its daughter Directives, established standards in the period up to 2004 for a range of pollutants including NO₂ in ambient air. The three first daughter directives were consolidated into a single ambient air quality Directive adopted as 2008/50/EC (EC, 2008a) and together with the fourth daughter directive 2004/107/EC they provide the current framework for the control of ambient concentrations of air pollution in the UK. However, the need for greater reductions in NO₂ mixing ratios has led to further directives, which gradually aimed to decrease the emission levels directly from vehicles (EC, 2008b; 2011). In the UK, evidence indicates that new Euro limits (Euro 5 and Euro 6), in conjunction with new after-treatment technologies (see section 1.2) have had a positive impact in the reduction of roadside PM₂.₅ (Harrison and Beddows, 2017) and NOₓ (DEFRA, 2017), while factors such as aging of catalysts
leading to reduced oxidative capacity via thermal deactivation might also play a role in affecting primary NO\textsubscript{2} emissions from traffic (Carslaw et al., 2016b).

Here, we analyse trends in ambient NO\textsubscript{X} and NO\textsubscript{2} mixing ratios between 2009 and 2016 measured at urban monitoring stations in the UK, where NO\textsubscript{X} mixing ratios are dominated by local traffic emissions. We assess changes in the ambient NO\textsubscript{2}/NO\textsubscript{X} ratio, and analyse the ambient data to infer potential trends in the primary (directly emitted) NO\textsubscript{2}/NO\textsubscript{X} ratio from vehicles. The NO\textsubscript{X} data are coupled with meteorological observations and a methodology is introduced to assess potential changes in vehicle emissions associated with “cold start” operation, as indicated by ambient temperature, and the impact of this behaviour upon ambient air quality.

1.2 Controls of vehicle NO\textsubscript{X} and NO\textsubscript{2} emissions

Internal combustion vehicle technologies have developed to reduce fuel consumption, improve engine nitrogen oxides (NO and NO\textsubscript{2}, collectively NO\textsubscript{X}) derived from vehicle exhausts, are critical pollutants with significant implications for urban air quality and human and environmental health. In this study, we investigate trends in measured ambient nitrogen dioxide (NO\textsubscript{2}) and NO\textsubscript{X} mixing ratios at urban traffic-dominated monitoring sites in the UK for the period 2009-2016. We apply an oxidant analysis approach alongside a number of assumptions to the ambient data to determine trends in the inferred primary NO\textsubscript{2}/NO\textsubscript{X} ratio, and examine evidence for enhanced vehicle "cold start" effects upon these inferred emissions. Ambient NO\textsubscript{2} and NO\textsubscript{X} mixing ratios have experienced an overall decrease of 17.2% and 11.3% respectively for the locations considered over this time period. The inferred primary NO\textsubscript{2}/NO\textsubscript{X} ratio for the majority of the study locations is found to have fallen by 29% (from 0.175 to 0.125) as a monthly mean from 2009 to 2016, with a statistically significant median decrease of 0.32 percentage points per year. However, during cold weather (temperatures less than or equal to 5 °C), the inferred primary NO\textsubscript{2}/NO\textsubscript{X} ratio averaged across all locations, when compared with normal conditions (temperatures higher than 5 °C) increased from 0.062 (±0.004) to 0.102 (±0.001) (64.5% higher) and from 0.056 (±0.004) to 0.098 (±0.001) (75% higher) for cold morning and evening rush hours, with substantially greater increases at some sites. This "cold start" result suggests that the combination of recent vehicle driving history and ambient weather conditions, in conjunction with technological constraints on the operating temperature range of emission
control systems in some vehicles, affects NOx emissions and hence has a detrimental impact upon air quality in urban environments. Increased cold start emissions imply an increased NO2-derived health burden from air pollution, under certain conditions, assessment of which should consider changes in vehicle use as a result of weather, and hence altered personal exposure. performance, and (primarily through the addition of after-treatment systems) reduce emissions of air pollutants such as NOx. Of the two principal categories of internal combustion engine, the emission problem is more straightforward to address for gasoline (spark ignition) vehicles in comparison to diesel (compression ignition) power units. Most gasoline vehicles now employ a three-way catalyst (TWC), a key abatement technology introduced in the 1980s and applied widely from the 1990s to reduce vehicle tailpipe emissions. TWC are designed to simultaneously convert carbon monoxide (CO) to carbon dioxide (CO2), hydrocarbons (HC) to water and NOx species to nitrogen. Theoretically, TWC can cut CO, HC and NOx emissions by over 99% (under stoichiometric conditions) if the air to fuel ratio in the exhaust stream is accurately controlled, although they have been associated with emissions of the greenhouse gas nitrous oxide (N2O) (Berges et al., 1993; Jimenez et al., 2000).

Diesel after-treatment systems face more challenges for the reduction of emissions. Diesel vehicles (Euro 3 and later) use diesel oxidation catalysts (DOC), which normally contain palladium, platinum and aluminium oxide, all of which serve as catalysts to oxidize HC and CO to CO2 and H2O. However, this oxidation can lead to increased NO2 emissions when no further after-treatment technology is applied.

Exhaust gas recirculation (EGR) was introduced as a further emission control technology in larger size Euro 3 engines, and became the standard in Euro 4 and later diesel passenger cars and light duty vehicles (LDV). The EGR system channels and recirculates a portion of the exhaust gas into the filtered, high-pressure, fresh combustion air at the engine intake. The higher the engine load the better the EGR performance and the greater the NOx reduction (Yokomura et al., 2003).

Diesel particle filters (DPF), introduced in 2009 to achieve Euro 5 limits, physically capture diesel particles and prevent their release to the atmosphere. However, the stored PM must be oxidized in order to avoid blocking the filter. This is achieved via reaction with O2 at high temperatures (600 °C) and via reaction with NO2 at low temperatures (250 – 450 °C). Owing to the amount of NO2 needed in the DPF to burn the soot, the DPF is attached after the DOC system, forming a continuously regenerated trap (CRT) or catalyzed continuously regenerated
trap (CCRT), which reduces PM, CO and HC. The secondary NO$_2$ formation as a by-product of the catalysis, however, is a major issue in these systems and can lead to increased NO$_2$ emissions from the vehicle.

The latest after-treatment technologies involve Lean NO$_x$ trap (LNT) and Selective catalytic reduction (SCR) technologies, which can achieve Euro 6 limits. LNT technology achieves NO$_x$ storage during lean engine operation, and NO$_x$ reduction during rich operation phases. During lean engine operation, NO$_x$ is retained in the storage components in the form of nitrates and nitrites. In a subsequent short fuel-rich period, the NO$_x$ trap is regenerated by NO$_x$ release and reaction with HCs achieves reduction to N$_2$. Since fuel consumption for NO$_x$ trap regeneration depends on the regeneration frequency, which is a function of NO$_x$ trap performance parameters, the impact of catalyst aging must be considered in the operation strategy.

Selective catalytic reduction (SCR) is an after-treatment system which catalyzes NO$_x$ (NO + NO$_2$) reduction by addition of reactive nitrogen compounds, such as ammonia or urea-based mixtures. In SCR, the mixture of ammonia/urea reacts with NO$_x$ to form N$_2$, CO$_2$, and H$_2$O. The SCR process requires precise control of the ammonia injection rate, because an insufficient injection rate may result in unacceptably low NO$_x$ conversion, while an excessive injection rate results in releases of ammonia (undesirable “ammonia slip”) to the atmosphere and increased SCR reductant consumption.

All these after-treatment systems need to reach a certain temperature threshold (i.e. regular operating conditions) in order to effectively reduce NO$_x$ emissions. This difference in the temperature, for both the engine and the catalytic converter, under which the vehicle is initially operated comparing to regular operating conditions can be expressed as a “cold start” when the engine is operated with the temperature of the oil, coolant and all elements of the engine at the ambient temperature. At lower ambient temperatures, the engine and catalyst warm up period is prolonged and this can have an adverse effect on vehicle emissions. For modern gasoline and diesel vehicles equipped with TWC and DOC after-treatment systems, under cold operation, this implies dis-proportionally higher release of gaseous pollutants, since the temperature of the catalyst is not sufficient to ensure efficient NO$_x$ conversion. Currently in the EU, only the emissions from gasoline Euro 3/4 vehicles under cold-start in low ambient temperature are regulated under the directive 98/69/EC (EC, 1998), as identified elsewhere (e.g. Dardiotis et al., 2013; Bielaczyc et al., 2011; 2012).
1.3 NO\textsubscript{2} and NO\textsubscript{X} emission measurement approaches

There are several different approaches to estimate vehicle combustion (tailpipe) emissions – see e.g. the review of Franco et al., (2013). Here, we briefly introduce the key approaches to provide context for the methodology used in this work. Most widely known are approved bench (chassis dynamometer) tests, where the tested vehicle follows a certain driving cycle (sequence of speed/acceleration/deceleration over a pre-defined period of time that corresponds to notional urban driving or extra-urban driving behaviour) and relevant analyzers sample directly from the exhaust to determine (e.g.) NO\textsubscript{X} emissions (Nine et al., 1999; Yanowitz et al, 2000). However, such tests are very short (approximately 20 min each test) and, as has been widely reported, fail to capture the real world operation NO\textsubscript{X} emissions either by accident or design (Andersson et al., 2014; Degraeuwe and Weiss, 2017). Thus, it is thought that historical emission factors based solely upon such tests may not be representative of real-world on-road vehicle behaviour.

Secondly, portable emission measurement systems (PEMS) are devices mounted to individual test vehicles which measure directly from the exhaust/tailpipe during on-road driving (Weiss et al, 2011). PEMS capture individual vehicle emissions under real driving conditions, but are expensive, can only be fitted in one car at a time, normally require tailpipe adaptations to sample directly, and may suffer power limitations if powered by the vehicle on-board low voltage power supply system. A related approach is the chase measurement method. In this approach, instruments are mounted in a second, monitoring vehicle and an inlet is used in order to sample from ambient air, while following individual (or groups of) target vehicles (Brantley et al., 2014). Chase approaches can, compared with test bench measurements and PEMS approaches, more readily give accurate information about fleet emissions from a number of vehicles and variations with driving behaviour (e.g. urban, rural, motorway), but suffer from limitations of the need to account for mixing with background air (commonly achieved via use of CO\textsubscript{2} as an exhaust tracer), and overlap of multiple vehicle plumes.

Thirdly, remote sensing technologies (Bishop et al, 1989), where a light beam passes through the exhaust plume of an individual or series of target vehicles prior to measurement at a detector, wherein the amount of light absorbed is proportional to the concentration of gases in the plume (Carslaw and Rhys-Tyler, 2013). Those approaches are commonly coupled with vehicle
sensing and number plate recognition tools to identify speed, acceleration and vehicle/engine characteristics. Although remote sensing methodologies are in many senses the “gold standard” approach, in that they can measure the real-world on-road emissions from large numbers of individual vehicles under favourable operating conditions, they suffer from constraints of cost, complexity and potentially perturbations to traffic flow/behaviour. Furthermore, such techniques have issues when located on multiple lane roads as emissions from vehicles alongside the target vehicle can interfere with the result, in particular when the wind is in an unfavourable direction - an alternative top-down geometry, which can sample individual, parallel vehicle lanes, has recently been demonstrated (Ropkins et al., 2017).

Lastly, vehicle emissions may be inferred from analysis of ambient air quality measurements, from monitoring sites located in suitable proximity to the road. This method has the advantage of utilizing the data that in most cases are used to report ambient air pollution levels, so no additional experiments are needed, and is able to exploit long term observations to assess the efficacy of policy measures. However, it cannot give detailed information for the vehicle fleet or driving behaviour. In this study we adopt this last approach, exploiting the extensive UK air quality network to infer trends in cumulative UK fleet NOx emissions and their response to temperature, building upon previous, related work applying a similar approach to infer changes in relative vehicle emissions (e.g. Carslaw et al., 2016b; Carslaw and Beevers, 2005; Jenkin, 2004), and potential signatures of increased diesel vehicle penetration and tightening of emission standards (e.g. Carslaw et al., 2016b; Grange et al., 2017).

2. Data and Methodology

2.1 Experimental data

Atmospheric mixing ratios of NOx and O3 are monitored across the UK by the Automatic Urban and Rural Network (AURN), which is operated and maintained by the Department for Environment, Food and Rural Affairs (DEFRA), the Scottish Executive, the National Assembly for Wales and the Department of the Environment for Northern Ireland. Ambient mixing ratios are reported at hourly resolution, with measurements made by well-established conventional techniques, UV photometry for O3 and chemiluminescence for NOx with a molybdenum converter (see comments below, section 2.2, re NO2 selectivity). The measurement uncertainty
for NO\textsubscript{x} and O\textsubscript{3} from the AURN stations is <15\%, following the European Committee for Standardisation (documents BS EN14211:2012 -NO\textsubscript{x} and BS EN14625:2012 -O\textsubscript{3}).

The analysis presented here uses hourly data from every urban-traffic monitoring station (defined as stations that are located at roadside and kerbside locations) in the UK AURN network. For each urban-traffic station, background data were obtained from a nearby background site, defined as the urban or rural background site (applying the AURN classification) closest to the location of the urban traffic monitoring station. Further data availability constraints of coverage from the start of 2009 to the end of 2016, and overall data capture greater than 75\% were applied (75 \% selected as this is the minimum requirement for a valid aggregated value over a day and a year according to the EU air quality reports (EEA, 2016; Font and Fuller, 2016)). Additionally, for each urban traffic monitoring site, meteorological measurements (UK Met-Office, downloaded from the British Atmospheric Data Centre (BADC, https://badc.nerc.ac.uk/data/)) were used, in order to couple the air pollution measurements with local meteorology. In total, we included 17 urban traffic stations, paired with 10 urban background sites and 5 rural sites from the AURN network, alongside the 14 meteorological sites. The rural stations were required as not all urban traffic sites have a proximate urban background station. The difference in the numbers of urban background and meteorological stations arises as for London two urban background sites were used for four urban traffic stations, and one meteorological station for the whole area. The map of the stations used is shown in Fig 1, and their details are listed in the supplementary materials (Table S1).

2.2 Data processing methods and assumptions

Monitored data were processed and displayed using ArcGIS and R version 2.15.1 (R Core Team, 2016) along with the R packages ggplot2 (Wickham, 2009), openair (Carslaw and Ropkins, 2012), and mcgv (Wood, 2003). The data were de-seasonalised by applying the smoothing LOESS function, which is a non-parametric regression method that combines multiple regression models in a k-nearest-neighbor-based meta-model (Cleveland et al., 1990). The statistical approach that we followed for trend calculation is a non-parametric Mann-Kendall approach, while the trend slope is calculated with the Theil-Sen method (Sen, 1968; Theil, 1950) available in the R-openair package. In this method, for a given set of n x, y pairs, the slopes between all pairs of points are calculated and the median is taken as an estimate of the most probable slope (trend). This method is robust to outliers and can be used in both non-normal and
heteroscedastic (non-constant error variance) data series. Bootstrap re-sampling was used for the calculation of confidence intervals at the 95% level and p-values. A statistically significant trend was assumed when \( p < 0.1 \) (represented with a '+' symbol), meaning that the trend was not random at a 90% chance; p-values of: \( p < 0.05 \), \( p < 0.01 \) and \( p < 0.001 \), marked by ‘**, ***’ and ‘****’, respectively, indicate very highly significant trends, while \( p > 0.1 \) shows insignificant trends.

To derive the inferred primary \( \text{NO}_2/\text{NO}_X \) ratio from ambient monitoring data we used the total oxidant \( (\text{Ox} = \text{NO}_2 + \text{O}_3) \) approach developed by Clapp and Jenkin (2001). It is well known that in the daytime atmosphere the interconversion of \( \text{O}_3 \) to \( \text{NO}_2 \) and vice versa is generally dominated by the following reactions:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (1)
\]
\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad (2)
\]
\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (3)
\]

which constitute a null cycle. Reactions (1) - (3) result in the cycling of \( \text{NO}_X \) between \( \text{NO} \) and \( \text{NO}_2 \) and total \( \text{Ox} \) between \( \text{O}_3 \) and \( \text{NO}_2 \), however the total mixing ratios of both \( \text{NO}_X \) and \( \text{Ox} \) remain constant. During daylight, the equilibrium that occurs in the above reactions determines the photo-stationary steady state (PSS). Clapp and Jenkin, (2001) illustrated that when in PSS there is a linear relation between \( \text{Ox} \) and \( \text{NO}_X \) for roadside station data, which may be interpreted as a \( \text{NO}_X \) - independent and a \( \text{NO}_X \) - dependent contribution to \( \text{Ox} \). The former is the regional contribution which corresponds to the regional background \( \text{O}_3 \) level, whereas the latter is effectively a local contribution that is associated with additional \( \text{NO}_2 \) (i.e. primary \( \text{NO}_2 \) emissions, under the assumption that no other sources are significant). While this analysis only holds in volume mixing ratio space, it should be noted that the AURN data-series are reported in \( \mu g/m^3 \), therefore before we apply the total oxidant approach, data were converted from \( \mu g/m^3 \) to ppb by applying EU/DEFRA conversion factors (20 °C temperature and 1013 hPa pressure). For the analysis presented here, “Daytime” was defined as all whole hours between sunrise and sunset, based on the local time in London.

In the case of vehicle emissions from ambient urban traffic monitoring data, Jenkin, (2004), demonstrated that by considering the ‘total oxidant’ slope, \( (\text{NO}_2 + \text{O}_3) / \text{NO}_X \) estimates could be drawn for the primary (direct) \( \text{NO}_2/\text{NO}_X \) ratio emitted from vehicles. However, most of
the AURN urban traffic monitoring sites in the UK do not have $O_3$ measurements which poses a limitation to the total oxidant approach and to the estimation of the primary NO$_2$/NO$_x$ ratio. In such cases, Carslaw and Beevers, (2005) suggested a methodology that calculates the NO$_2$/NO$_x$ ratio without the need of $O_3$ observations from the urban traffic site, but with additional observations (of NO$_2$, NO$_x$ and $O_3$) from a nearby urban background site. In general, this approach assumes that the increment in NO$_2$ mixing ratio between a given urban traffic monitoring site and a nearby urban background site is partitioned into NO$_2$ that is chemically derived through the reaction between NO and $O_3$, and NO$_2$ which is emitted directly by road vehicles. Therefore, data from paired sites (roadside and background/rural site) are used. Additionally, in the calculation of the primary NO$_2$/NO$_x$ ratio, the difference in NO$_x$ between the urban traffic and urban-background/rural stations is considered; therefore impacts from non-traffic related sources are essentially removed. The method uses a simple constrained model and basic set of chemical reactions to explain the time-dependent variation in NO, NO$_2$ and $O_3$ as vehicle plumes mix with background air. Carslaw and Beevers (2005), showed that the primary NO$_2$/NO$_x$ ratio may then be obtained from fitting the observed NO$_2$-NO$_x$ data to that predicted, whilst optimizing the primary NO$_2$ fraction and the mixing time between emission and observation at the urban site. Here, we follow this methodology, but note some limitations. Specifically, the approach assumes that the increment in NO$_2$ mixing ratio above a local background site is controlled by the availability of $O_3$ and directly emitted NO and NO$_2$ only and does not include additional chemical reactions (e.g. of peroxy radicals with NO). Furthermore, it should be mentioned that because the AURN analysers employ a heated molybdenum converter to detect NO$_2$ (as NO), other NOy species will be detected as NO$_2$. The influence of those interferences might lead to overestimation of NO$_2$ in urban areas (Dunlea et al., 2007; Harrison et al., 2012). In addition, direct emissions of HONO, thought to comprise a small, but still significant and uncertain, component of vehicle exhaust (Crilley et al., 2016; Jenkin et al., 2008; Kurtenbach et al., 2001), is also a potential interferent in NO$_2$ measurements. However, in our analysis (see section 2.3 below) all the above potential interferences would be expected, to a first approximation, to co-vary with NO$_2$ and hence have limited effect upon the inferred primary NO$_2$/NO$_x$ ratio.

2.3 Investigation of cold-start/emissions under low ambient temperature conditions.
To assess evidence for altered emissions under conditions of low ambient temperatures, we applied the total oxidant approach for rush hour periods during the morning (06:00-10:00) and afternoon (16:00-19:00) during winter time (November, December, January, February), with a temperature condition of 5 °C (i.e., $T \leq 5$ °C). We select rush hours because the vehicle fleet experiences less (and known) variations during those hours with respect to the rest of daytime. It should be noted here that, although we used the total oxidant approach (notionally daylight only, Clapp and Jenkin, 2001), by including morning pre-sunrise and evening post-sunset periods, sensitivity tests showed that this introduced a very small difference in the overall results (less than a 2% change in the inferred primary NO$_2$/NO$_x$ ratio; less than 2 ppb difference in the ozone background). According to European regulations, the bench/laboratory tests for standard vehicle emissions are made under an (air) temperature range of 20 – 30 °C (EC, 91/441/ECC) and normally at the fixed temperature value of 23 °C (DfT, 2016). The vehicle is given a standard pre-conditioning in a temperature control room so that the whole vehicle including engine oil and coolant is ‘soaked’ to the regulated temperature range. As a result, the selected temperature threshold method ($T \leq 5$ °C), is well below that for the tested/regulated range, and very close to the winter mean temperature in the UK (4.4 °C). Results for days that satisfied the temperature criterion were compared with those that did not (Matthaios et al., 2017), in order to examine any potential difference in emissions-driven air quality.

3. Results and Discussion

3.1 Ambient NO$_x$ and NO$_2$ trends and relationships

The annual averaged ambient NO$_x$ and NO$_2$ values for each urban traffic station are shown in Fig 2, normalised to their mean value (2009-2016). A clear decline in the levels of both NO$_x$ and NO$_2$ is evident, which based on the overall average from all sites is 11.3% for NO$_x$ (black dashed line, Fig 2a) and 17.2% for NO$_2$ (black dashed line, Fig 2b) across the time period considered (2009 - 2016). The larger NO$_2$ than NO$_x$ decline in the UK urban traffic sites might be due to an alteration in PSS, emissions or in the background ozone that contributes to the photochemical cycle. Fig 3 shows how the monthly mean rush hour NO$_2$ mixing ratios (normalized to 100 on 1/1/2009) varies for the examined period. An overall mean reduction of approximately 20% (see black line) in the NO$_2$ mixing ratios is apparent. This sharper NO$_2$
decrease cannot be explained by the changes in background ozone, since the background ozone has not changed significantly during the examined years (0.5% increase – see Fig S1 in the supplementary material). This decrease in NO$_2$ is somewhat counter-intuitive to that expected when considering the increase in the number of licensed diesel vehicles in the UK, which, according to the Department for Transport, have increased from about 39% (2009) to 52% (2016) in urban areas of the UK – and which are associated with higher NO$_2$ emissions than petrol vehicles. However, it should be highlighted that during the period studied here, new Euro limits came into force for the reduction of NO$_x$ and NO$_2$ vehicle emissions. Briefly, Euro 5 limits, first introduced in 2009, introduced a limit value of 0.18 g/km for NO$_x$ in passenger cars, while the tighter limits of Euro 6 for passenger cars (0.08 g/km for NO$_x$) came into force around 2014, driving the introduction of new after-treatment technologies such as SCR and LNT. Depending upon fleet penetration, these changes are beginning to play an important role in the (fleet averaged) primary NO$_2$/NO$_x$ ratio from vehicles (Carslaw et al., 2016b).

Figure 4 illustrates the variation in the ambient NO$_2$/NO$_x$ ratio over time, as a function of NO$_x$ abundance, for the ambient monitoring data from urban traffic locations. Fig 4a (top) shows the distribution of hourly mean NO$_x$ mixing ratios for 2009 and 2016; Fig 4b (right) the distribution in hourly mean NO$_2$/NO$_x$ ratios for the same years and Fig 4c (centre) the hourly mean NO$_2$/NO$_x$ ratio as a function of NO$_x$ abundance. The values of NO$_2$/NO$_x$ as a function of NO$_x$ (Fig 4c) tend towards a minimum value, which approximates the primary NO$_2$/NO$_x$ emission ratio (this asymptote can be used as an alternative to the total oxidant approach described above in order to estimate the primary NO$_2$/NO$_x$ emission fraction; Itano et al, (2007) used a similar approach to estimate the primary NO$_2$/NO$_x$ ratio from an urban traffic site in Osaka, Japan). From the distribution in Fig 4b (right) it can be seen that the NO$_2$/NO$_x$ ratio has reduced slightly between 2009 and 2016 (median falling from 0.46 to 0.43), while from the asymptotes in Fig 4c (centre) the primary NO$_2$/NO$_x$ emission can be seen to have fallen from 0.175 to 0.125.

Figure 4d shows the absolute changes in NO$_2$/NO$_x$ ratio as a function of the change in total NO$_x$ mixing ratio (hourly mean for corresponding date / time / location) between 2009 and 2016, for each urban traffic location. The greatest reduction in NO$_2$/NO$_x$ ratio has occurred in the locations where NO$_x$ mixing ratio has increased (i.e. sites which have become more polluted, or busy, with positive values on the x axis), while for the majority of sites where NO$_x$ abundance has decreased (negative x axis values), the NO$_2$/NO$_x$ ratio has increased. To assess whether the
observed changes in NO$_2$/NO$_x$ could be explained by NO$_x$-O$_3$ PSS chemistry alone a simple PSS model, based on reactions 1-3, was used. In the first instance the model was initiated with baseline conditions of 30 ppb of O$_3$, 100 ppb of NO$_x$ (75:25% NO:NO$_2$). In subsequent runs only the initial NO$_x$ mixing ratio was adjusted. In each case the model was run until NO, NO$_2$ and O$_3$ reached PSS and the difference in the final NO$_2$/NO$_x$ ratio between the baseline run and all other runs was plotted against the change in initial NO$_x$ (see Fig 4b – blue line). It is observed that as the NO$_x$ abundance grows (positive x axis values), the PSS-chemistry-derived changes in the NO$_2$/NO$_x$ ratio (blue line) deviate from the observed ambient behavior (black points). Further model runs (not shown here) demonstrated that if the PSS model was initiated with a higher NO$_2$ fraction of 0.45 (i.e. similar to the mean NO$_2$/NO$_x$ ratio observed in 2013 from Fig 4a) then the difference between PSS-only predicted and ambient observed NO$_2$/NO$_x$ differences becomes even larger. Additional model PSS simulations for different initial ozone values O$_3$ = 100 ppb (extreme case) also showed deviation from observations. The results of the model runs suggest that the response of the PSS-chemistry to changes in overall NO$_x$ emissions cannot, in isolation, explain the variation in the NO$_2$/NO$_x$ ratio observed between 2009 and 2016.

The observed changes in NO$_2$/NO$_x$, therefore are likely to be influenced primarily by changes in vehicle emissions, which might have resulted from the combined changes in: (1) policy, where new Euro limits came into force for new car passenger models (Euro 5 in 2009 and Euro 6 in 2014), and for London (4 stations included here), a low emission zone came into effect, and daily charges for the London congestion zone increased. (2) Diesel cars, where in 2009, 90% of diesel cars in the UK were Euro 3 and Euro 4, while in 2016, 69% of UK diesel cars were Euro 5 and Euro 6, according to the DfT / National Atmospheric Emissions Inventory NAEI, 2016). (3) After-treatment technologies, where new technologies such as LNT and SCR have been introduced (see section 1.2) and factors such as ‘catalyst thrifting’, where catalyst developers and manufacturers reduce the amount of platinum group metal (which will potentially affect the amount of NO$_2$ formed), or catalyst deactivation over time (where aged DOC catalyst technologies may have reduced oxidative capacity through thermal deactivation or poisoning and therefore less efficient conversion of NO to NO$_2$ (Carslaw et al., 2016b). Our results are in accordance with other monitoring observations which show trends from eight long-running urban traffic stations (1995 - 2015), and highlight that six out of eight stations show a downward trend in the ambient NO$_2$ concentrations (DEFRA, 2017). In a recent study across Europe, Grange et al. (2017) conclude that the ambient NO$_2$ levels measured at roadside monitoring sites have
fallen, and that the primary $\text{NO}_2/\text{NO}_x$ emission ratio is lower than assumed by some key emission inventories. This result is also in agreement with the findings of Font and Fuller (2016), who analysed trends from ambient measurements in London and found that $\text{NO}_2$ and PM show a declining trend from 2010 to 2015, attributed to a variety of factors, including a reduction of the primary $\text{NO}_2/\text{NO}_x$ emission ratio due to the absolute and relative reduction in numbers of older diesel passenger cars in the overall fleet. These studies represent a growing body of evidence that there has been a recent reduction in the ambient and primary emitted $\text{NO}_2/\text{NO}_x$ ratio in UK urban environments.

3.2 Trends in inferred primary $\text{NO}_2/\text{NO}_x$ ratio

The trend in inferred primary $\text{NO}_2/\text{NO}_x$ ratio is presented in Fig 5 (monthly daytime values from all urban traffic sites, calculated using the methodology of Palmgren et al., (1996) / Carslaw and Beevers, (2005), after removing the observed seasonality (see section 2.1; Carslaw, 2016a)). Despite some individual monthly increases (mainly in 2011), the inferred primary $\text{NO}_2/\text{NO}_x$ ratio, shows a clear downward trend, with a change (median value) of -0.32%/year with 95% confidence interval from -0.45% to -0.2% per year, significant to the 0.001 level ($p <0.001$).

Fig 5 shows an overall reduction in the inferred primary $\text{NO}_2/\text{NO}_x$ ratio from 17.5% to 12.5% between 2009 and 2016. Despite the increases reported for the urban traffic monitoring sites in the UK before 2009 (AQEG, 2004, 2007), the inferred primary emitted $\text{NO}_2/\text{NO}_x$ experiences an overall reduction of 5 percentage points over the 2009 – 2016 period. In detail, from 2009 until 2011, a small reduction in the emissions is evident (from 17.5% to 15%). From 2011 until mid-2013 no significant changes are observed and the mean inferred primary $\text{NO}_2/\text{NO}_x$ ratio is steady. At that period the Euro 5a and Euro 5b limits for passenger and light duty vehicles, as well as the Euro IV standards for heavy duty vehicles came into force for sales of new vehicles in September 2011 and January 2013 for light and heavy-duty vehicles respectively. Standards, which set a prerequisite for diesel vehicles to have a DPF after-treatment system (Euro 5 diesel cars constituted 20% of the UK diesel fleet in 2011 and they reached 52% by 2014 according to NAEI, 2016)). This technology, as discussed in section 1.2, uses $\text{NO}_2$ in order to burn the collected soot/PM in the filters, thus can also impact $\text{NO}_2$ emissions in the exhaust. In September 2014, the most recent and stricter limits of Euro 6 came into force. The introduction of new Euro-limit-driven emissions control technologies and their penetration through the fleet (Euro 5 and Euro 6...
passenger cars) may therefore have contributed to this decrease of 2.5 percentage points in the mean primary NO$_2$/NO$_x$ ratio from early 2014, and the overall decrease of 5 percentage points that is apparent from early 2009. This 29% relative decrease in inferred primary NO$_2$/NO$_x$ ratio in the last period has to be taken into account in the emission inventories for future modelling estimates of exposure and policy making which currently they estimate an increase until 2015 for UK (NAEI, 2016) and Europe (Kiesewetter et al., 2014; Grange et al., 2017).

The change in inferred primary NO$_2$/NO$_x$ ratio between 2009 and 2016 shows some variability with geographic region across the UK (Fig 6). With few exceptions, the primary NO$_2$/NO$_x$ ratio has fallen in the majority of the regions, by a range from 0.5 to 10 % (Table 1). The observed increases in the ratio in some regions (e.g York, Swansea) are difficult to explain individually - they may be associated with other local factors such as changing road layouts and urban infrastructure. A decline in the median inferred primary NO$_2$/NO$_x$ emission for London of 5% is apparent, in agreement with Carslaw et al., (2016b), who found a decrease of about 7% in the primary NO$_2$/NO$_x$ ratio for inner London from 2009/10 to 2014/15. However, these variations were not always consistent with the monthly primary NO$_2$/NO$_x$ trend (calculated for the whole data series) (Table 1), indicating that the trends are not significant in every area and more data (i.e. a longer time series) are needed in order for a clear conclusion to be drawn. This potentially reflects that the oxidant analysis assumptions (essentially, that the NO$_x$/O$_3$ PSS represents a fully closed system) may be less valid for some locations and highlights the complexity and the heterogeneity in the implementation and outcome of policy interventions to control air pollution.

3.3 Low temperature primary NO$_2$ emissions – evidence for “cold start” effects

The inferred NO$_2$/NO$_x$ emission ratios for cold (T ≤ 5°C) and non-cold/normal (T > 5°C) conditions during winter (November, December, January, February) morning and evening rush hours are depicted in Fig 7. The change in gradient between cold (Fig 7b, 7d) and non-cold/normal (Figs 7a, 7c) conditions is clearly apparent, with the O$_3$-NO$_x$ analysis indicating an increase of 64.5% (mornings) and 75% (evenings) in the inferred primary NO$_2$/NO$_x$ ratio for the former compared with the latter. The increase in overall NO$_x$ abundance (greater x-axis range, most likely arising primarily from lower and more stable atmospheric boundary layer/mixing heights under cold conditions, alongside reduced winter month NO$_2$ photolysis) is also apparent.
The 64.5% increase in inferred primary NO\textsubscript{2}/NO\textsubscript{x} ratio is statistically significant (p < 0.001), changing by over 4 percentage points from 6.2 (±0.4) %, for normal winter mornings to 10.2 (±0.1) %, for cold winter mornings. Similar behaviour is observed for evenings (75% increase from normal to cold conditions), where the difference is slightly higher at 4.2 percentage points, from 5.6 (±0.4) to 9.8(±0.1) % (values in the parenthesis indicate the standard error). For individual locations the difference between cold and normal conditions ranges over a factor of 1.6 to 3.8 (Table 2).

Atmospheric photochemical processes (i.e., chemical reaction rate constants and to a lesser extent photolysis frequencies) are dependent upon temperature, which can introduce changes in concentrations, as a function of temperature, under otherwise constant conditions i.e. without any emission change. To assess the extent to which this may contribute to the observed trends, a series of tests were performed using a simple chemical box-model including a full inorganic chemical mechanism (taken from the MCM, http://mcm.leeds.ac.uk/, Saunders et al., 2003) (described in detail in the supplementary material). The model was run for a 24-hour period for a notional winter day (15\textsuperscript{th} December), for a range of temperatures (-10 to +30 °C), to assess the impact of the temperature dependence of chemical processes (alone) upon the ambient NO\textsubscript{2}/NO\textsubscript{x} ratio. The results showed that the daytime and nighttime average primary NO\textsubscript{2}/NO\textsubscript{x} ratios during the rush hour period (i.e., the period examined here for the cold starts) varied by between 0.5% and 8.4%, with a mean relative change of 2.4%, due to the effect of temperature-dependent chemical kinetics (see supplementary material Fig S4, S5). The model results indicate that the observed increments in the inferred primary NO\textsubscript{2}/NO\textsubscript{x} ratio with low temperatures, of 64.5% and 75%, are substantially larger than can be accounted for by the temperature-dependence of the atmospheric photochemistry. We suggest therefore that changed vehicle emissions with operating temperature are contributing towards the observed difference in inferred NO\textsubscript{2}/NO\textsubscript{x} emission ratio with temperature. While the ambient data will contain contributions from vehicles which have been operating for some time and hence are not under “cold start” conditions, statistics on mode of transport from the UK DfT National Travel Survey in 2016 indicate that 20% of all trips under 1 mile (1.6 km), were by car (either as driver or passenger), increasing to 77% for trips between 1 and 5 miles (1.6 – 8 km) (DfT, 2017). For urban journeys, distances tend to be shorter than these UK mean values suggest. Short urban trip duration alongside the reduced efficiency or designed deactivation of emission control systems at temperatures below 250 °C may contribute to the substantial increase in the inferred
primary NO$_2$/NO$_x$ ratio, and hence reduced attainment of NO$_2$ air quality standards, under cold weather conditions. Recent testing of vehicles in Germany conducted in 2016 found that over half of ca. 50 vehicles tested had their EGR system inoperative under low ambient temperatures, for engine protection purposes (BMVI, 2016). Such differences in the vehicle NO$_x$ emissions under low temperatures are observed in Euro 6 passenger cars (Suarez-Bertoa and Astorga, 2018). During regulated laboratory tests Suarez-Bertoa and Astorga (2018) observed that Euro 6 gasoline and diesel vehicles emitted two to more than three times more NO$_x$ at pre-conditioned initial engine temperatures of $-7$ °C, compared to emissions at $23$ °C. These results underline the lower effectiveness in the performance of the after-treatment systems under the low initial operating temperatures found in some real driving conditions. However, the relative contribution of gasoline and diesel vehicles, or passenger cars vs light- and heavy-goods vehicles, to the change in inferred primary NO$_2$/NO$_x$ ratio cannot be readily determined from these data. At intermediate temperatures ($5 – 15$ °C) reduced changes in the inferred primary NO$_2$/NO$_x$ ratio were found (see Fig S2, S3 in supplementary material).

Fig 8 shows the relationship between inferred mean primary NO$_2$/NO$_x$ ratio and mean ambient temperature, for the cold months (November, December, January and February). The primary NO$_2$/NO$_x$ ratio is significantly negatively correlated with temperature ($R^2 = 0.54$), according to the inverse relationship $f_{NO_2} = 15\% - [0.77 \pm 0.15] \times (T / °C)$. Similar results to those presented here were reported by Degraeuwe and Weiss (2017), who found that for on-road tests, Euro 5 and Euro 6 cars emit four and three times higher NO$_x$ at low ambient temperatures than the legislative limits, respectively. For Euro 6 cars, similar results were reported by Kwon et al. (2017), who compared NO$_x$ emissions at lower ambient temperatures ($0 – 5$ °C) with higher ambient temperatures ($15 – 20$ °C) and found a difference of $82 – 192\%$.

These literature results, along with the analysis presented here, support the finding that higher vehicle emissions at lower ambient temperatures may have a measurable impact upon ambient air quality. Vehicle emissions effects are likely exacerbated by meteorology during wintertime (lower boundary layer height, and increasing tendency to stable conditions (temperature inversions) during the worst pollution episodes and coldest weather); reduced photolysis frequencies (shifting the NO$_x$ PSS towards NO$_2$), and potentially greater vehicle use during low temperature conditions in the UK, relative to other travel options.
4. Conclusions

This study presents an analysis of ambient NO$_x$ and NO$_2$ mixing ratios, to derive inferred NO$_2$/NO$_x$ emission ratios from urban traffic monitoring stations in the UK, for the period from 2009 until 2016. The analysis showed:

- In keeping with other recent results, a decrease in the mean ambient NO$_2$ mixing ratio at selected urban roadside measurement sites between 2009 and 2016, alongside a smaller reduction in NO$_x$ mixing ratios.

- Direct emissions are not measured in this work, and a number of assumptions are made in deducing emitted NO$_x$ ratios from ambient data for a finite number of measurement stations. The mean inferred primary NO$_2$/NO$_x$ ratio shows an overall reduction of 5 percentage points from 17.5% to 12.5%, with a calculated reduction of -0.32 percentage points/year (95% confidence interval of -0.2 to -0.45 percentage points/year), over this time period. The period of this reduction corresponds to the combined development of policy (new Euro limits), changes in fleet composition and, to some extent, to the initial penetration of new after-treatment technologies introduced in the last eight years. However, this reduction is not evident in every location, underling the complexity of the problem and implying that more stringent measures may be needed to further reduce ambient NO$_2$ in urban environments, a challenge that will be heightened by increasing vehicle numbers.

- Enhanced “cold-start” emissions, inferred from ambient monitoring data under low temperature conditions. The results imply that the overall vehicle primary NO$_2$/NO$_x$ ratios increase on average by 64.5% and 75% for morning and evening rush hours under cold (≤ 5°C) conditions, compared with (for the UK) normal conditions (> 5°C), while this difference can be 1.6 - 3.8 times higher, when examining individual urban traffic monitoring stations. An inverse relationship is found between ambient temperature and primary NO$_2$/NO$_x$ ratio.

These results suggest that the combination of (short duration) driving patterns and the temperature dependence of the current after-treatment systems under low ambient temperatures leads to measurable impacts upon ambient air quality. They also highlight the importance of consideration of cold-start emissions within vehicle test cycles, as these may cause a measurable deterioration in air quality in urban areas. Assessment of the related health
burden – which must integrate personal exposure considerations – should combine the impact of meteorological factors on both vehicle performance, and public behaviour vs transport choices.

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<th>Region</th>
<th>Median 2009 primary NO$_2$/NO (%)</th>
<th>Median 2016 primary NO$_2$/NO (%)</th>
<th>Difference primary NO$_2$/NO (%)</th>
<th>Monthly trend with 95% confidence limits (%/year)</th>
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<td>-0.8 (-1.61, -0.06) *</td>
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Table 1. Median inferred primary NO$_2$/NO$_x$ ratios, difference and monthly trend (percentage points/year) for individual urban traffic monitoring sites in the UK from 2009 to 2016. Symbols (***, **, *, +) indicate the level of significance $p$ (0.001, 0.01, 0.05, 0.1). Note that the median primary NO$_2$/NO$_x$ values were acquired with a localised fitted regression model, while the monthly trend was calculated with a fitted linear regression model.
Aberdeen & 12.3±0.17*** & 13.1±0.18*** & 12.0±0.3 & 13.0±0.3 & 2.5 & 0.1 & \\
Birmingham & 10±0.14*** & 10.4±0.23*** & 7.2±0.4 & 8.2±0.3 & 38.8 & 26.8 & \\
Cambridge & 8.5±0.36*** & 7.2±0.36*** & 3.6±0.7 & 4.7±0.5 & 136.1 & 53.2 & \\
Carlisle & 12.6±0.43*** & 13.2±0.47*** & 10.1±0.8 & 7.0±0.5 & 24.8 & 88.5 & \\
Chepstow & 9.7±0.62*** & 11.9±0.1**** & 9.9±0.9 & 12.0±0.8 & - & 0.1 & \\
Exeter & 12.1±0.19*** & 11.7±0.33*** & 6.5±0.3 & 6.8±0.4 & 86.2 & 72.1 & \\
Leeds & 8.5±0.2*** & 8.0±0.3*** & 4.6±0.4 & 3.2±0.3 & 84.8 & 150 & \\
Liverpool & 9.4±0.3*** & 11.3±0.48*** & 7.8±0.7 & 11.2±0.6 & 20.5 & 0.1 & \\
London Camden & 15±0.27*** & 14.2±0.4*** & 12.2±0.3 & 11.1±0.3 & 22.9 & 27.9 & \\
London Haringey & 6.8±0.2*** & 6.9±0.04*** & 1.4±0.5 & 3.3±0.3 & 385.7 & 109.1 & \\
London Marylebone & 12.3±0.1*** & 13.7±0.2*** & 12±0.2 & 13.7±0.2 & 2.5 & - & \\
London tower hamlet & 13.5±0.3*** & 13.8±0.7*** & 12.6±0.6 & 13.8±0.5 & 7.1 & - & \\
Newcastle & 10.7±0.1*** & 11.4±0.2*** & 7.9±0.4 & 8.3±0.3 & 35.4 & 25.3 & \\
Sandys & 16.3±0.3*** & 15.1±0.3*** & 15±0.7 & 13.2±0.6 & 8.7 & 14.3 & \\
Stanford le hope & 7.0±0.3*** & 8.2±0.4*** & 4.8±0.9 & 7.8±0.6 & 45.8 & 12.8 & \\
Swansea & 24.4±0.3*** & 23.4±0.4*** & 15±0.4 & 13.2±0.4 & 62.7 & 77.2 & \\
York & 13.8±0.3*** & 13.5±0.4*** & 5.7±0.7 & 5.3±0.4 & 142.1 & 158.4 & \\

Table 2. Primary NO$_2$/NO$_x$ ratio during cold weather rush hours (representing cold start emissions) and normal weather rush hours (representing normal emissions) and the corresponding increment for individual areas across the UK. Symbols (***, **, *, +) indicate the level of significance of the slope $p$ (0.001, 0.01, 0.05, 0.1).
Fig 1. Monitoring sites used in this study. Blue indicates the meteorological stations, red the urban traffic sites, yellow the urban background and green the rural sites.
Fig 2. Annual average NO$_x$ (left) and NO$_2$ (right) values for urban traffic stations in the UK normalized to their mean value. Black dashed line is the average from all sites used.
Fig 3. Monthly NO\textsubscript{2} mixing ratios during rush hour periods (06:00-10:00, 16:00-19:00), normalized to their 1/1/2009 value, for urban traffic monitoring sites across the UK. Black line indicates the mean value across all stations used.
Fig 4. Daytime hourly mean ambient (a) NO\textsubscript{x} and (b) NO\textsubscript{2}/NO\textsubscript{x} distributions for 2009 and 2016 from all urban traffic monitoring sites in the UK. (c) NO\textsubscript{2}/NO\textsubscript{x} ratio vs NO\textsubscript{x}: the green (2016) and red (2009) lines indicate the baselines of the distributions and can be used to estimate the primary NO\textsubscript{2} (see text). (d) ambient NO\textsubscript{2}/NO\textsubscript{x} ratio as a function of the difference in NO\textsubscript{x} mixing ratio for each location, between 2009 and 2016. The yellow line indicates the locally fitted regression (LOESS) line with associated 95% confidence interval, while the blue line indicates the variation in NO\textsubscript{2}/NO\textsubscript{x} expected, for a change in overall NO\textsubscript{x} abundance, on the basis of the NO\textsubscript{2}-O\textsubscript{3} PSS chemistry alone (see text for details).
Fig 5. Mean overall trend of the inferred primary NO$_2$/NO$_x$ ratio averaged over all UK urban traffic monitoring sites. The error bars indicate the standard error of the slope estimates. The local regression fitted line (red solid line) is weighted by taking into account the standard errors of the individual slopes. The shaded area indicates the 95% confidence intervals.
Fig 6. Box-whisker plots for the inferred primary NO$_2$/NO$_x$ ratio for the individual urban traffic monitoring sites considered in this study, during 2009 and 2016. Green indicates a reduction in the median value between the two dates for each location, red an increase, between 2009 and 2016. S1: Aberdeen, S2: Birmingham, S3: Cambridge, S4: Carlisle, S5: Chepstow, S6: Exeter, S7: Leeds, S8: Liverpool, S9: Newcastle, S10: Sandy, S11: Stanford le Hope, S12: Swansea, S13: York, S14: London.
Fig 7. Ox -NO\textsubscript{x} plots during normal winter morning and evening rush hours (Fig 7a, Fig 7c, green) and during cold (T ≤ 5 \degree C) morning and evening rush hours (Fig 7b, Fig 7d, blue), representing normal and potential cold start emissions. The shaded areas indicate the 95% confidence intervals of the linear regression fit.
Fig 8. Inferred mean monthly primary NO$_2$/NO$_x$ ratio (%fNO$_2$) and its dependence on mean ambient temperature in the UK. The grey shaded areas indicate the 95% confidence intervals of the regression relationship.

%fNO$_2$ = 15 - [0.77 ± 0.15]T (°C)

R$^2$ = 0.54
Highlights

- A methodology is developed to assess enhanced “cold-start” primary NO\textsubscript{2} emissions from vehicles.

- Ambient mixing ratios of NO\textsubscript{2} and NO\textsubscript{x} measured at selected UK urban traffic sites have fallen over the period from 2009-2016.

- Overall inferred primary NO\textsubscript{2}/NO\textsubscript{x} ratio experiences a statistically significant decrease from 17.5% to 12.5% between 2009 and 2016.

- Inferred cold-start morning and evening primary NO\textsubscript{2} vehicle emissions are significantly higher than those found under warmer conditions

- Inferred cold-start primary NO\textsubscript{2} vehicle emissions have measurable impacts upon urban air quality in the UK.