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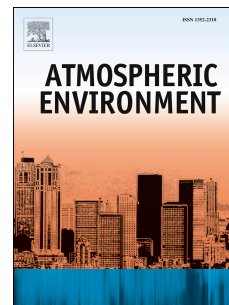
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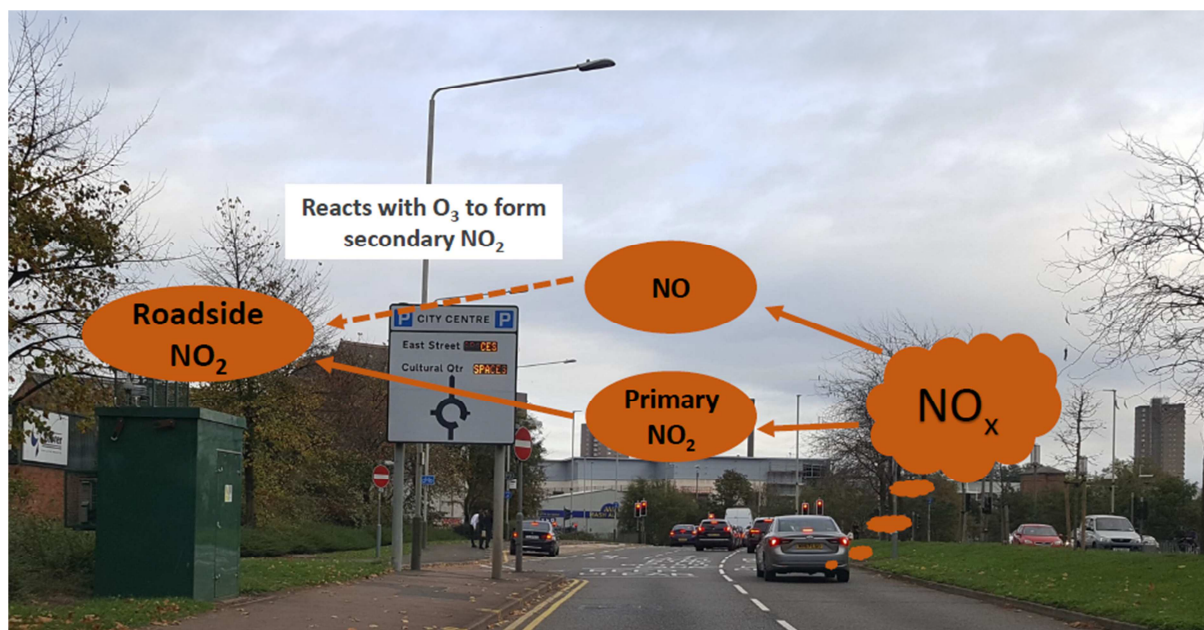
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ACCEPTED MANUSCRIPT

1 **Investigation of vehicle cold start primary NO₂ emissions from ambient monitoring data in the**
2 **UK and their implications for urban air quality**

3
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9 Bloss)

10 **Abstract**

11 Nitrogen oxides (NO and NO₂, collectively NO_x) derived from vehicle exhausts are critical
12 pollutants with significant implications for urban air quality and human and environmental
13 health. In this study, we investigate trends in measured ambient nitrogen dioxide (NO₂) and NO_x
14 mixing ratios at urban traffic - dominated monitoring sites in the UK for the period 2009-2016.
15 We apply an oxidant analysis approach alongside a number of assumptions to the ambient data
16 to determine trends in the inferred primary NO₂/NO_x ratio, and examine evidence for enhanced
17 vehicle "cold start" effects upon these inferred emissions. Ambient NO₂ and NO_x mixing ratios
18 have experienced an overall decrease of 17.2% and 11.3% respectively for the locations
19 considered over this time period. The inferred primary NO₂/NO_x ratio for the majority of the
20 study locations is found to have fallen by 29% (from 0.175 to 0.125) as a monthly mean from
21 2009 to 2016, with a statistically significant median decrease of 0.32 percentage points per year.
22 However, during cold weather (temperatures less than or equal to 5 °C), the inferred primary
23 NO₂/NO_x ratio averaged across all locations, when compared with normal conditions
24 (temperatures higher than 5 °C) increased from 0.062 (±0.004) to 0.102 (±0.001) (64.5% higher)
25 and from 0.056 (±0.004) to 0.098 (±0.001) (75% higher) for cold morning and evening rush
26 hours, with substantially greater increases at some sites. This "cold start" result suggests that the
27 combination of recent vehicle driving history and ambient weather conditions, in conjunction
28 with technological constraints on the operating temperature range of emission control systems
29 in some vehicles, affects NO_x emissions and hence has a detrimental impact upon air quality in
30 urban environments. Increased cold start emissions imply an increased NO₂ - derived health
31 burden from air pollution, under certain conditions, assessment of which should consider
32 changes in vehicle use as a result of weather, and hence altered personal exposure.

33

34 **Key words:** Urban air quality, Nitrogen oxides - primary NO_x , vehicle cold starts, trend analysis,
35 vehicle emissions, low temperature emissions

36

37 **1. Introduction**

38 1.1 Background and objectives

39 Vehicle emissions are a dominant source of air pollution in urban environments in
40 developed nations. Direct emissions include nitrogen oxides (NO_x , the sum of nitrogen monoxide
41 (NO) and nitrogen dioxide (NO_2)) and particulate matter (PM). NO_x emissions are of particular
42 importance to urban air quality, since they not only contribute to local and regional scale air
43 pollution, but also to the formation of secondary pollutants such as ozone (O_3) and secondary
44 PM. Vehicular pollutants have been reported to have substantial adverse impacts on human
45 health (Papapostolou et al., 2011), with exposure to NO_2 known to lead to reduced lung function
46 and increased risk of cancer (Adam et al., 2015; Hamra et al., 2015; WHO, 2013), and is
47 responsible for tens of thousands of premature deaths each year across Europe (EEA, 2016; RCP,
48 2016; COMEAP, 2010). The International Agency for Research on Cancer has recently classified
49 diesel engine exhaust as a Group I carcinogen, based on its association with lung cancer
50 incidence (Attfield et al., 2012; Silverman et al., 2012).

51 Within the EU, a series of legislative measures have been introduced to address this
52 challenge. The first directive 96/62/EC (EC, 1996), which is commonly referred as the Air Quality
53 Framework Directive, and its daughter Directives, established standards in the period up to 2004
54 for a range of pollutants including NO_2 in ambient air. The three first daughter directives were
55 consolidated into a single ambient air quality Directive adopted as 2008/50/EC (EC, 2008a) and
56 together with the fourth daughter directive 2004/107/EC they provide the current framework
57 for the control of ambient concentrations of air pollution in the UK. However, the need for
58 greater reductions in NO_2 mixing ratios has led to further directives, which gradually aimed to
59 decrease the emission levels directly from vehicles (EC, 2008b; 2011). In the UK, evidence
60 indicates that new Euro limits (Euro 5 and Euro 6), in conjunction with new after-treatment
61 technologies (see section 1.2) have had a positive impact in the reduction of roadside $\text{PM}_{2.5}$
62 (Harrison and Beddows, 2017) and NO_x (DEFRA, 2017), while factors such as aging of catalysts

63 leading to reduced oxidative capacity via thermal deactivation might also play a role in affecting
64 primary NO₂ emissions from traffic (Carslaw et al., 2016b).

65 Here, we analyse trends in ambient NO_x and NO₂ mixing ratios between 2009 and 2016
66 measured at urban monitoring stations in the UK, where NO_x mixing ratios are dominated by
67 local traffic emissions. We assess changes in the ambient NO₂/NO_x ratio, and analyse the
68 ambient data to infer potential trends in the primary (directly emitted) NO₂/NO_x ratio from
69 vehicles. The NO_x data are coupled with meteorological observations and a methodology is
70 introduced to assess potential changes in vehicle emissions associated with "cold start"
71 operation, as indicated by ambient temperature, and the impact of this behaviour upon ambient
72 air quality.

73

74 1.2 Controls of vehicle NO_x and NO₂ emissions

75 Internal combustion vehicle technologies have developed to reduce fuel consumption,
76 improve engineNitrogen oxides (NO and NO₂, collectively NO_x) derived from vehicle exhausts,
77 are critical pollutants with significant implications for urban air quality and human and
78 environmental health. In this study, we investigate trends in measured ambient nitrogen dioxide
79 (NO₂) and NO_x mixing ratios at urban traffic - dominated monitoring sites in the UK for the
80 period 2009-2016. We apply an oxidant analysis approach alongside a number of assumptions to
81 the ambient data to determine trends in the inferred primary NO₂/NO_x ratio, and examine
82 evidence for enhanced vehicle "cold start" effects upon these inferred emissions. Ambient NO₂
83 and NO_x mixing ratios have experienced an overall decrease of 17.2% and 11.3% respectively for
84 the locations considered over this time period. The inferred primary NO₂/NO_x ratio for the
85 majority of the study locations is found to have fallen by 29% (from 0.175 to 0.125) as a monthly
86 mean from 2009 to 2016, with a statistically significant median decrease of 0.32 percentage
87 points per year. However, during cold weather (temperatures less than or equal to 5 OC), the
88 inferred primary NO₂/NO_x ratio averaged across all locations, when compared with normal
89 conditions (temperatures higher than 5 OC) increased from 0.062 (±0.004) to 0.102 (±0.001)
90 (64.5% higher) and from 0.056 (±0.004) to 0.098 (±0.001) (75% higher) for cold morning and
91 evening rush hours, with substantially greater increases at some sites. This "cold start" result
92 suggests that the combination of recent vehicle driving history and ambient weather conditions,
93 in conjunction with technological constraints on the operating temperature range of emission

94 control systems in some vehicles, affects NO_x emissions and hence has a detrimental impact
95 upon air quality in urban environments. Increased cold start emissions imply an increased NO₂ -
96 derived health burden from air pollution, under certain conditions, assessment of which should
97 consider changes in vehicle use as a result of weather, and hence altered personal exposure.
98 performance, and (primarily through the addition of after-treatment systems) reduce emissions
99 of air pollutants such as NO_x. Of the two principal categories of internal combustion engine, the
100 emission problem is more straightforward to address for gasoline (spark ignition) vehicles in
101 comparison to diesel (compression ignition) power units. Most gasoline vehicles now employ a
102 three-way catalyst (TWC), a key abatement technology introduced in the 1980s and applied
103 widely from the 1990s to reduce vehicle tailpipe emissions. TWC are designed to simultaneously
104 convert carbon monoxide (CO) to carbon dioxide (CO₂), hydrocarbons (HC) to water and NO_x
105 species to nitrogen. Theoretically, TWC can cut CO, HC and NO_x emissions by over 99% (under
106 stoichiometric conditions) if the air to fuel ratio in the exhaust stream is accurately controlled,
107 although they have been associated with emissions of the greenhouse gas nitrous oxide (N₂O)
108 (Berges et al., 1993; Jimenez et al., 2000).

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

114 Exhaust gas recirculation (EGR) was introduced as a further emission control technology
115 in larger size Euro 3 engines, and became the standard in Euro 4 and later diesel passenger cars
116 and light duty vehicles (LDV). The EGR system channels and recirculates a portion of the exhaust
117 gas into the filtered, high-pressure, fresh combustion air at the engine intake. The higher the
118 engine load the better the EGR performance and the greater the NO_x reduction (Yokomura et al.,
119 2003).

120 Diesel particle filters (DPF), introduced in 2009 to achieve Euro 5 limits, physically
121 capture diesel particles and prevent their release to the atmosphere. However, the stored PM
122 must be oxidized in order to avoid blocking the filter. This is achieved via reaction with O₂ at high
123 temperatures (600 °C) and via reaction with NO₂ at low temperatures (250 – 450 °C). Owing to
124 the amount of NO₂ needed in the DPF to burn the soot, the DPF is attached after the DOC
125 system, forming a continuously regenerated trap (CRT) or catalyzed continuously regenerated

126 trap (CCRT), which reduces PM, CO and HC. The secondary NO₂ formation as a by-product of the
127 catalysis, however, is a major issue in these systems and can lead to increased NO₂ emissions
128 from the vehicle.

129 The latest after-treatment technologies involve Lean NO_x trap (LNT) and Selective
130 catalytic reduction (SCR) technologies, which can achieve Euro 6 limits. LNT technology achieves
131 NO_x storage during lean engine operation, and NO_x reduction during rich operation phases.
132 During lean engine operation, NO_x is retained in the storage components in the form of nitrates
133 and nitrites. In a subsequent short fuel-rich period, the NO_x trap is regenerated by NO_x release
134 and reaction with HCs achieves reduction to N₂. Since fuel consumption for NO_x trap
135 regeneration depends on the regeneration frequency, which is a function of NO_x trap
136 performance parameters, the impact of catalyst aging must be considered in the operation
137 strategy.

138 Selective catalytic reduction (SCR) is an after-treatment system which catalyzes NO_x (NO
139 + NO₂) reduction by addition of reactive nitrogen compounds, such as ammonia or urea-based
140 mixtures. In SCR, the mixture of ammonia/urea reacts with NO_x to form N₂, CO₂, and H₂O. The
141 SCR process requires precise control of the ammonia injection rate, because an insufficient
142 injection rate may result in unacceptably low NO_x conversion, while an excessive injection rate
143 results in releases of ammonia (undesirable “ammonia slip”) to the atmosphere and increased
144 SCR reductant consumption.

145 All these after-treatment systems need to reach a certain temperature threshold (i.e.
146 regular operating conditions) in order to effectively reduce NO_x emissions. This difference in the
147 temperature, for both the engine and the catalytic converter, under which the vehicle is initially
148 operated comparing to regular operating conditions can be expressed as a “cold start” when the
149 engine is operated with the temperature of the oil, coolant and all elements of the engine at the
150 ambient temperature. At lower ambient temperatures, the engine and catalyst warm up period
151 is prolonged and this can have an adverse effect on vehicle emissions. For modern gasoline and
152 diesel vehicles equipped with TWC and DOC after-treatment systems, under cold operation, this
153 implies dis-proportionally higher release of gaseous pollutants, since the temperature of the
154 catalyst is not sufficient to ensure efficient NO_x conversion. Currently in the EU, only the
155 emissions from gasoline Euro 3/4 vehicles under cold-start in low ambient temperature are
156 regulated under the directive 98/69/EC (EC, 1998), as identified elsewhere (e.g. Dardiotis et al.,
157 2013; Bielaczyc et al., 2011; 2012).

158

159 1.3 NO₂ and NO_x emission measurement approaches

160 There are several different approaches to estimate vehicle combustion (tailpipe)
161 emissions – see e.g. the review of Franco et al., (2013). Here, we briefly introduce the key
162 approaches to provide context for the methodology used in this work. Most widely known are
163 approved bench (chassis dynamometer) tests, where the tested vehicle follows a certain driving
164 cycle (sequence of speed/acceleration/deceleration over a pre-defined period of time that
165 corresponds to notional urban driving or extra-urban driving behaviour) and relevant analyzers
166 sample directly from the exhaust to determine (e.g.) NO_x emissions (Nine et al., 1999; Yanowitz
167 et al, 2000). However, such tests are very short (approximately 20 min each test) and, as has
168 been widely reported, fail to capture the real world operation NO_x emissions either by accident
169 or design (Andersson et al., 2014; Degraeuwe and Weiss, 2017). Thus, it is thought that historical
170 emission factors based solely upon such tests may not be representative of real-world on-road
171 vehicle behaviour.

172 Secondly, portable emission measurement systems (PEMS) are devices mounted to
173 individual test vehicles which measure directly from the exhaust/tailpipe during on-road driving
174 (Weiss et al, 2011). PEMS capture individual vehicle emissions under real driving conditions, but
175 are expensive, can only be fitted in one car at a time, normally require tailpipe adaptations to
176 sample directly, and may suffer power limitations if powered by the vehicle on-board low voltage
177 power supply system. A related approach is the chase measurement method. In this approach,
178 instruments are mounted in a second, monitoring vehicle and an inlet is used in order to sample
179 from ambient air, while following individual (or groups of) target vehicles (Brantley et al., 2014).
180 Chase approaches can, compared with test bench measurements and PEMS approaches, more
181 readily give accurate information about fleet emissions from a number of vehicles and variations
182 with driving behaviour (e.g. urban, rural, motorway), but suffer from limitations of the need to
183 account for mixing with background air (commonly achieved via use of CO₂ as an exhaust tracer),
184 and overlap of multiple vehicle plumes.

185 Thirdly, remote sensing technologies (Bishop et al, 1989), where a light beam passes
186 through the exhaust plume of an individual or series of target vehicles prior to measurement at a
187 detector, wherein the amount of light absorbed is proportional to the concentration of gases in
188 the plume (Carslaw and Rhys-Tyler, 2013). Those approaches are commonly coupled with vehicle

189 sensing and number plate recognition tools to identify speed, acceleration and vehicle/engine
190 characteristics. Although remote sensing methodologies are in many senses the “gold standard”
191 approach, in that they can measure the real-world on-road emissions from large numbers of
192 individual vehicles under favourable operating conditions, they suffer from constraints of cost,
193 complexity and potentially perturbations to traffic flow/behaviour. Furthermore, such
194 techniques have issues when located on multiple lane roads as emissions from vehicles
195 alongside the target vehicle can interfere with the result, in particular when the wind is in an
196 unfavourable direction - an alternative top-down geometry, which can sample individual, parallel
197 vehicle lanes, has recently been demonstrated (Ropkins et al., 2017).

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

209

210 **2. Data and Methodology**

211 2.1 Experimental data

212 Atmospheric mixing ratios of NO_x and O₃ are monitored across the UK by the Automatic
213 Urban and Rural Network (AURN), which is operated and maintained by the Department for
214 Environment, Food and Rural Affairs (DEFRA), the Scottish Executive, the National Assembly for
215 Wales and the Department of the Environment for Northern Ireland. Ambient mixing ratios are
216 reported at hourly resolution, with measurements made by well-established conventional
217 techniques, UV photometry for O₃ and chemiluminescence for NO_x with a molybdenum
218 converter (see comments below, section 2.2, re NO₂ selectivity). The measurement uncertainty

219 for NO_x and O₃ from the AURN stations is <15%, following the European Committee for
220 Standardisation (documents BS EN14211:2012 -NO_x and BS EN14625:2012 -O₃).

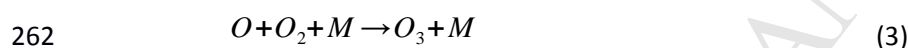
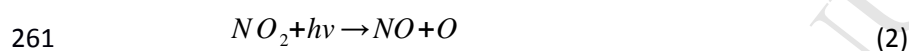
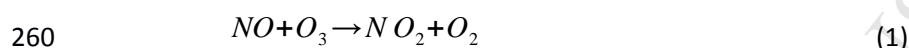
221 The analysis presented here uses hourly data from every urban-traffic monitoring station
222 (defined as stations that are located at roadside and kerbside locations) in the UK AURN
223 network. For each urban-traffic station, background data were obtained from a nearby
224 background site, defined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

239 2.2 Data processing methods and assumptions

240 Monitored data were processed and displayed using ArcGIS and R version 2.15.1 (R Core
241 Team, 2016) along with the R packages ggplot2 (Wickham, 2009), openair (Carslaw and Ropkins,
242 2012), and mcgv (Wood, 2003). The data were de-seasonalised by applying the smoothing LOESS
243 function, which is a non-parametric regression method that combines multiple regression
244 models in a k-nearest-neighbor-based meta-model (Cleveland et al., 1990). The statistical
245 approach that we followed for trend calculation is a non-parametric Mann-Kendall approach,
246 while the trend slope is calculated with the Theil-Sen method (Sen, 1968; Theil, 1950) available
247 in the R-openair package. In this method, for a given set of n x, y pairs, the slopes between all
248 pairs of points are calculated and the median is taken as an estimate of the most probable slope
249 (trend). This method is robust to outliers and can be used in both non-normal and

250 heteroscedastic (non-constant error variance) data series. Bootstrap re-sampling was used for
 251 the calculation of confidence intervals at the 95% level and p-values. A statistically significant
 252 trend was assumed when $p < 0.1$ (represented with a '+' symbol), meaning that the trend was
 253 not random at a 90% chance; p-values of: $p < 0.05$, $p < 0.01$ and $p < 0.001$, marked by '*', '**'
 254 and '***', respectively, indicate very highly significant trends, while $p > 0.1$ shows insignificant
 255 trends.

256 To derive the inferred primary NO_2/NO_x ratio from ambient monitoring data we used the
 257 total oxidant ($\text{Ox} = \text{NO}_2 + \text{O}_3$) approach developed by Clapp and Jenkin (2001). It is well known
 258 that in the daytime atmosphere the interconversion of O_3 to NO_2 and vice versa is generally
 259 dominated by the following reactions:



263 which constitute a null cycle. Reactions (1) - (3) result in the cycling of NO_x between NO and NO_2
 264 and total Ox between O_3 and NO_2 , however the total mixing ratios of both NO_x and Ox remain
 265 constant. During daylight, the equilibrium that occurs in the above reactions determines the
 266 photo-stationary steady state (PSS). Clapp and Jenkin, (2001) illustrated that when in PSS there is
 267 a linear relation between Ox and NO_x for roadside station data, which may be interpreted as a
 268 NO_x - independent and a NO_x - dependent contribution to Ox. The former is the regional
 269 contribution which corresponds to the regional background O_3 level, whereas the latter is
 270 effectively a local contribution that is associated with additional NO_2 (i.e. primary NO_2 emissions,
 271 under the assumption that no other sources are significant). While this analysis only holds in
 272 volume mixing ratio space, it should be noted that the AURN data-series are reported in $\mu\text{g}/\text{m}^3$,
 273 therefore before we apply the total oxidant approach, data were converted from $\mu\text{g}/\text{m}^3$ to ppb
 274 by applying EU/DEFRA conversion factors (20 °C temperature and 1013 hPa pressure). For the
 275 analysis presented here, "Daytime" was defined as all whole hours between sunrise and sunset,
 276 based on the local time in London.

277 In the case of vehicle emissions from ambient urban traffic monitoring data, Jenkin,
 278 (2004), demonstrated that by considering the 'total oxidant' slope, $(\text{NO}_2 + \text{O}_3) / \text{NO}_x$, estimates
 279 could be drawn for the primary (direct) NO_2/NO_x ratio emitted from vehicles. However, most of

280 the AURN urban traffic monitoring sites in the UK do not have O_3 measurements which poses a
281 limitation to the total oxidant approach and to the estimation of the primary NO_2/NO_x ratio. In
282 such cases, Carslaw and Beevers, (2005) suggested a methodology that calculates the NO_2/NO_x
283 ratio without the need of O_3 observations from the urban traffic site, but with additional
284 observations (of NO_2 , NO_x and O_3) from a nearby urban background site. In general, this
285 approach assumes that the increment in NO_2 mixing ratio between a given urban traffic
286 monitoring site and a nearby urban background site is partitioned into NO_2 that is chemically
287 derived through the reaction between NO and O_3 , and NO_2 which is emitted directly by road
288 vehicles. Therefore, data from paired sites (roadside and background/rural site) are used.
289 Additionally, in the calculation of the primary NO_2/NO_x ratio, the difference in NO_x between the
290 urban traffic and urban-background/rural stations is considered; therefore impacts from non-
291 traffic related sources are essentially removed. The method uses a simple constrained model
292 and basic set of chemical reactions to explain the time-dependent variation in NO , NO_2 and O_3 as
293 vehicle plumes mix with background air. Carslaw and Beevers (2005), showed that the primary
294 NO_2/NO_x ratio may then be obtained from fitting the observed NO_2 - NO_x data to that predicted,
295 whilst optimizing the primary NO_2 fraction and the mixing time between emission and
296 observation at the urban site. Here, we follow this methodology, but note some limitations.
297 Specifically, the approach assumes that the increment in NO_2 mixing ratio above a local
298 background site is controlled by the availability of O_3 and directly emitted NO and NO_2 only and
299 does not include additional chemical reactions (e.g. of peroxy radicals with NO). Furthermore, it
300 should be mentioned that because the AURN analysers employ a heated molybdenum converter
301 to detect NO_2 (as NO), other NO_y species will be detected as NO_2 . The influence of those
302 interferences might lead to overestimation of NO_2 in urban areas (Dunlea et al., 2007; Harrison
303 et al., 2012). In addition, direct emissions of HONO, thought to comprise a small, but still
304 significant and uncertain, component of vehicle exhaust (Crilley et al., 2016; Jenkin et al., 2008;
305 Kurtenbach et al., 2001), is also a potential interferent in NO_2 measurements. However, in our
306 analysis (see section 2.3 below) all the above potential interferences would be expected, to a
307 first approximation, to co-vary with NO_2 and hence have limited effect upon the inferred primary
308 NO_2/NO_x ratio.

309 2.3 Investigation of cold-start/emissions under low ambient temperature conditions.

310 To assess evidence for altered emissions under conditions of low ambient temperatures,
311 we applied the total oxidant approach for rush hour periods during the morning (06:00-10:00)
312 and afternoon (16:00-19:00) during winter time (November, December, January, February), with
313 a temperature condition of 5 °C (i.e., $T \leq 5$ °C). We select rush hours because the vehicle fleet
314 experiences less (and known) variations during those hours with respect to the rest of daytime.
315 It should be noted here that, although we used the total oxidant approach (notionally daylight
316 only, Clapp and Jenkin, 2001), by including morning pre-sunrise and evening post-sunset periods,
317 sensitivity tests showed that this introduced a very small difference in the overall results (less
318 than a 2% change in the inferred primary NO₂/NO_x ratio; less than 2 ppb difference in the ozone
319 background). According to European regulations, the bench/laboratory tests for standard vehicle
320 emissions are made under an (air) temperature range of 20 – 30 °C (EC, 91/441/ECC) and
321 normally at the fixed temperature value of 23 °C (DfT, 2016). The vehicle is given a standard pre-
322 conditioning in a temperature control room so that the whole vehicle including engine oil and
323 coolant is 'soaked' to the regulated temperature range. As a result, the selected temperature
324 threshold method ($T \leq 5$ °C), is well below that for the tested/regulated range, and very close to
325 the winter mean temperature in the UK (4.4 °C). Results for days that satisfied the temperature
326 criterion were compared with those that did not (Matthaios et al., 2017), in order to examine
327 any potential difference in emissions-driven air quality.

328

329 **3. Results and Discussion**

330 **3.1 Ambient NO_x and NO₂ trends and relationships**

331 The annual averaged ambient NO_x and NO₂ values for each urban traffic station are
332 shown in Fig 2, normalised to their mean value (2009-2016). A clear decline in the levels of both
333 NO_x and NO₂ is evident, which based on the overall average from all sites is 11.3% for NO_x (black
334 dashed line, Fig 2a) and 17.2% for NO₂ (black dashed line, Fig 2b) across the time period
335 considered (2009 - 2016). The larger NO₂ than NO_x decline in the UK urban traffic sites might be
336 due to an alteration in PSS, emissions or in the background ozone that contributes to the
337 photochemical cycle. Fig 3 shows how the monthly mean rush hour NO₂ mixing ratios
338 (normalized to 100 on 1/1/2009) varies for the examined period. An overall mean reduction of
339 approximately 20% (see black line) in the NO₂ mixing ratios is apparent. This sharper NO₂

340 decrease cannot be explained by the changes in background ozone, since the background ozone
341 has not changed significantly during the examined years (0.5% increase – see Fig S1 in the
342 supplementary material). This decrease in NO_2 is somewhat counter-intuitive to that expected
343 when considering the increase in the number of licensed diesel vehicles in the UK, which,
344 according to the Department for Transport, have increased from about 39% (2009) to 52%
345 (2016) in urban areas of the UK – and which are associated with higher NO_2 emissions than
346 petrol vehicles. However, it should be highlighted that during the period studied here, new Euro
347 limits came into force for the reduction of NO_x and NO_2 vehicle emissions. Briefly, Euro 5 limits,
348 first introduced in 2009, introduced a limit value of 0.18 g/km for NO_x in passenger cars, while
349 the tighter limits of Euro 6 for passenger cars (0.08 g/km for NO_x) came into force around 2014,
350 driving the introduction of new after-treatment technologies such as SCR and LNT. Depending
351 upon fleet penetration, these changes are beginning to play an important role in the (fleet
352 averaged) primary NO_2/NO_x ratio from vehicles (Carslaw et al., 2016b).

353 Figure 4 illustrates the variation in the ambient NO_2/NO_x ratio over time, as a function of
354 NO_x abundance, for the ambient monitoring data from urban traffic locations. Fig 4a (top) shows
355 the distribution of hourly mean NO_x mixing ratios for 2009 and 2016; Fig 4b (right) the
356 distribution in hourly mean NO_2/NO_x ratios for the same years and Fig 4c (centre) the hourly
357 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
358 (Fig 4c) tend towards a minimum value, which approximates the primary NO_2/NO_x emission ratio
359 (this asymptote can be used as an alternative to the total oxidant approach described above in
360 order to estimate the primary NO_2/NO_x emission fraction; Itano et al, (2007) used a similar
361 approach to estimate the primary NO_2/NO_x ratio from an urban traffic site in Osaka, Japan). From
362 the distribution in Fig 4b (right) it can be seen that the NO_2/NO_x ratio has reduced slightly
363 between 2009 and 2016 (median falling from 0.46 to 0.43), while from the asymptotes in Fig 4c
364 (centre) the primary NO_2/NO_x emission can be seen to have fallen from 0.175 to 0.125.

365 Figure 4d shows the absolute changes in NO_2/NO_x ratio as a function of the change in
366 total NO_x mixing ratio (hourly mean for corresponding date / time / location) between 2009 and
367 2016, for each urban traffic location. The greatest reduction in NO_2/NO_x ratio has occurred in the
368 locations where NO_x mixing ratio has increased (i.e. sites which have become more polluted, or
369 busy, with positive values on the x axis), while for the majority of sites where NO_x abundance has
370 decreased (negative x axis values), the NO_2/NO_x ratio has increased. To assess whether the

371 observed changes in NO_2/NO_x could be explained by $\text{NO}_x\text{-O}_3$ PSS chemistry alone a simple PSS
372 model, based on reactions 1-3, was used. In the first instance the model was initiated with
373 baseline conditions of 30 ppb of O_3 , 100 ppb of NO_x (75:25% $\text{NO}:\text{NO}_2$). In subsequent runs only
374 the initial NO_x mixing ratio was adjusted. In each case the model was run until NO , NO_2 and O_3
375 reached PSS and the difference in the final NO_2/NO_x ratio between the baseline run and all other
376 runs was plotted against the change in initial NO_x (see Fig 4b – blue line). It is observed that as
377 the NO_x abundance grows (positive x axis values), the PSS-chemistry-derived changes in the
378 NO_2/NO_x ratio (blue line) deviate from the observed ambient behavior (black points). Further
379 model runs (not shown here) demonstrated that if the PSS model was initiated with a higher
380 NO_2 fraction of 0.45 (i.e. similar to the mean NO_2/NO_x ratio observed in 2013 from Fig 4a) then
381 the difference between PSS-only predicted and ambient observed NO_2/NO_x differences becomes
382 even larger. Additional model PSS simulations for different initial ozone values $\text{O}_3 = 100$ ppb
383 (extreme case) also showed deviation from observations. The results of the model runs suggest
384 that the response of the PSS-chemistry to changes in overall NO_x emissions cannot, in isolation,
385 explain the variation in the NO_2/NO_x ratio observed between 2009 and 2016.

386 The observed changes in NO_2/NO_x therefore are likely to be influenced primarily by
387 changes in vehicle emissions, which might have resulted from the combined changes in: (1)
388 policy, where new Euro limits came into force for new car passenger models (Euro 5 in 2009 and
389 Euro 6 in 2014), and for London (4 stations included here), a low emission zone came into effect,
390 and daily charges for the London congestion zone increased. (2) Diesel cars, where in 2009, 90%
391 of diesel cars in the UK were Euro 3 and Euro 4, while in 2016, 69% of UK diesel cars were Euro 5
392 and Euro 6, according to the DfT / National Atmospheric Emissions Inventory NAEI, 2016). (3)
393 After-treatment technologies, where new technologies such as LNT and SCR have been
394 introduced (see section 1.2) and factors such as ‘catalyst thrifting’, where catalyst developers and
395 manufacturers reduce the amount of platinum group metal (which will potentially affect the
396 amount of NO_2 formed), or catalyst deactivation over time (where aged DOC catalyst
397 technologies may have reduced oxidative capacity through thermal deactivation or poisoning
398 and therefore less efficient conversion of NO to NO_2 (Carslaw et al., 2016b). Our results are in
399 accordance with other monitoring observations which show trends from eight long-running
400 urban traffic stations (1995 - 2015), and highlight that six out of eight stations show a downward
401 trend in the ambient NO_2 concentrations (DEFRA, 2017). In a recent study across Europe, Grange
402 et al. (2017) conclude that the ambient NO_2 levels measured at roadside monitoring sites have

403 fallen, and that the primary NO_2/NO_x emission ratio is lower than assumed by some key emission
404 inventories. This result is also in agreement with the findings of Font and Fuller (2016), who
405 analysed trends from ambient measurements in London and found that NO_2 and PM show a
406 declining trend from 2010 to 2015, attributed to a variety of factors, including a reduction of the
407 primary NO_2/NO_x emission ratio due to the absolute and relative reduction in numbers of older
408 diesel passenger cars in the overall fleet. These studies represent a growing body of evidence
409 that there has been a recent reduction in the ambient and primary emitted NO_2/NO_x ratio in UK
410 urban environments.

411

412 3.2 Trends in inferred primary NO_2/NO_x ratio

413 The trend in inferred primary NO_2/NO_x ratio is presented in Fig 5 (monthly daytime
414 values from all urban traffic sites, calculated using the methodology of Palmgren et al., (1996) /
415 Carslaw and Beevers, (2005), after removing the observed seasonality (see section 2.1; Carslaw,
416 2016a)). Despite some individual monthly increases (mainly in 2011), the inferred primary
417 NO_2/NO_x ratio, shows a clear downward trend, with a change (median value) of -0.32%/year with
418 95% confidence interval from -0.45% to -0.2% per year, significant to the 0.001 level ($p < 0.001$).
419 Fig 5 shows an overall reduction in the inferred primary NO_2/NO_x ratio from 17.5% to 12.5%
420 between 2009 and 2016. Despite the increases reported for the urban traffic monitoring sites in
421 the UK before 2009 (AQEG, 2004, 2007), the inferred primary emitted NO_2/NO_x experiences an
422 overall reduction of 5 percentage points over the 2009 – 2016 period. In detail, from 2009 until
423 2011, a small reduction in the emissions is evident (from 17.5% to 15%). From 2011 until mid-
424 2013 no significant changes are observed and the mean inferred primary NO_2/NO_x ratio is steady.
425 At that period the Euro 5a and Euro 5b limits for passenger and light duty vehicles, as well as the
426 Euro IV standards for heavy duty vehicles came into force for sales of new vehicles in September
427 2011 and January 2013 for light and heavy-duty vehicles respectively. Standards, which set a
428 prerequisite for diesel vehicles to have a DPF after-treatment system (Euro 5 diesel cars
429 constituted 20% of the UK diesel fleet in 2011 and they reached 52% by 2014 according to NAEI,
430 (2016)). This technology, as discussed in section 1.2, uses NO_2 in order to burn the collected
431 soot/PM in the filters, thus can also impact NO_2 emissions in the exhaust. In September 2014,
432 the most recent and stricter limits of Euro 6 came into force. The introduction of new Euro-limit-
433 driven emissions control technologies and their penetration through the fleet (Euro 5 and Euro 6

434 passenger cars) may therefore have contributed to this decrease of 2.5 percentage points in the
435 mean primary NO_2/NO_x ratio from early 2014, and the overall decrease of 5 percentage points
436 that is apparent from early 2009. This 29% relative decrease in inferred primary NO_2/NO_x ratio in
437 the last period has to be taken into account in the emission inventories for future modelling
438 estimates of exposure and policy making which currently they estimate an increase until 2015
439 for UK (NAEI, 2016) and Europe (Kiesewetter et al., 2014; Grange et al., 2017).

440 The change in inferred primary NO_2/NO_x ratio between 2009 and 2016 shows some
441 variability with geographic region across the UK (Fig 6). With few exceptions, the primary
442 NO_2/NO_x ratio has fallen in the majority of the regions, by a range from 0.5 to 10 % (Table 1). The
443 observed increases in the ratio in some regions (e.g York, Swansea) are difficult to explain
444 individually - they may be associated with other local factors such as changing road layouts and
445 urban infrastructure. A decline in the median inferred primary NO_2/NO_x emission for London of
446 5% is apparent, in agreement with Carslaw et al., (2016b), who found a decrease of about 7% in
447 the primary NO_2/NO_x ratio for inner London from 2009/10 to 2014/15. However, these variations
448 were not always consistent with the monthly primary NO_2/NO_x trend (calculated for the whole
449 data series) (Table 1), indicating that the trends are not significant in every area and more data
450 (i.e. a longer time series) are needed in order for a clear conclusion to be drawn. This potentially
451 reflects that the oxidant analysis assumptions (essentially, that the NO_x/O_3 PSS represents a fully
452 closed system) may be less valid for some locations and highlights the complexity and the
453 heterogeneity in the implementation and outcome of policy interventions to control air
454 pollution.

455

456 3.3 Low temperature primary NO_2 emissions – evidence for “cold start” effects

457 The inferred NO_2/NO_x emission ratios for cold ($T \leq 5^\circ\text{C}$) and non-cold/normal ($T > 5^\circ\text{C}$)
458 conditions during winter (November, December, January, February) morning and evening rush
459 hours are depicted in Fig 7. The change in gradient between cold (Fig 7b, 7d) and non-
460 cold/normal (Figs 7a, 7c) conditions is clearly apparent, with the $\text{O}_x\text{-NO}_x$ analysis indicating an
461 increase of 64.5% (mornings) and 75% (evenings) in the inferred primary NO_2/NO_x ratio for the
462 former compared with the latter. The increase in overall NO_x abundance (greater x-axis range,
463 most likely arising primarily from lower and more stable atmospheric boundary layer/mixing
464 heights under cold conditions, alongside reduced winter month NO_2 photolysis) is also apparent.

465 The 64.5% increase in inferred primary NO_2/NO_x ratio is statistically significant ($p < 0.001$),
466 changing by over 4 percentage points from 6.2 (± 0.4) %, for normal winter mornings to 10.2
467 (± 0.1) %, for cold winter mornings. Similar behaviour is observed for evenings (75% increase
468 from normal to cold conditions), where the difference is slightly higher at 4.2 percentage points,
469 from 5.6 (± 0.4) to 9.8(± 0.1) % (values in the parenthesis indicate the standard error). For
470 individual locations the difference between cold and normal conditions ranges over a factor of
471 1.6 to 3.8 (Table 2).

472 Atmospheric photochemical processes (i.e., chemical reaction rate constants and to a
473 lesser extent photolysis frequencies) are dependent upon temperature, which can introduce
474 changes in concentrations, as a function of temperature, under otherwise constant conditions
475 i.e. without any emission change. To assess the extent to which this may contribute to the
476 observed trends, a series of tests were performed using a simple chemical box-model including a
477 full inorganic chemical mechanism (taken from the MCM, <http://mcm.leeds.ac.uk/>, Saunders et
478 al., 2003) (described in detail in the supplementary material). The model was run for a 24-hour
479 period for a notional winter day (15th December), for a range of temperatures (-10 to +30 °C), to
480 assess the impact of the temperature dependence of chemical processes (alone) upon the
481 ambient NO_2/NO_x ratio. The results showed that the daytime and nighttime average primary
482 NO_2/NO_x ratios during the rush hour period (i.e., the period examined here for the cold starts)
483 varied by between 0.5% and 8.4%, with a mean relative change of 2.4%, due to the effect of
484 temperature-dependent chemical kinetics (see supplementary material Fig S4, S5). The model
485 results indicate that the observed increments in the inferred primary NO_2/NO_x ratio with low
486 temperatures, of 64.5% and 75%, are substantially larger than can be accounted for by the
487 temperature-dependence of the atmospheric photochemistry. We suggest therefore that
488 changed vehicle emissions with operating temperature are contributing towards the observed
489 difference in inferred NO_2/NO_x emission ratio with temperature. While the ambient data will
490 contain contributions from vehicles which have been operating for some time and hence are not
491 under “cold start” conditions, statistics on mode of transport from the UK DfT National Travel
492 Survey in 2016 indicate that 20% of all trips under 1 mile (1.6 km), were by car (either as driver
493 or passenger), increasing to 77% for trips between 1 and 5 miles (1.6 – 8 km) (DfT, 2017). For
494 urban journeys, distances tend to be shorter than these UK mean values suggest. Short urban
495 trip duration alongside the reduced efficiency or designed deactivation of emission control
496 systems at temperatures below 250 °C may contribute to the substantial increase in the inferred

497 primary NO₂/NO_x ratio, and hence reduced attainment of NO₂ air quality standards, under cold
498 weather conditions. Recent testing of vehicles in Germany conducted in 2016 found that over
499 half of ca. 50 vehicles tested had their EGR system inoperative under low ambient temperatures,
500 for engine protection purposes (BMVI, 2016). Such differences in the vehicle NO_x emissions
501 under low temperatures are observed in Euro 6 passenger cars (Suarez-Bertoa and Astorga,
502 2018). During regulated laboratory tests Suarez-Bertoa and Astorga (2018) observed that Euro 6
503 gasoline and diesel vehicles emitted two to more than three times more NO_x at pre-conditioned
504 initial engine temperatures of $-7\text{ }^{\circ}\text{C}$, compared to emissions at $23\text{ }^{\circ}\text{C}$. These results underline
505 the lower effectiveness in the performance of the after-treatment systems under the low initial
506 operating temperatures found in some real driving conditions. However, the relative
507 contribution of gasoline and diesel vehicles, or passenger cars vs light- and heavy-goods vehicles,
508 to the change in inferred primary NO₂/NO_x ratio cannot be readily determined from these data.
509 At intermediate temperatures ($5 - 15\text{ }^{\circ}\text{C}$) reduced changes in the inferred primary NO₂/NO_x ratio
510 were found (see Fig S2, S3 in supplementary material).

511 Fig 8 shows the relationship between inferred mean primary NO₂/NO_x ratio and mean
512 ambient temperature, for the cold months (November, December, January and February). The
513 primary NO₂/NO_x ratio is significantly negatively correlated with temperature ($R^2 = 0.54$),
514 according to the inverse relationship $f\text{NO}_2 = 15\% - [0.77 \pm 0.15] \times (T / ^{\circ}\text{C})$. Similar results to those
515 presented here were reported by Degraeuwe and Weiss (2017), who found that for on-road
516 tests, Euro 5 and Euro 6 cars emit four and three times higher NO_x at low ambient temperatures
517 than the legislative limits, respectively. For Euro 6 cars, similar results were reported by Kwon et
518 al. (2017), who compared NO_x emissions at lower ambient temperatures ($0 - 5\text{ }^{\circ}\text{C}$) with higher
519 ambient temperatures ($15 - 20\text{ }^{\circ}\text{C}$) and found a difference of $82 - 192\%$.

520 These literature results, along with the analysis presented here, support the finding that
521 higher vehicle emissions at lower ambient temperatures may have a measurable impact upon
522 ambient air quality. Vehicle emissions effects are likely exacerbated by meteorology during
523 wintertime (lower boundary layer height, and increasing tendency to stable conditions
524 (temperature inversions) during the worst pollution episodes and coldest weather); reduced
525 photolysis frequencies (shifting the NO_x PSS towards NO₂), and potentially greater vehicle use
526 during low temperature conditions in the UK, relative to other travel options.

527

528 4. Conclusions

529 This study presents an analysis of ambient NO_x and NO₂ mixing ratios, to derive inferred
530 NO₂/NO_x emission ratios from urban traffic monitoring stations in the UK, for the period from
531 2009 until 2016. The analysis showed:

- 532 • In keeping with other recent results, a decrease in the mean ambient NO₂ mixing ratio at
533 selected urban roadside measurement sites between 2009 and 2016, alongside a
534 smaller reduction in NO_x mixing ratios.
- 535 • Direct emissions are not measured in this work, and a number of assumptions are made
536 in deducing emitted NO_x ratios from ambient data for a finite number of measurement
537 stations. The mean inferred primary NO₂/NO_x ratio shows an overall reduction of 5
538 percentage points from 17.5% to 12.5%, with a calculated reduction of -0.32 percentage
539 points/year (95% confidence interval of -0.2 to -0.45 percentage points/year), over this
540 time period. The period of this reduction corresponds to the combined development of
541 policy (new Euro limits), changes in fleet composition and, to some extent, to the initial
542 penetration of new after-treatment technologies introduced in the last eight years.
543 However, this reduction is not evident in every location, underling the complexity of the
544 problem and implying that more stringent measures may be needed to further reduce
545 ambient NO₂ in urban environments, a challenge that will be heightened by increasing
546 vehicle numbers.
- 547 • Enhanced “cold-start” emissions, inferred from ambient monitoring data under low
548 temperature conditions. The results imply that the overall vehicle primary NO₂/NO_x
549 ratios increase on average by 64.5% and 75% for morning and evening rush hours under
550 cold (≤ 5 °C) conditions, compared with (for the UK) normal conditions (> 5 °C), while
551 this difference can be 1.6 - 3.8 times higher, when examining individual urban traffic
552 monitoring stations. An inverse relationship is found between ambient temperature and
553 primary NO₂/NO_x ratio.

554 These results suggest that the combination of (short duration) driving patterns and the
555 temperature dependence of the current after-treatment systems under low ambient
556 temperatures leads to measurable impacts upon ambient air quality. They also highlight the
557 importance of consideration of cold-start emissions within vehicle test cycles, as these may
558 cause a measurable deterioration in air quality in urban areas. Assessment of the related health

559 burden – which must integrate personal exposure considerations – should combine the impact
560 of meteorological factors on both vehicle performance, and public behaviour vs transport
561 choices.

562

563

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569

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TABLES

Region	Median 2009 primary NO ₂ /NO _x (%)	Median 2016 primary NO ₂ /NO _x (%)	Difference primary NO ₂ /NO _x (%)	Monthly trend with 95% confidence limits (%/year)
Aberdeen	19	10	-9	-1.33 (-1.52, -1.1) ***
Birmingham	20	10	-10	0.24 (-0.29, 0.78)
Cambridge	12	8	-4	-0.83 (-1.04, -0.6) ***
Carlisle	21.5	17	-4.5	-0.16 (-0.51, 0.18)
Chepstow	14	16	2	0.06 (-0.28, 0.34)
Exeter	18	15	-3	-0.45 (-0.75, -0.13) **
Leeds	16	13	-3	-0.17 (-0.5, 0.2)
Liverpool	21	19	-2	0.42 (-0.13, 1.01)
London	15	10	-5	-0.78 (-1.08, -0.38) **
Newcastle	11	10	-1	-0.5 (-1.26, 0.37)
Sandy	10	15	5	0.68 (0.39, 0.96) ***
Stanford le hope	20	17.5	-2.5	-1.79 (-2.45, -1.13) ***
Swansea	27	26.5	-0.5	0.16 (-0.12, 0.43)
York	8	15	7	-0.8 (-1.61, -0.06) *

Table 1. Median inferred primary NO₂/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 NO₂/NO_x values were acquired with a localised fitted regression model, while the monthly trend was calculated with a fitted linear regression model.

Region	Cold start primary NO ₂ emissions (%)		Primary NO ₂ emissions (%)		Relative increment (%)	
	Morning	Evening	Morning	Evening	Morning	Evening
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±0.2***	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
Sandy	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 NO₂/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).

FIGURES

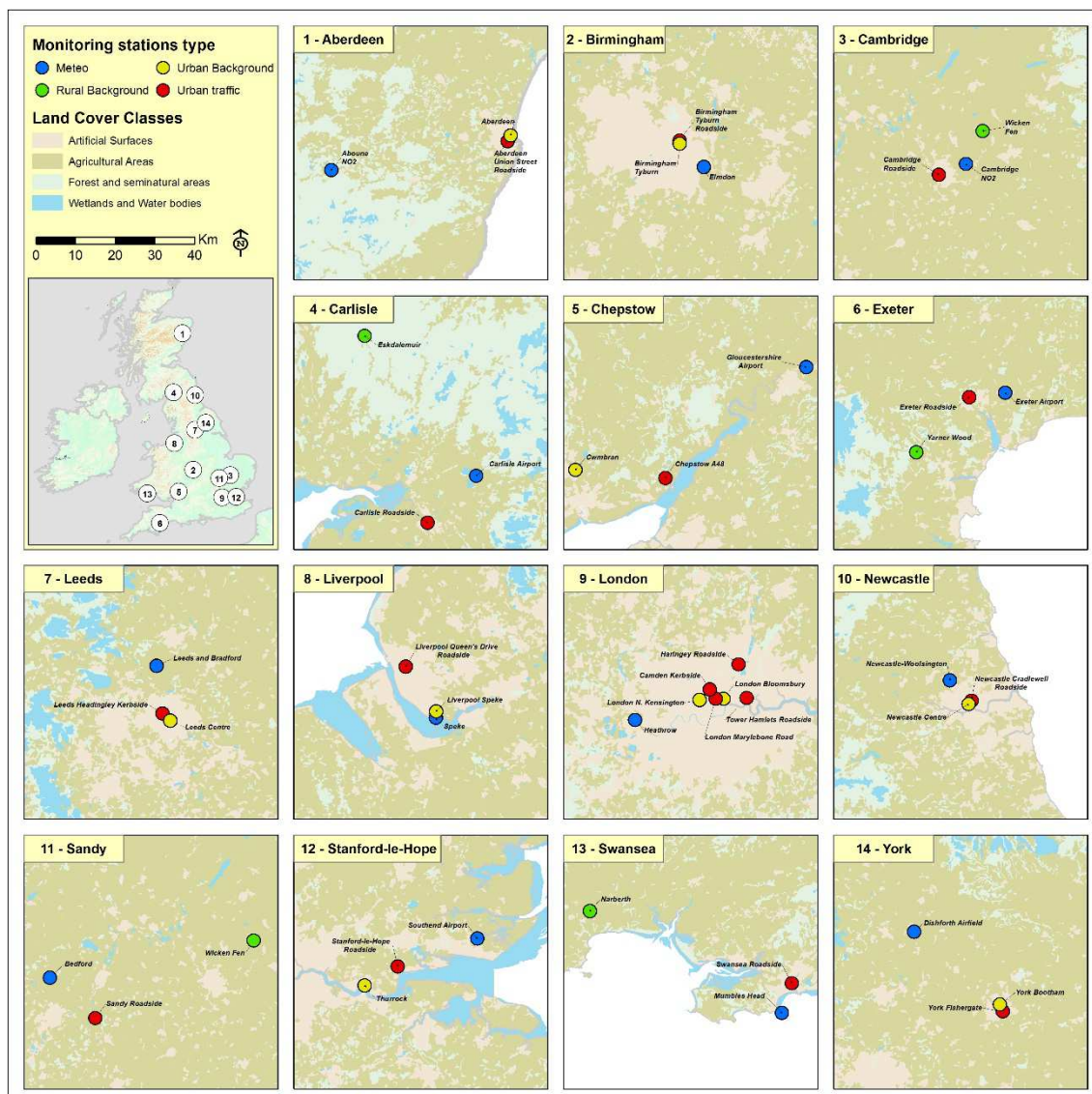


Fig 1. Monitoring sites used in this study. Blue indicates the meteorological stations, red the urban traffic sites, yellow the urban background and green the rural sites.

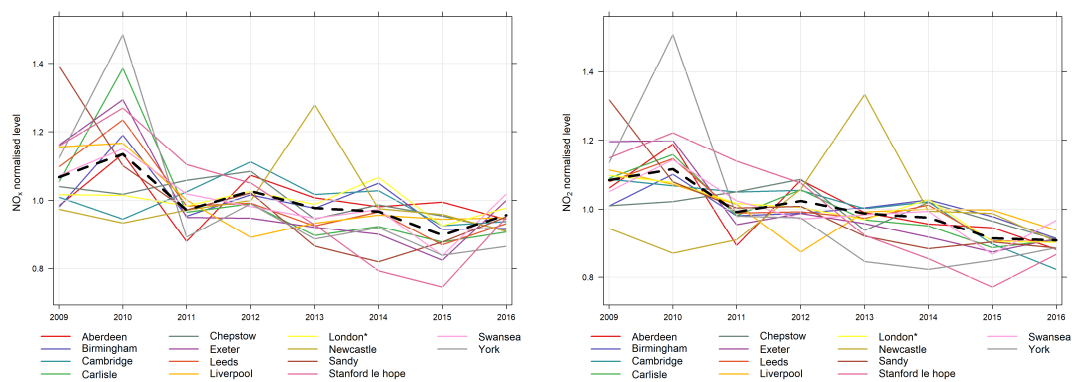


Fig 2. Annual average NO_x (left) and NO_2 (right) values for urban traffic stations in the UK normalized to their mean value. Black dashed line is the average from all sites used.

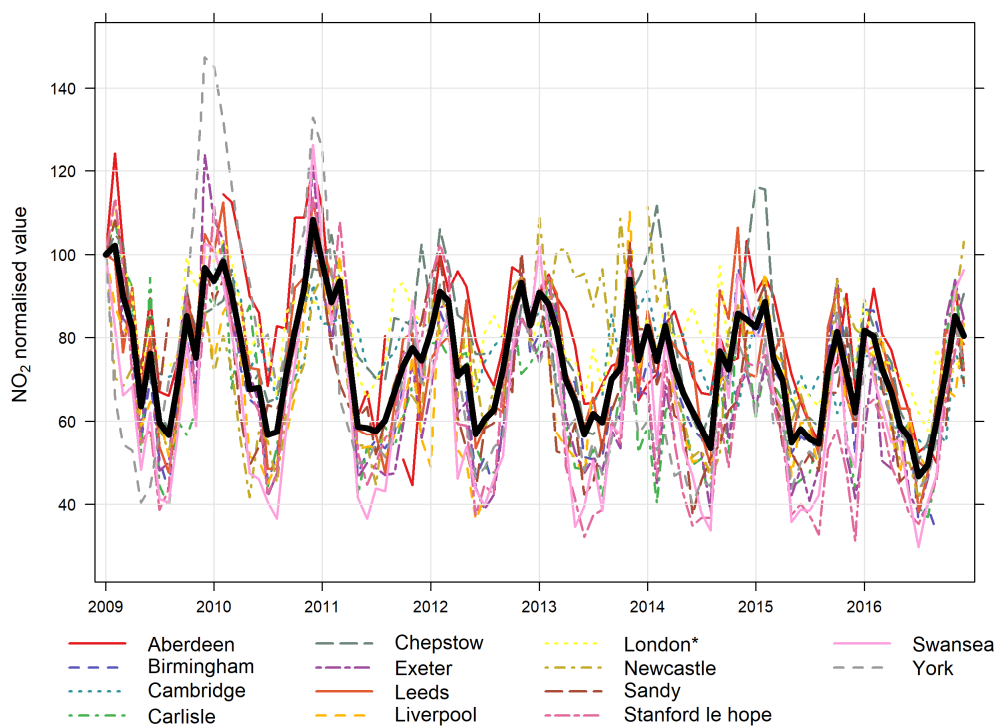


Fig 3. Monthly NO₂ mixing ratios during rush hour periods (06:00-10:00, 16:00-19:00), normalized to their 1/1/2009 value, for urban traffic monitoring sites across the UK. Black line indicates the mean value across all stations used.

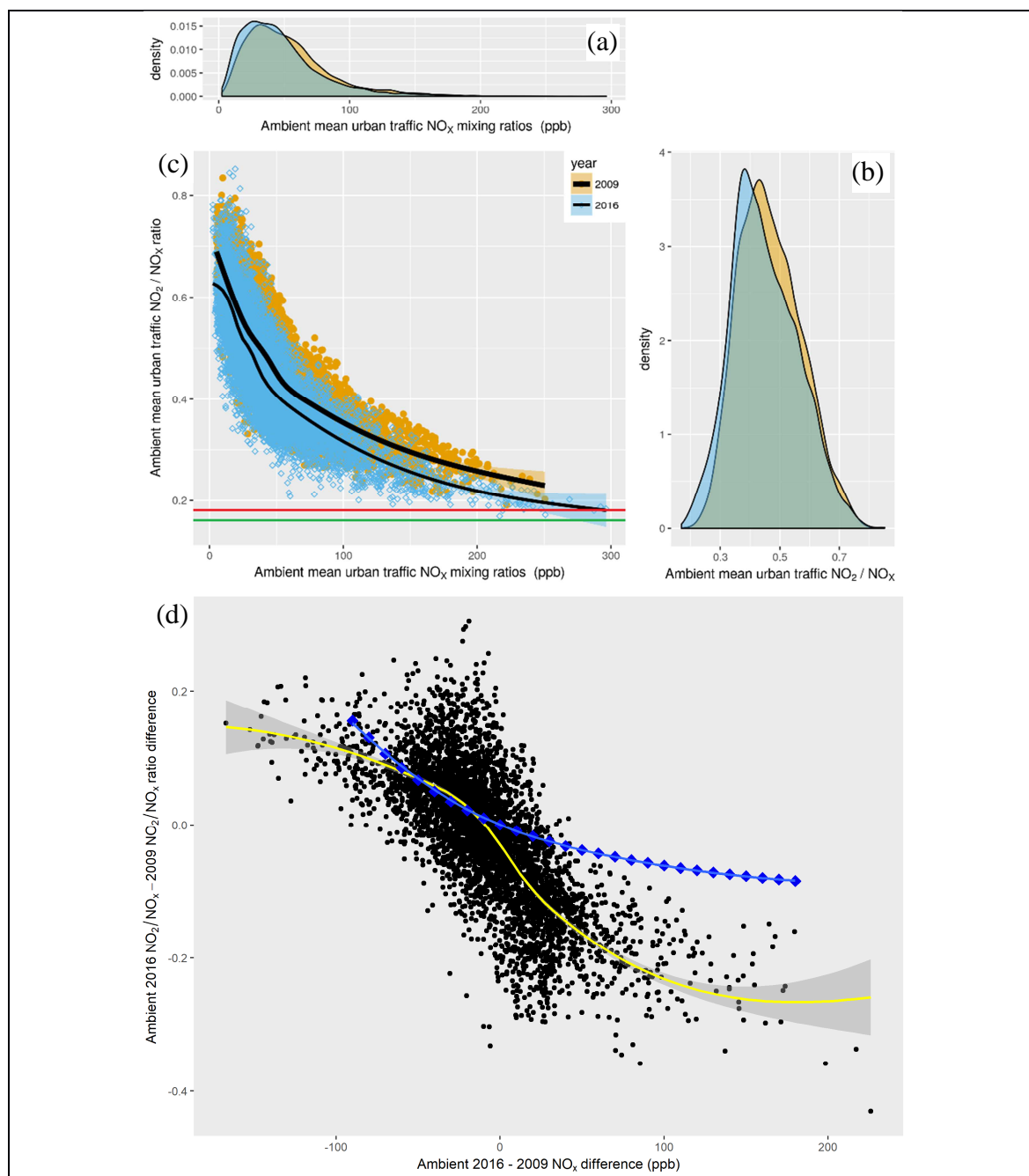


Fig 4. Daytime hourly mean ambient (a) NO_x and (b) NO_2/NO_x distributions for 2009 and 2016 from all urban traffic monitoring sites in the UK. (c) NO_2/NO_x ratio vs NO_x : the green (2016) and red (2009) lines indicate the baselines of the distributions and can be used to estimate the primary NO_2 (see text). (d) ambient NO_2/NO_x ratio as a function of the difference in NO_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_2/NO_x expected, for a change in overall NO_x abundance, on the basis of the $\text{NO}_x\text{-O}_3$ PSS chemistry alone (see text for details).

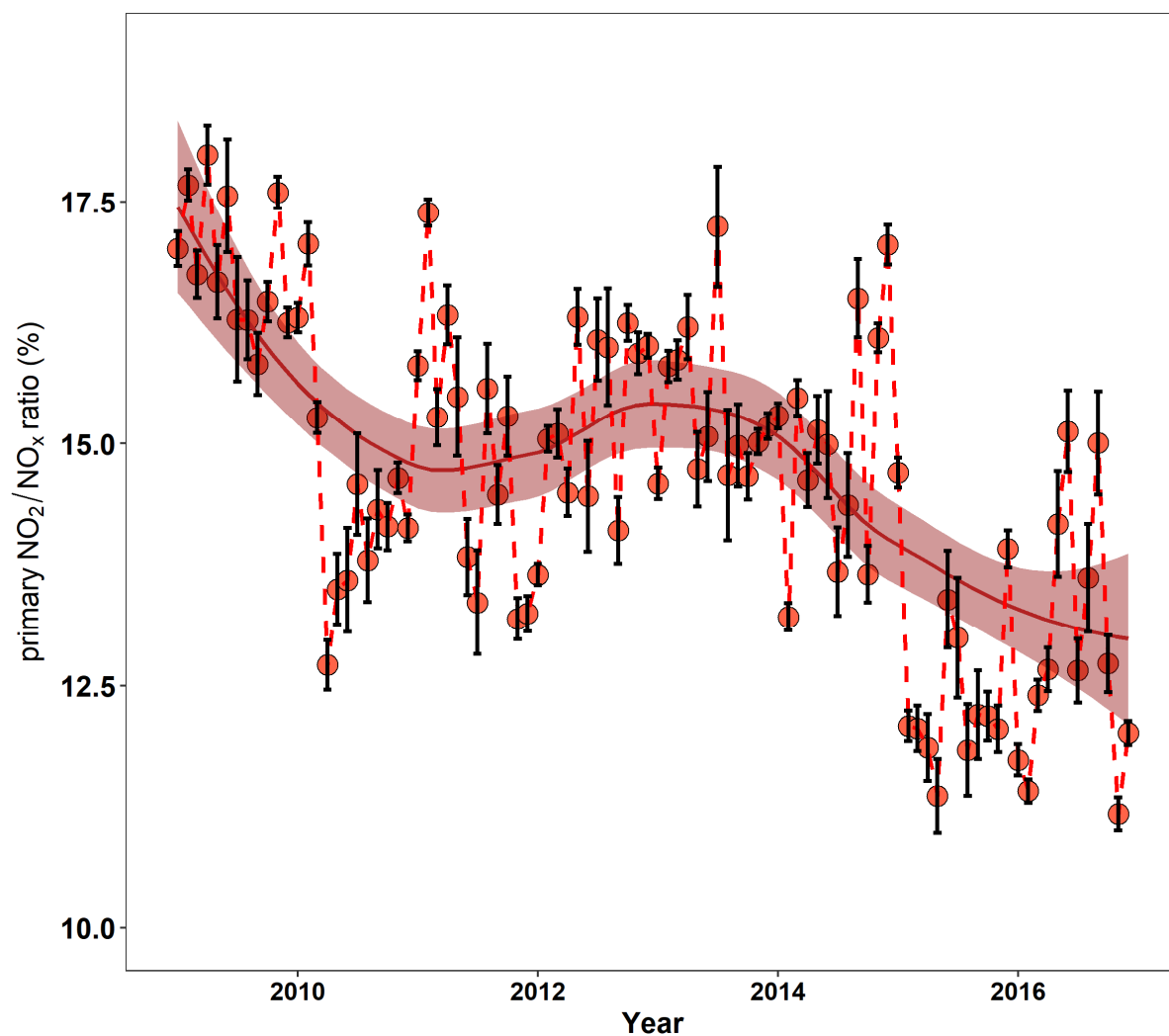


Fig 5. Mean overall trend of the inferred primary NO₂/NO_x ratio averaged over all UK urban traffic monitoring sites. The error bars indicate the standard error of the slope estimates. The local regression fitted line (red solid line) is weighted by taking into account the standard errors of the individual slopes. The shaded area indicates the 95% confidence intervals.

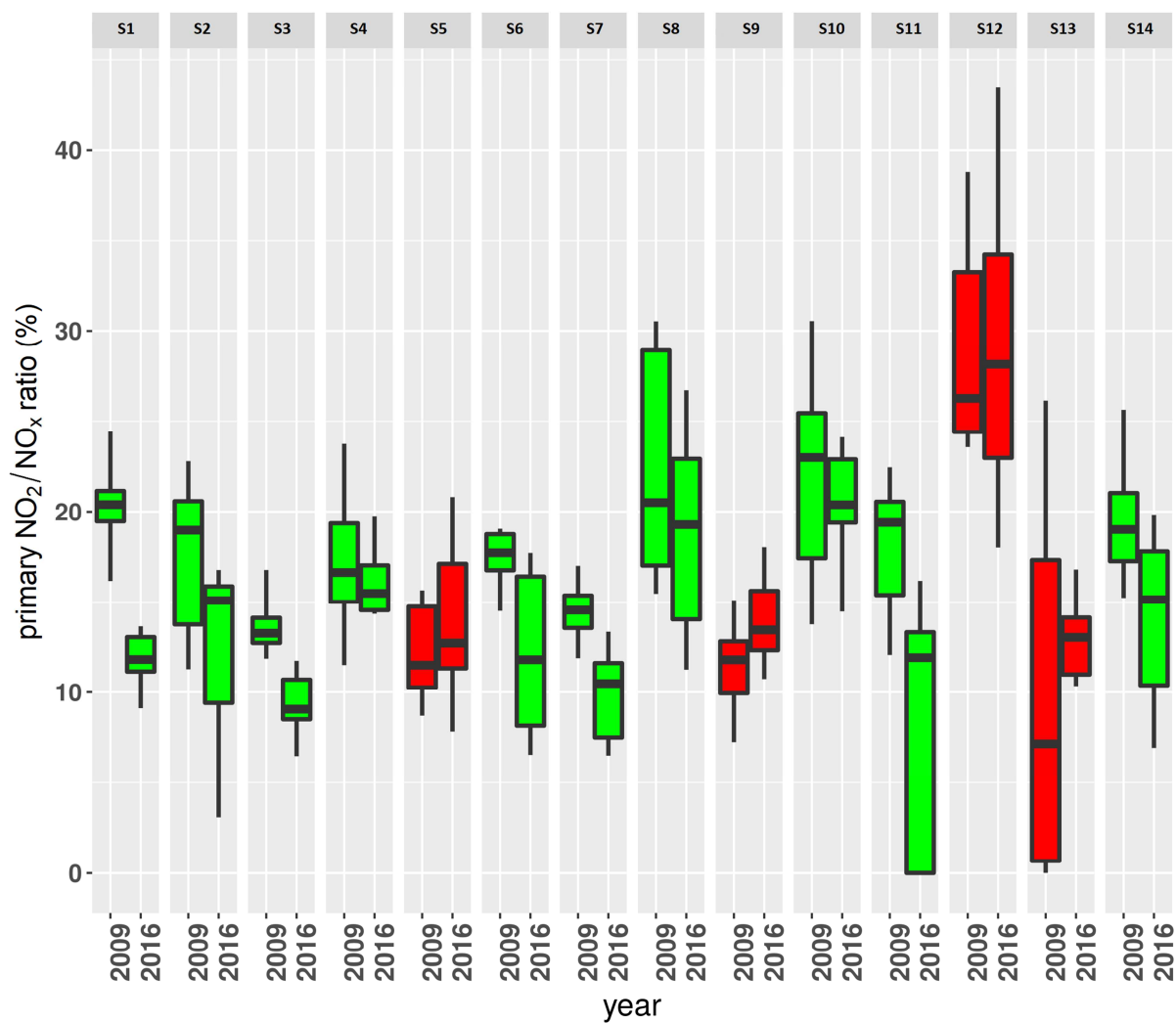


Fig 6. Box-whisker plots for the inferred primary NO₂/NO_x ratio for the individual urban traffic monitoring sites considered in this study, during 2009 and 2016. Green indicates a reduction in the median value between the two dates for each location, red an increase, between 2009 and 2016. S1: Aberdeen, 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.

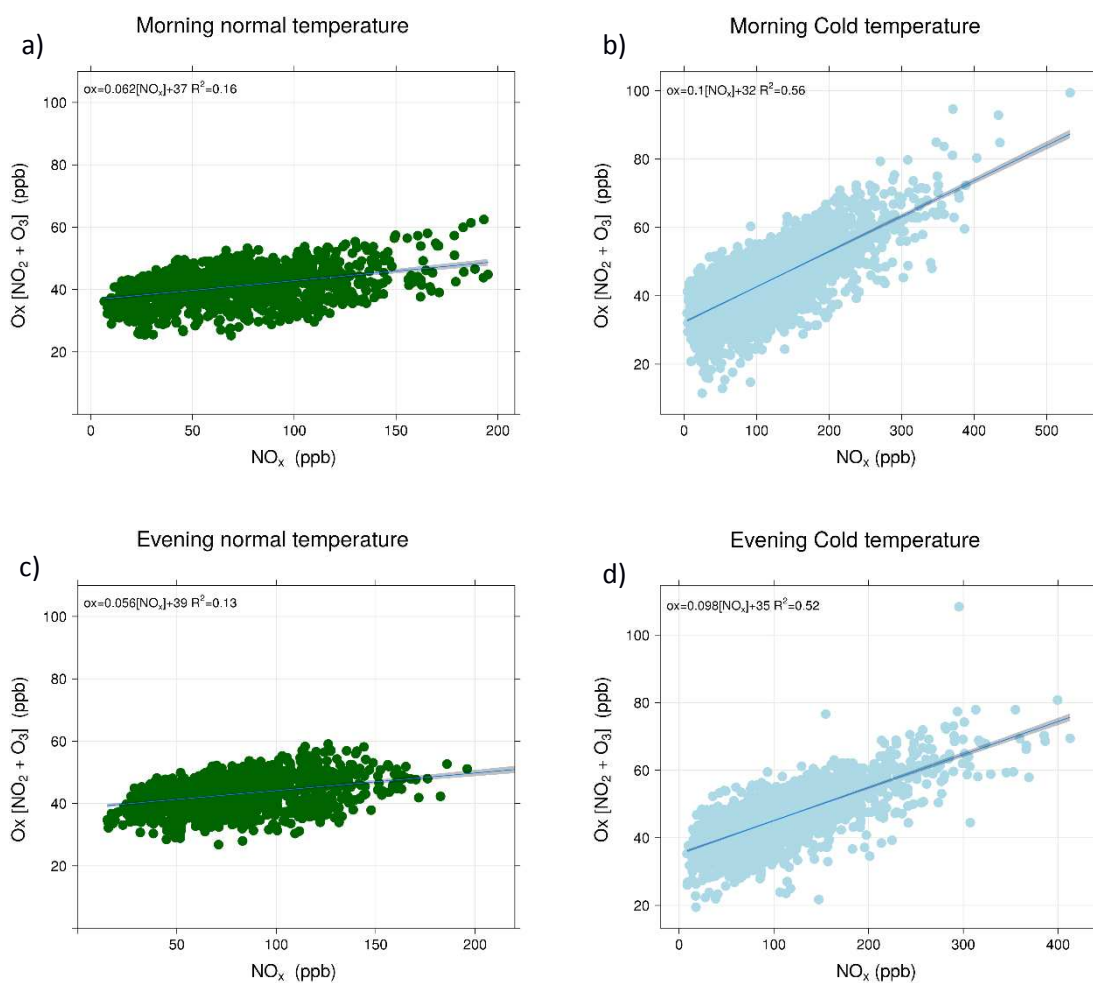


Fig 7. Ox -NO_x plots during normal winter morning and evening rush hours (Fig 7a, Fig 7c, green) and during cold ($T \leq 5$ °C) morning and evening rush hours (Fig 7b, Fig 7d, blue), representing normal and potential cold start emissions. The shaded areas indicate the 95% confidence intervals of the linear regression fit.

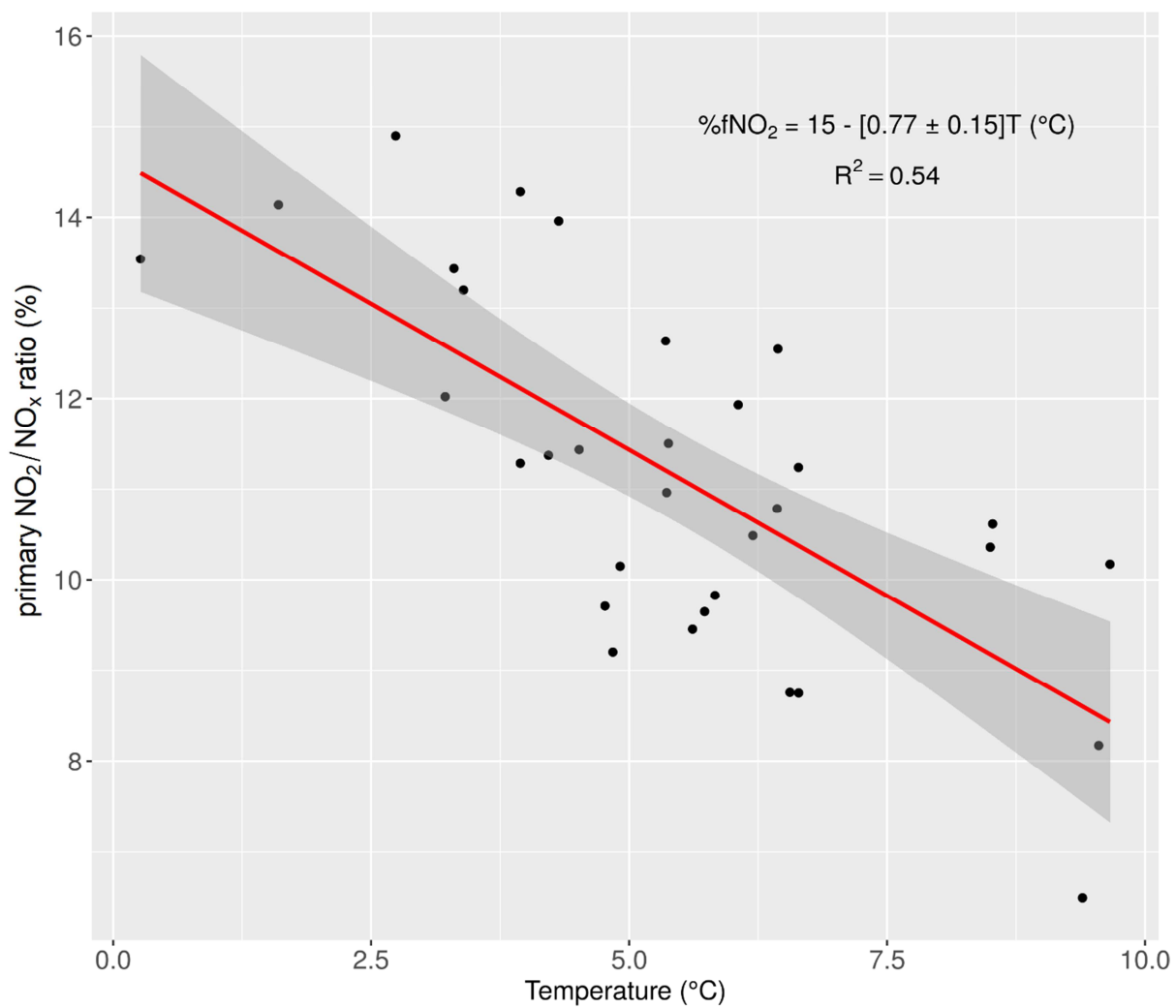


Fig 8. Inferred mean monthly primary NO₂/NO_xratio (%fNO₂) and its dependence on mean ambient temperature in the UK. The grey shaded areas indicate the 95% confidence intervals of the regression relationship.

Highlights

- A methodology is developed to assess enhanced “cold-start” primary NO₂ emissions from vehicles.
- Ambient mixing ratios of NO₂ and NO_x measured at selected UK urban traffic sites have fallen over the period from 2009-2016.
- Overall inferred primary NO₂/NO_x ratio experiences a statistically significant decrease from 17.5% to 12.5% between 2009 and 2016.
- Inferred cold-start morning and evening primary NO₂ vehicle emissions are significantly higher than those found under warmer conditions
- Inferred cold-start primary NO₂ vehicle emissions have measurable impacts upon urban air quality in the UK.