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# Lower vehicular primary emissions of NO<sub>2</sub> in Europe than assumed in policy projections

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Many European countries do not currently meet legal air quality standards for ambient nitrogen dioxide (NO<sub>2</sub>) near roads; a problem that has been forecast to persist to 2030. Whereas European air quality standards regulate NO<sub>2</sub> concentrations, emissions standards for new vehicles instead set limits for NO<sub>x</sub> – the combination of nitric oxide (NO) and NO<sub>2</sub>. From around 1990 onwards, total emissions of NO<sub>x</sub> declined significantly in Europe, but roadside concentrations of NO<sub>2</sub> – a regulated species – declined much less than expected. This discrepancy has been attributed largely to the increasing usage of diesel vehicles in Europe and more directly-emitted tailpipe NO<sub>2</sub>. Here we apply a data filtering technique to 130 million hourly measurements of NO<sub>x</sub>, NO<sub>2</sub> and ozone (O<sub>3</sub>) from roadside monitoring stations across 61 urban areas in Europe

over the period 1990 to 2015 to estimate the continent-wide trends of directly emitted  $\text{NO}_2$ . We find that the ratio of  $\text{NO}_2$  to  $\text{NO}_x$  emissions increased from 1995 to around 2010 but has since stabilised at a level that is substantially lower than is assumed in some key emissions inventories. The proportion of  $\text{NO}_x$  now being emitted directly from road transport as  $\text{NO}_2$  is up to a factor of two smaller than the estimates used in policy projections. We therefore conclude that there may be a faster attainment of roadside  $\text{NO}_2$  air quality standards across Europe than is currently expected.

1 Since the mid-1990s the European vehicle fleet has undergone considerable diesellisation<sup>1-4</sup>  
2 with incentivisation over other fuels and technologies on the basis of predicted fuel effi-  
3 ciency, lower  $\text{CO}_2$  emissions, and increased driving performance.<sup>5-7</sup> By 2014 diesel vehicles  
4 accounted for an average of 53 % of new European passenger vehicle sales compared to  
5 14 % in 1990, in contrast to little increase in their adoption into US fleets.<sup>3,4</sup> The pro-  
6 portion of diesel powered vehicles across Europe has contributed to widely published  
7 problems where legal ambient air quality standards are breached, usually near roads. Of  
8 particular concern in recent years is nitrogen dioxide ( $\text{NO}_2$ ) although particulate matter  
9 (PM) is also important.<sup>8</sup> Many European Union (EU) member states are struggling to  
10 comply with the 2008/50/EC Air Quality Directive which sets legal limits for hourly and  
11 annual average  $\text{NO}_2$  concentrations.<sup>8-10</sup> While total national emissions of  $\text{NO}_x$  ( $\text{NO} +$   
12  $\text{NO}_2$ ) have shown reductions in Europe, urban concentrations of  $\text{NO}_2$  have decreased less  
13 than expected and this has been attributed to the growth in diesel fuelled vehicles.<sup>11-19</sup>

14 The impacts on public health of  $\text{NO}_2$  are significant both through direct harm on  
15 inhalation and as a precursor to secondary pollutants ozone ( $\text{O}_3$ ) and PM.<sup>20</sup> Published  
16 estimates of premature deaths due to  $\text{NO}_2$  in 28 EU countries were reported to be 72 000

17 annually, based on a 2012 analysis year.<sup>21</sup> Roadside locations are perhaps the most im-  
18 portant places where NO<sub>2</sub> must be controlled because this is where human exposure is  
19 at its highest. These are challenging locations from a legal compliance perspective — of  
20 all the reported exceedances of EU hourly and annual limit values in 2016, 94 % of those  
21 occurred at roadside monitoring locations.<sup>22</sup>

22 NO<sub>2</sub> concentrations at roadside locations are primarily controlled by local road trans-  
23 port and are influenced by, firstly, the total amount of NO<sub>x</sub> emitted and then the fraction  
24 of that NO<sub>x</sub> that is directly emitted as NO<sub>2</sub>.<sup>23</sup> A shift towards higher NO<sub>2</sub>/NO<sub>x</sub> emissions  
25 from road transport can lead to a counter intuitive situation where total NO<sub>x</sub> emissions  
26 can fall over time, yet roadside concentrations of NO<sub>2</sub> do not decline. The influence of  
27 this key ratio in driving trends and forecasts has already been shown in central London.<sup>16</sup>  
28 Predictions of future NO<sub>2</sub> concentrations in Europe must make assumptions about this  
29 NO<sub>2</sub>/NO<sub>x</sub> ratio, and predicted increases in this ratio are in part, behind a predicted lack  
30 of air quality standard attainment in many cities until 2025–2030.<sup>15</sup> Despite the critical  
31 importance of the NO<sub>2</sub>/NO<sub>x</sub> ratio in controlling urban roadside concentrations, specific  
32 limits do not exist as part of European vehicular emission standards tests. New European  
33 vehicle tests report only total NO<sub>x</sub> (NO + NO<sub>2</sub>) in exhaust gases and whilst emission stan-  
34 dards set limits for total NO<sub>x</sub> they do not speciate between NO and NO<sub>2</sub>. Beyond initial  
35 new vehicle tests little is known about how technologies such as diesel oxidation catalysts  
36 (DOC) and diesel particulate filters (DPF) influence this ratio in the real-world, despite  
37 the high profile given to the topic since the Volkswagen (VW) emissions scandal.<sup>7,24</sup> The  
38 implications of not correctly estimating NO<sub>2</sub>/NO<sub>x</sub> ratios in policy support tools such as  
39 COPERT and HBEFA have been described by others.<sup>25–28</sup>

40 Although recent NO<sub>x</sub> emission underestimates from passenger cars have received most

41 media attention, other vehicles such as heavy duty vehicles (HDVs) and buses are also  
42 important in controlling roadside NO<sub>2</sub> because they are predominately diesel fuelled. In  
43 this study, which focuses on NO<sub>2</sub> trends in urban areas, it is expected that light duty  
44 vehicles (LDVs) and urban buses will make significant contributions to vehicle emissions.  
45 It should also be noted that in terms of emissions data availability there is considerably  
46 more information available on passenger cars compared with other types of vehicles. As a  
47 consequence, there is uncertainty in both the absolute and relative contributions to NO<sub>x</sub>  
48 and NO<sub>2</sub> from these additional transport sources.

49 The NO<sub>2</sub>/NO<sub>x</sub> ratio from diesel vehicles is controlled by both engine and exhaust  
50 control technologies that have advanced in response to the ‘Euro’ series of emissions stan-  
51 dards. The introduction of Euro 3 in 2000 saw the introduction of DOC into passenger  
52 vehicles; where in the presence of excess oxygen, NO can be oxidised to NO<sub>2</sub> over DOC  
53 metal catalysts resulting in more direct NO<sub>2</sub> being emitted.<sup>16,29,30</sup> The introduction of  
54 DPF in 2009 for compliance with the Euro 5 emission standards introduced a further  
55 technology that could lead to additional direct tailpipe NO<sub>2</sub>.<sup>31</sup> However, as each pro-  
56 gressive Euro standard has been introduced there have been no systemic observations of  
57 how new exhaust technologies might affect the NO<sub>2</sub>/NO<sub>x</sub> ratio in real world emissions,  
58 or evaluation of whether the emissions inventories that need this ratio for forecasts, and  
59 that unpin policy, are performing well.

## 60 **Ambient observations to determine the NO<sub>2</sub>/NO<sub>x</sub> trend**

61 Using the measured roadside atmospheric ratio of NO<sub>2</sub> to NO<sub>x</sub> (NO<sub>2</sub>/NO<sub>x</sub> ratio, expressed  
62 as a molar volume ratio) is one effective way of determining the influence on NO<sub>2</sub> of in-  
63 creased proportions of diesel vehicles in a fleet, as well as a method to detect change in

64 after treatment technologies resulting from progressive tightening of the Euro standards.  
65 Since there is no systematic set of vehicle exhaust measurements that show  $\text{NO}_2/\text{NO}_x$   
66 trends we look instead at the combined national data sets of ambient monitoring infor-  
67 mation which measure NO and  $\text{NO}_2$  in air. We carefully filter these datasets for roadside  
68 locations where the ratio of these two species can be taken as a proxy for the exhaust  
69 emission ratio. We note that there is considerable diversity in the penetration and uptake  
70 of diesel vehicles, typical vehicle lifespans, and climates when considering Europe as a  
71 whole. The analysis in this section uses data from roadside monitoring sites across 61  
72 European urban areas between 1990 and 2015. The combined European trend (Fig. 1)  
73 for the 61 areas demonstrates a clear increase in annual mean  $\text{NO}_2/\text{NO}_x$  ratio between  
74 1995 and 2010. The aggregation was performed on the mean for each city in each year to  
75 ensure the results were not biased towards cities with more measurement locations, such  
76 as London.

77 Figure 1 shows three distinct periods where  $\text{NO}_2/\text{NO}_x$  ratio behaviour differed. The  
78 first, from 1990 to 1994 coincides with a pre-Euro 3 fleet that did not use diesel oxidation  
79 catalysts (DOCs) and the ratio was stable within the uncertainty of the slope estimate  
80 and less than 10 % (Supplementary Table 2). The second period from 1995 to 2008 is a  
81 period where there was a clear, sustained, and significant increase in the  $\text{NO}_2/\text{NO}_x$  ratio  
82 corresponding to a period of growth in diesel passenger cars numbers and the introduction  
83 of DOC to new vehicles via Euro 3 and Euro 4. Over this period the ratio increased to a  
84 peak value of approximately 16 % in 2010. The third period is characterized by a stabili-  
85 sation in the  $\text{NO}_2/\text{NO}_x$  ratio and coincides with the introduction of Euro 5 vehicles fitted  
86 with diesel particle filters (DPFs). The second period is the only period that shows a  
87 statistically significant change  $\text{NO}_2/\text{NO}_x$  ratio. The trends shown in Fig. 1 broadly follow

88 the pattern of reported changes in emissions seen from sporadic remote sensing measure-  
89 ments of almost 70 000 vehicles in London (during 2012), with a progressive increase in  
90  $\text{NO}_2/\text{NO}_x$  ratio for diesel passenger cars and light vans from pre-Euro to Euro 5.<sup>32</sup>

91 Although the ambient derived  $\text{NO}_2/\text{NO}_x$  ratio turning points in Fig. 1 broadly coincide  
92 with identifiable regulatory landmarks, the changes are more complex than they would  
93 first appear. First, when a new Euro class is introduced, it takes time for those new  
94 vehicles to significantly penetrate the vehicle fleet and affect overall emissions. Second,  
95 the emissions characteristics of vehicles will be expected to change as they age. For  
96 example, a Euro 3 car introduced in year 2000 will be  $\approx 5$ –6 years old at the end of the  
97 Euro 3 period. Analysis of vehicle emission remote sensing data has shown that vehicle  
98 ageing tends to decrease the  $\text{NO}_2/\text{NO}_x$  ratio of diesel passenger cars (and likely other  
99 types of vehicles fitted with DOC).<sup>16,33</sup> All these influences, as well as other local effects,  
100 contribute to the overall pattern seen in Fig. 1. Nevertheless, it is clear that on average,  
101 across Europe, the ratio has not continued to increase after 2010 and is now declining.

102 At an European level, mean annual roadside  $\text{NO}_x$  concentrations demonstrated an  
103 overall decrease from 1998 to 2015 with mean  $\text{NO}_x$  concentrations reducing from 338 to  
104  $228 \mu\text{g m}^{-3}$  (Fig. 2). Before 1998, the  $\text{NO}_x$  means are scattered due to fewer sites and  
105 observations and larger uncertainties concerning the quality of the measurements. This  
106 decrease can be attributed to improved vehicular  $\text{NO}_x$  emission control during this period.  
107 Fig. 2 shows that mean  $\text{NO}_x$  concentrations have remained stable since 2010, however,  
108 the trend in  $\text{NO}_2$  concentrations (the regulated species of  $\text{NO}_x$ ) differs from total  $\text{NO}_x$  in  
109 several important ways. First,  $\text{NO}_2$  concentrations tended to increase over the period from  
110 around 1997 to 2009 (despite concentrations of  $\text{NO}_x$  decreasing). Second, concentrations  
111 of  $\text{NO}_2$  have tended to decrease from around 2009 at a time when concentrations of

112 NO<sub>x</sub> have been stable. These changes in concentrations are consistent with the changes  
113 calculated for the NO<sub>2</sub>/NO<sub>x</sub> ratio, shown in Fig. 1.

## 114 **Spatial analysis of roadside NO<sub>2</sub>/NO<sub>x</sub> over Europe**

115 The Europe-wide aggregation displayed in Fig. 1 hides the diversity of trends in the  
116 NO<sub>2</sub>/NO<sub>x</sub> ratio across European roadside monitoring sites, urban areas, and countries.  
117 When estimates of the NO<sub>2</sub>/NO<sub>x</sub> ratio were aggregated at an urban level, a peak ratio  
118 was observed at or near 2010 in most European urban areas (Fig. 3). The trends in  
119 NO<sub>2</sub>/NO<sub>x</sub> ratio are shown for two periods 2005 to 2010 and 2010 to 2015. Over the first  
120 period most urban areas showed an increase in NO<sub>2</sub>/NO<sub>x</sub>, most pronounced in western  
121 and central Europe. For the later period the majority of regions showed a declining trend  
122 in NO<sub>2</sub>/NO<sub>x</sub> albeit generally smaller than the earlier increases.

123 Seven percent of the urban areas however showed opposing trends most likely reflect-  
124 ing unique and localised site or urban area conditions. Some of these urban areas includ-  
125 ing Amsterdam (Netherlands), Barcelona (Spain), Milan (Italy), and Krakow (Poland)  
126 demonstrate a levelling-off of the NO<sub>2</sub>/NO<sub>x</sub> ratio but had not shown decreasing trends  
127 by 2015. Other urban areas such as Dublin (Ireland which had the largest delta), Rotter-  
128 dam (Netherlands), some urban areas in central United Kingdom, and Helsinki (Finland)  
129 showed further increases in NO<sub>2</sub>/NO<sub>x</sub> by 2015. Some urban areas, most conspicuously  
130 in Reykjavík (Iceland), are not shown in the 2010–2015 panel (b) in Fig. 3. This was  
131 due to the absence of more-recent observations, usually due to O<sub>3</sub> or NO<sub>x</sub> monitoring site  
132 closures or when the EU member state stopped reporting NO<sub>x</sub> and NO alongside NO<sub>2</sub>. It  
133 is very difficult to attempt attribute the underlying causes of the 7 % outliers; it may be  
134 associated with fleet makeup or indeed other local factors such as changing road layouts,

135 new sources and urban infrastructure. In the absence of consistent information across  
136 Europe on these factors we do not speculate further.

137 The overwhelming consistency seen in the 93 % of urban areas and across the whole  
138 of the continent is however strongly suggestive of a European-scale influence on primary  
139  $\text{NO}_2$ , not that this change in  $\text{NO}_2/\text{NO}_x$  is a result of a series of uncoordinated local factors.  
140 These changes are consistent with a steady evolution of the European fleet as a whole, for  
141 example, the effect of Euro standards and technologies, rather than trends driven by city  
142 or country specific interventions such as changes to local urban public transport fleets,  
143 introduction of congestion zones, and so on.

#### 144 **Potential factors controlling recent declines in $\text{NO}_2/\text{NO}_x$**

145 Whilst the periods of increase in the  $\text{NO}_2/\text{NO}_x$  ratio can be rationalised based on previous  
146 evidence, the recent declines in ratio from around 2010 are more difficult to understand  
147 because diesel vehicles continue to use DOC with DPF. We raise here some potential  
148 factors that could explain this result. Remote sensing measurement of selected vehicles  
149 has showed that selective catalytic reduction (SCR) control systems introduced on heavy  
150 duty vehicles have improved, resulting in both lower overall emissions of  $\text{NO}_x$  and a better  
151 control of  $\text{NO}_2$ .<sup>16</sup> Although the numbers of heavy duty vehicles passing each monitor is  
152 unknown across Europe, this technology working on part of the fleet may have contributed  
153 to the ratio declining. A second potential factor is the ageing of exhaust control systems  
154 themselves, and an engineering shift towards ‘catalytic thriftiness’. This refers to vehicle  
155 manufacturers and catalyst developers progressively reducing the amount of platinum  
156 group metals used in exhaust systems which in turn has a consequence of reducing the  
157 amount of  $\text{NO}_2$  generated. Finally, evidence from vehicle emission remote sensing shows

158 that as light duty diesel vehicles age, the  $\text{NO}_2/\text{NO}_x$  ratio does decrease over time although  
159 the extent of this is uncertain.<sup>16</sup> It would seem plausible that all of these poorly understood  
160 factors could, in combination, contribute to the stabilisation and decline seen in  $\text{NO}_2/\text{NO}_x$   
161 ratio since 2010. However, with ambient data alone, it is impossible to quantify the  
162 individual contributions robustly.

## 163 **Comparisons to emissions inventories**

164 The Europe-wide primary  $\text{NO}_2/\text{NO}_x$  estimated by the observational filtering method here  
165 differs substantially from previous works which report roadside  $\text{NO}_2/\text{NO}_x$  ratio trends.  
166 Other inventories estimate higher  $\text{NO}_2/\text{NO}_x$  than what we see in the real world. A  
167 modelled estimate of traffic emissions at a national and European level in five year intervals  
168 between 2000 and 2030<sup>15</sup> predicted  $\text{NO}_2/\text{NO}_x$  to increase  $\approx 25\%$  by 2020 and stay at this  
169 level until 2030 (Fig. 4). Using these model estimates of  $\text{NO}_2/\text{NO}_x$  around 30 monitoring  
170 areas were then forecast to still be in breach of the European  $\text{NO}_2$  air quality standard in  
171 2030. The current United Kingdom (UK) vehicular primary  $\text{NO}_2$  emission factors are also  
172 predicted up to 2030 in the National Atmospheric Emissions Inventory (NAEI).<sup>34</sup> The UK  
173 emission factors are derived from the COPERT database with modelling of predicted fleet  
174 changes in the future. The UK primary  $\text{NO}_2$  emission factors for all UK urban areas are  
175 currently predicted to reach a peak  $\text{NO}_2/\text{NO}_x$  ratio in 2015 at 23% (Fig. 4). After 2015,  
176 the UK emission factors decrease until 2030 to a minimum ratio of 17%.

177 Both emission estimates appear to substantially overstate the current fraction of emis-  
178 sions that is directly released as  $\text{NO}_2$ , in one case by nearly a factor two for the year 2015,  
179 and the measured vs. modelled trends are currently diverging further from one another.  
180 If primary  $\text{NO}_2$  emissions remain similar or even further decreases as the current analysis

181 suggests, the use of these inventory estimates for air quality modelling purposes would  
182 result in overly pessimistic future predictions of compliance with European NO<sub>2</sub> ambient  
183 air quality standards.

## 184 **Impact on the attainment of air quality standards**

185 Policy projections of air quality that use too high a value for the NO<sub>2</sub>/NO<sub>x</sub> ratio will  
186 predict higher concentrations of roadside NO<sub>2</sub> than may actually occur for the same  
187 total amount of NO<sub>x</sub> emitted. As an example of the potential changes brought about  
188 by using different NO<sub>2</sub>/NO<sub>x</sub> ratios, we compare how ambient concentrations would vary  
189 based on the current range of estimates. The most recent ratio reported here by the  
190 filtering method was 14.5 % in 2015 while the other reported estimates ranged from 25  
191 to 22 % (Fig. 4). To estimate the influence of differing primary NO<sub>2</sub> assumptions on  
192 roadside annual mean NO<sub>2</sub> concentrations, we have considered the roadside increment of  
193 NO<sub>x</sub> concentration at each measurement site *i.e.* the increment in NO<sub>x</sub> concentration  
194 above urban background values of NO<sub>2</sub>. Two scenarios have been considered: first, that  
195 the roadside NO<sub>x</sub> increment is associated with a NO<sub>2</sub>/NO<sub>x</sub> ratio of 14.5 % and second,  
196 that it is associated with a ratio of 23 %. Considering all European roadside sites, the  
197 mean difference in NO<sub>2</sub> concentration between these two scenarios is 6.6 μg m<sup>-3</sup>. The  
198 current analysis, which applies data filtering techniques, is not strictly consistent with  
199 the changes expected to annual mean NO<sub>2</sub> concentrations because only a subset of data  
200 have been analysed. However, the changes in the NO<sub>2</sub>/NO<sub>x</sub> ratio identified will have a  
201 strong influence on annual mean NO<sub>2</sub> concentrations close to roads.

202 The impact of differing primary NO<sub>2</sub> assumptions will clearly vary depending on indi-  
203 vidual sites. However, for the most polluted NO<sub>2</sub> sites in Europe, examples being Brixton

204 Road and Farringdon Street in London, the annual mean difference in NO<sub>2</sub> from the traffic  
205 contribution could be as much as 19 µg m<sup>-3</sup>. Differences in projected NO<sub>2</sub> of this kind of  
206 magnitude are highly significant when compared against targets for compliance with the  
207 European annual NO<sub>2</sub> ambient standard which is currently 40 µg m<sup>-3</sup>. In this respect, cur-  
208 rent air quality modelling of roadside NO<sub>2</sub> that uses these unrealistically high NO<sub>2</sub>/NO<sub>x</sub>  
209 ratios for the future will tend to also be overly pessimistic. Should NO<sub>2</sub>/NO<sub>x</sub> ratios of  
210 the kind now being observed across Europe be projected forward for the next decade then  
211 attainment of annual roadside NO<sub>2</sub> standards in many places might be achieved sooner  
212 than is currently predicted.

213 We note however the substantial disconnections that still exist between the legislative  
214 controls being placed on reporting vehicle emissions and air quality standards designed  
215 to protect public health. By only requiring the reporting of total NO<sub>x</sub> from new vehicles,  
216 and not NO and NO<sub>2</sub> as separate quantities, the later impacts of those vehicles, and how  
217 they influence the regulate pollutant NO<sub>2</sub>, cannot be assessed. The continued lack of any  
218 systematic collection of information on changes to NO and NO<sub>2</sub> emissions as vehicles age  
219 is a further gap in evidence that if filled would greatly improve the reliability of future  
220 forecasts of air quality in cities.

## 221 **Methods**

### 222 **Data**

223 The primary data sources for the air quality data used in this study were the European  
224 Environment Agency (EEA) AirBase and air quality e-Reporting (AQER) data repos-  
225 itories.<sup>35,36</sup> These two repositories cover all European Union (EU) member states and  
226 other cooperating countries such as those in the European Economic Area (EEA) and  
227 Switzerland. The AirBase repository contains observational data during 1969–2012 but  
228 from 2013 onwards, the AirBase system was superseded with the more comprehensive  
229 AQER reporting system. AQER uses new data vocabulary, file formats, and requires  
230 EEA member states to report a range of observational units called “data flows” which  
231 were not required for AirBase. The AQER system uses the XML (Extensible Markup  
232 Language) file format to transfer data but it is common for other file formats to be used  
233 alongside XML for some data flows.

234 The AirBase and AQER data were cleaned and inserted into a single database with  
235 a simple data model.<sup>37</sup> The AirBase data are available in well-formatted tabular text  
236 files which only required decoding of their file names to be used. However, the AQER  
237 XML documents were a far greater challenge due to the need to parse different obser-  
238 vational units to create a coherent and decoded data model. Despite AQER formalising  
239 XML schemas, many variations were found across the member states’ files which required  
240 significant development to ensure that the variations were handled correctly.

241 The database was also supplemented with other data where available. London for  
242 example, has a much larger air quality monitoring network which is not represented by  
243 AirBase and the AQER repositories because these monitoring activities are coordinated

244 by other bodies and do not form part of the national network. Therefore, these additional  
245 sites and data were accessed using **openair**, which accesses data from King’s College Lon-  
246 don.<sup>38,39</sup> These additional sites follow equivalent quality assurance and quality procedures  
247 as the national network. Many countries have not reported the full complement of NO,  
248 NO<sub>2</sub>, and NO<sub>x</sub> presumably due to a lack of a legal obligation and file size concerns. The  
249 analysis reported here required both hourly NO<sub>2</sub> and NO<sub>x</sub> to be present for a monitor-  
250 ing site and therefore the missing variables were derived from the other components if  
251 possible. In the case of Paris, the additional NO<sub>x</sub> was accessed through the Airparif web  
252 portal.<sup>40</sup> Once the cleaning and tidying was complete, the database contained  $2.7 \times 10^9$   
253 observations from 8 400 air quality monitoring sites.<sup>37,41</sup>

254 The data import, transformation, and tidying was conducted with R and the database  
255 technology used was PostgreSQL.<sup>42,43</sup> NO<sub>x</sub> data spanned from 1973 to 2015, but the  
256 analysis focused on years between 1990 and 2015 when the operation of chemiluminescent  
257 NO<sub>x</sub> instrumentation was wide-spread throughout Europe.

## 258 **NO<sub>x</sub> filtering method**

259 To isolate the primary NO<sub>2</sub> component, a multi-step filtering process was conducted which  
260 was similar to past calculation of CO/NO<sub>x</sub> ratios by other authors (for example see<sup>44,45</sup>).  
261 The first step was to choose urban areas and these were generally identified by the Euro-  
262 pean Commission’s Functional Urban Area definition.<sup>46</sup> A Functional Urban Area includes  
263 a city and their commuting zones, which is approximately equivalent to a metropolitan  
264 area. The spatial boundaries (polygons) for these urban areas were obtained from the  
265 AQER zones data flow which form the official EU air quality management zones. When  
266 the polygons were not available or not suitable for use in the AQER repository, the appro-

267 priate administrative boundaries were scraped from OpenStreetMap.<sup>47,48</sup> These polygons  
268 were then used as a spatial boundary for an urban area and only monitoring sites within  
269 the boundary were selected and used. Seventy-six urban areas were identified and used  
270 but after the filtering process, 61 urban areas had the variables and volume of data needed  
271 for the analysis. An European urban area map can be found in Supplementary Fig. 1.

272 For each urban area that was defined with a boundary, a representative ozone ( $O_3$ )  
273 background site was identified. The representative  $O_3$  site had the requirements of having  
274 a continuous monitoring operation, *i.e.* not a seasonal site and having an hourly time  
275 series of at least five years. These  $O_3$  time series were used to represent the typical urban  
276 background concentrations of  $O_3$  for each urban area. In some situations, an unbroken  
277 time series was unavailable, usually due to monitoring site closures, therefore more than  
278 one representative  $O_3$  site was used to gain a minimum of five years of  $O_3$  data. No data  
279 capture filters were applied to the observations. Sites classified as urban background were  
280 prioritised over other site types but for seven urban areas this was not possible and an  
281 industrial or roadside site was used. One-hundred and thirty million hourly measurements  
282 of  $NO_2$ ,  $NO_x$ , and  $O_3$  were evaluated from 488 sites. Details on the urban areas and the  
283  $O_3$  monitoring sites can be found in Supplementary Table 3.

284 After a representative  $O_3$  site was identified for an urban area, hourly  $NO_2$  and  $NO_x$   
285 observations from traffic, roadside, and kerbside sites were filtered to include only traffic-  
286 dominated periods between 06:00–18:00 (Coordinated Universal Time, Eastern European  
287 Time, or Central European Time depending on location; Supplementary Table 3) for week-  
288 days (Monday–Friday), and when the representative  $O_3$  background concentrations were  
289 low. Low- $O_3$  conditions were considered when hourly concentrations were  $\leq 10 \mu\text{g m}^{-3}$   
290 (5 ppb). The low- $O_3$  threshold was varied to determine the effect on the calculated ratio of

291 NO<sub>2</sub> to NO<sub>x</sub>. Varying the absolute value of the threshold between 5 and 30 µg m<sup>-3</sup> did not  
292 alter the patterns which were determined, only the absolute values of the NO<sub>2</sub>/NO<sub>x</sub> ratio  
293 due to an increase of contamination of non-primary NO<sub>2</sub> (Supplementary Fig. 2). The  
294 10 µg m<sup>-3</sup> threshold allowed for more recent years with higher urban O<sub>3</sub> concentrations  
295 when compared to earlier time periods to have an adequate number of observations which  
296 could be used to estimate the NO<sub>2</sub>/NO<sub>x</sub> ratio which was not the case for the 5 µg m<sup>-3</sup>  
297 threshold.

298 The filtering process removed many of the total NO<sub>2</sub> and NO<sub>x</sub> observations but had  
299 the goal of isolating the times when the influence of the NO + O<sub>3</sub> reaction was negligible.  
300 These conditions would therefore represent those when the roadside increment in NO<sub>2</sub>  
301 above background would be dominated by primary NO<sub>2</sub> emissions from vehicles using the  
302 road. A potential source of uncertainty is the use of chemiluminescent NO<sub>x</sub> analysers with  
303 molybdenum catalysts in most analysers for compliance monitoring. These instruments  
304 are affected by interference due to NO<sub>y</sub> species, which are detected as NO<sub>2</sub>. However, at  
305 roadside locations, and in particular for increments above local background concentrations  
306 with very little ageing of the airmass, the influence of NO<sub>y</sub> species is expected to be  
307 negligible.<sup>49</sup> A potentially more important interferent is the direct emission of nitrous  
308 acid (HONO), which would also be detected as NO<sub>2</sub> in these instruments. Measurements  
309 of HONO in vehicle exhausts suggests only low amounts are emitted and its effect would  
310 be small. For example,<sup>50</sup> measured a HONO/NO<sub>x</sub> ratio of  $2.9 \pm 0.5 \times 10^{-3}$ .

### 311 **NO<sub>2</sub>/NO<sub>x</sub> ratio estimation**

312 After the filters had been applied, for each site and year combination, the NO<sub>2</sub>/NO<sub>x</sub> ratio  
313 was calculated with robust linear regression with an MM-estimator. The use of the linear

314 model in this way allowed for the slope to be estimated, which represents an estimate of  
315 the the primary  $\text{NO}_2/\text{NO}_x$  ratio. The robust linear regression functions were provided  
316 with the **MASS** R package.<sup>51</sup> The robust regression technique is hardened against out-  
317 liers by a high breakdown point which helped handle noisy observations before 2000 in  
318 some locations. When ratios were sequentially aggregated to urban area, country, and  
319 European level the arithmetic mean was used as the summary function. For  $n$  values, see  
320 Supplementary Table 2. After the  $\text{NO}_2/\text{NO}_x$  ratio estimates were aggregated to European  
321 level, the trend was non-monotonic. The breakpoints in the trend were identified with the  
322 **segmented** R package and three linear least squares regression models were calculated  
323 to represent the pieces of the trend.<sup>52,53</sup>

## 324 **Method validation**

325 The filtering method employed was tested with a total oxidant ( $\text{OX} = \text{NO}_2 + \text{O}_3$ ) method  
326 reported by Jenkin<sup>54</sup>. OX can be thought of as the sum of regional and local oxidant  
327 contributions at a monitoring site. Like the filtering method, if the OX method is applied  
328 to a roadside site, the local oxidant component can provide an estimate of the primary  
329  $\text{NO}_2/\text{NO}_x$  ratio. Therefore the estimates of the filtering and OX methods can be directly  
330 compared. The OX method has the limitation of requiring  $\text{O}_3$  observations as well as  $\text{NO}_x$   
331 observations. However, the measurement of  $\text{O}_3$  at roadside sites is uncommon. The two  
332 methods showed very good agreement and for London Marylebone Road, a monitoring site  
333 reported by Jenkin<sup>54</sup>, the methods demonstrated near-equivalence for the years 1997–2014  
334 (Supplementary Fig. 3).

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482 and the maintenance of a PostgreSQL database server.

## 483 **Author contributions**

484 DCC designed the research questions and with SKG developed and evaluated the appro-  
485 priate methods. SKG processed the European air quality data and with DCC conducted  
486 the data analysis. SKG, DCC, ACL and SJM wrote the paper.

## 487 **Data availability**

488 The datasets analysed in the current study are publicly available, are referenced in  
489 the text, and can be accessed from the AirBase ([https://www.eea.europa.eu/data-and-](https://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-8)  
490 [maps/data/airbase-the-european-air-quality-database-8](https://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-8)) and the European Environment  
491 Agency's Central Data Repository (<http://cdr.eionet.europa.eu>) repositories.

## 492 **Code availability**

493 The code used to estimate the NO<sub>2</sub>/NO<sub>x</sub> ratios and to aggregate the ratios are available  
494 from the corresponding author on reasonable request. All software used for data storage  
495 and analysis is referenced in text and is open-source.

## 496 **Competing financial interests**

497 The authors declare no competing financial interests.

498 **Figure captions**

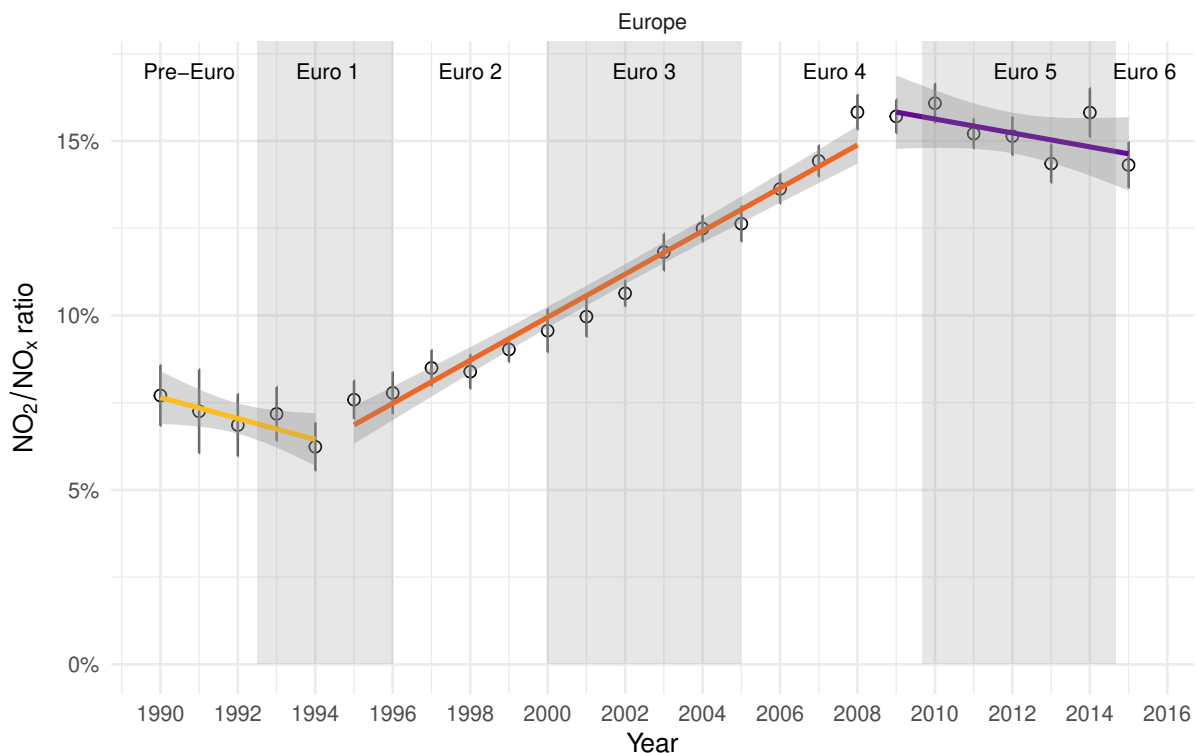


Figure 1: Mean  $\text{NO}_2/\text{NO}_x$  ratio for all roadside monitoring sites for the 61 European urban areas analysed between 1990 and 2015. The error bars represent the 95% confidence intervals of the slope estimates based on the number of samples (for extra details see Supplementary Table 1). Linear regression models were applied to three separate periods: 1990–1994, 1995–2008, and 2009–2015 identified by segmented regression (see Supplementary Table 2).

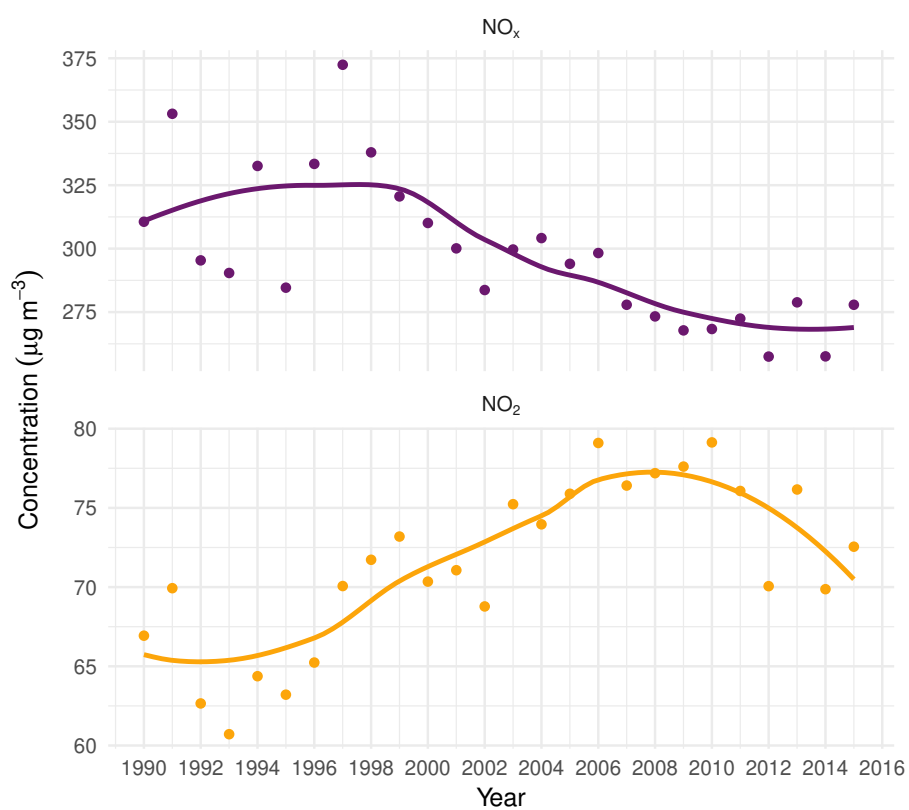


Figure 2: Mean  $\text{NO}_x$  and  $\text{NO}_2$  concentrations after the filtering method was applied (see Methods section) for all roadside monitoring sites for the 61 European urban areas analysed between 1990 and 2015. These concentration data were used for the calculation of the  $\text{NO}_2/\text{NO}_x$  ratio displayed in Fig. 1. The smoothed lines are loess (local regression) fits.

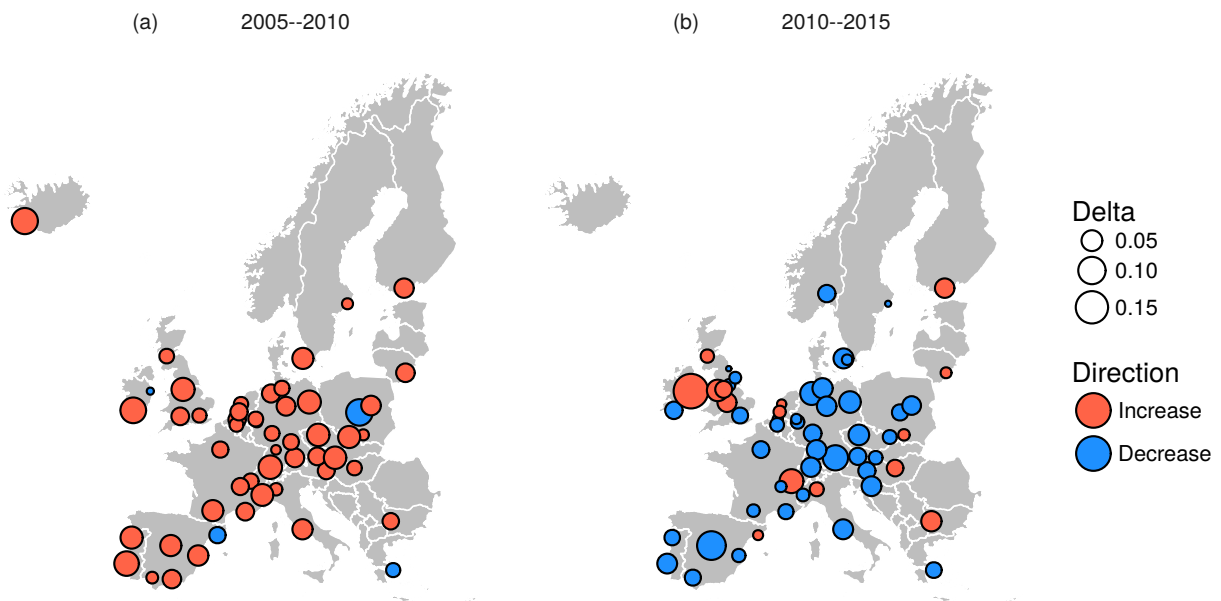


Figure 3: The change in the  $\text{NO}_2/\text{NO}_x$  ratio for each urban area for two time periods, the five years leading up to 2010, and the five years after 2010 (2010 is the year with the highest  $\text{NO}_2/\text{NO}_x$  ratio). Plot (a) shows the change in the  $\text{NO}_2/\text{NO}_x$  ratios from 2005 to 2010 and the plot (b) displays the change in ratio from 2010 to 2015. The size of the dots indicates the magnitude of the change.

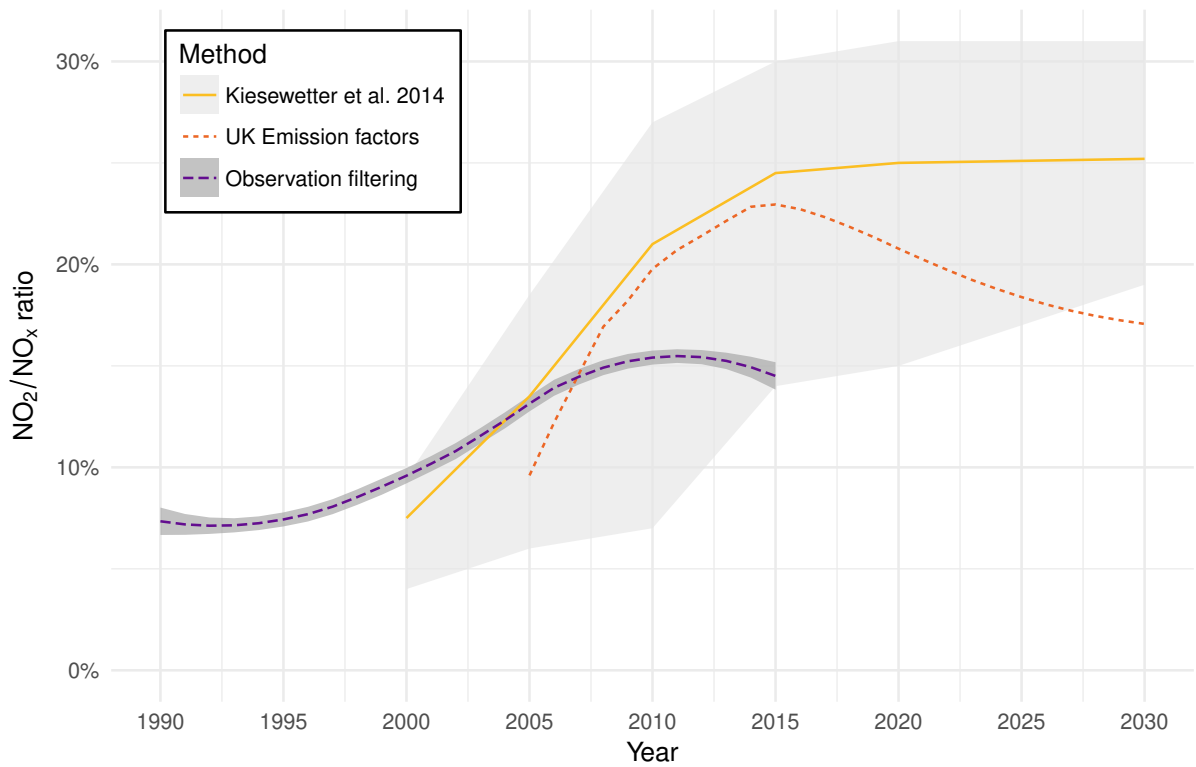


Figure 4: Comparison of three methods which estimate roadside primary  $\text{NO}_2$  as a  $\text{NO}_2/\text{NO}_x$  ratio and forecasts from two other sources.<sup>15,34</sup> Shaded zones are the individual EU member state range in Kiesewetter et al. 2014<sup>15</sup> and the 95 % confidence interval of the observation filtering method's loess fit.