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Lower vehicular primary emissions of NO_2 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_2) near roads; a problem that has been forecast to persist to 2030. Whereas European air quality standards regulate NO_2 concentrations, emissions standards for new vehicles instead set limits for NO_x – the combination of nitric oxide (NO) and NO_2. From around 1990 onwards, total emissions of NO_x declined significantly in Europe, but roadside concentrations of NO_2 – 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_2. Here we apply a data filtering technique to 130 million hourly measurements of NO_x, NO_2 and ozone (O_3) 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 NO_2. We find that the ratio of NO_2 to 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 NO_x now being emitted directly from road transport as 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 NO_2 air quality standards across Europe than is currently expected.

Since the mid-1990s the European vehicle fleet has undergone considerable dieselisation[1–4] with incentivisation over other fuels and technologies on the basis of predicted fuel efficiency, lower CO_2 emissions, and increased driving performance.[5–7] By 2014 diesel vehicles accounted for an average of 53 % of new European passenger vehicle sales compared to 14 % in 1990, in contrast to little increase in their adoption into US fleets.[3,4] The proportion of diesel powered vehicles across Europe has contributed to widely published problems where legal ambient air quality standards are breached, usually near roads. Of particular concern in recent years is nitrogen dioxide (NO_2) although particulate matter (PM) is also important.[8] Many European Union (EU) member states are struggling to comply with the 2008/50/EC Air Quality Directive which sets legal limits for hourly and annual average NO_2 concentrations.[8–10] While total national emissions of NO_x (NO + NO_2) have shown reductions in Europe, urban concentrations of NO_2 have decreased less than expected and this has been attributed to the growth in diesel fuelled vehicles.[11–19]

The impacts on public health of NO_2 are significant both through direct harm on inhalation and as a precursor to secondary pollutants ozone (O_3) and PM.[20] Published estimates of premature deaths due to NO_2 in 28 EU countries were reported to be 72 000 annually, based on a 2012 analysis year.[21] Roadside locations are perhaps the most important places where NO_2 must be controlled because this is where human exposure is at its highest. These are challenging locations from a legal compliance perspective — of all the reported exceedances of EU hourly and annual limit values in 2016, 94 % of those occurred at roadside monitoring locations.[22]

NO_2 concentrations at roadside locations are primarily controlled by local road transport and are influenced by, firstly, the total amount of NO_x emitted and then the fraction of that NO_x that is directly emitted as NO_2.[23] A shift towards higher NO_2/NO_x emissions from road transport can lead to a counter intuitive situation where total NO_x emissions can fall over time, yet roadside concentrations of NO_2 do not decline. The influence of this key ratio in driving trends and forecasts has already been shown in central London.[16] Predictions of future NO_2 concentrations in Europe must make assumptions about this NO_2/NO_x ratio, and predicted increases in this ratio are in part, behind a predicted lack of air quality standard attainment in many cities until 2025–2030.[15] Despite the critical importance of the NO_2/NO_x ratio in controlling urban roadside concentrations, specific limits do not exist as part of European vehicular emission standards tests. New European vehicle tests report only total NO_x ($NO + NO_2$) in exhaust gases and whilst emission standards set limits for total NO_x they do not speciate between NO and NO_2. Beyond initial new vehicle tests little is known about how technologies such as diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) influence this ratio in the real-world, despite the high profile given to the topic since the Volkswagen (VW) emissions scandal.[7,24] The implications of not correctly estimating NO_2/NO_x ratios in policy support tools such as COPERT and HBEFA have been described by others.[25–28]

Although recent NO_x emission underestimates from passenger cars have received most media attention, other vehicles such as heavy duty vehicles (HDVs) and buses are also important in controlling roadside NO_2 because they are predominately diesel fuelled. In this study, which focuses on NO_2 trends in urban areas, it is expected that light duty vehicles (LDVs) and urban buses will make significant contributions to vehicle emissions. It should also be noted that in terms of emissions data availability there is considerably more information available on passenger cars compared with other types of vehicles. As a consequence, there is uncertainty in both the absolute and relative contributions to NO_x and NO_2 from these additional transport sources.

The NO_2/NO_x ratio from diesel vehicles is controlled by both engine and exhaust control technologies that have advanced in response to the 'Euro' series of emissions standards. The introduction of Euro 3 in 2000 saw the introduction of DOC into passenger vehicles; where in the presence of excess oxygen, NO can be oxidised to NO_2 over DOC metal catalysts resulting in more direct NO_2 being emitted.[16,29,30] The introduction of DPF in 2009 for compliance with the Euro 5 emission standards introduced a further technology that could lead to additional direct tailpipe NO_2.[31] However, as each progressive Euro standard has been introduced there have been no systemic observations of how new exhaust technologies might affect the NO_2/NO_x ratio in real world emissions, or evaluation of whether the emissions inventories that need this ratio for forecasts, and that unpin policy, are preforming well.

Ambient observations to determine the NO_2/NO_x trend

Using the measured roadside atmospheric ratio of NO_2 to NO_x (NO_2/NO_x ratio, expressed as a molar volume ratio) is one effective way of determining the influence on NO_2 of increased proportions of diesel vehicles in a fleet, as well as a method to detect change in after treatment technologies resulting from progressive tightening of the Euro standards. Since there is no systematic set of vehicle exhaust measurements that show NO_2/NO_x trends we look instead at the combined national data sets of ambient monitoring information which measure NO and NO_2 in air. We carefully filter these datasets for roadside locations where the ratio of these two species can be taken as a proxy for the exhaust emission ratio. We note that there is considerable diversity in the penetration and uptake of diesel vehicles, typical vehicle lifespans, and climates when considering Europe as a whole. The analysis in this section uses data from roadside monitoring sites across 61 European urban areas between 1990 and 2015. The combined European trend (Fig. 1) for the 61 areas demonstrates a clear increase in annual mean NO_2/NO_x ratio between 1995 and 2010. The aggregation was performed on the mean for each city in each year to ensure the results were not biased towards cities with more measurement locations, such as London.

Figure 1 shows three distinct periods where NO_2/NO_x ratio behaviour differed. The first, from 1990 to 1994 coincides with a pre-Euro 3 fleet that did not use diesel oxidation catalysts (DOCs) and the ratio was stable within the uncertainty of the slope estimate and less than 10 % (Supplementary Table 2). The second period from 1995 to 2008 is a period where there was a clear, sustained, and significant increase in the NO_2/NO_x ratio corresponding to a period of growth in diesel passenger cars numbers and the introduction of DOC to new vehicles via Euro 3 and Euro 4. Over this period the ratio increased to a peak value of approximately 16 % in 2010. The third period is characterized by a stabilisation in the NO_2/NO_x ratio and coincides with the introduction of Euro 5 vehicles fitted with diesel particle filters (DPFs). The second period is the only period that shows a statistically significant change NO_2/NO_x ratio. The trends shown in Fig. 1 broadly follow the pattern of reported changes in emissions seen from sporadic remote sensing measurements of almost 70 000 vehicles in London (during 2012), with a progressive increase in NO_2/NO_x ratio for diesel passenger cars and light vans from pre-Euro to Euro 5.[32]

Although the ambient derived NO_2/NO_x ratio turning points in Fig. 1 broadly coincide with identifiable regulatory landmarks, the changes are more complex than they would first appear. First, when a new Euro class is introduced, it takes time for those new vehicles to significantly penetrate the vehicle fleet and affect overall emissions. Second, the emissions characteristics of vehicles will be expected to change as they age. For example, a Euro 3 car introduced in year 2000 will be $\approx$ 5–6 years old at the end of the Euro 3 period. Analysis of vehicle emission remote sensing data has shown that vehicle ageing tends to decrease the NO_2/NO_x ratio of diesel passenger cars (and likely other types of vehicles fitted with DOC).[16,33] All these influences, as well as other local effects, contribute to the overall pattern seen in Fig. 1. Nevertheless, it is clear that on average, across Europe, the ratio has not continued to increase after 2010 and is now declining.

At an European level, mean annual roadside NO_x concentrations demonstrated an overall decrease from 1998 to 2015 with mean NO_x concentrations reducing from 338 to 228 $\mu g\,m^{-3}$ (Fig. 2). Before 1998, the NO_x means are scattered due to fewer sites and observations and larger uncertainties concerning the quality of the measurements. This decrease can be attributed to improved vehicular NO_x emission control during this period. Fig. 2 shows that mean NO_x concentrations have remained stable since 2010, however, the trend in NO_2 concentrations (the regulated species of NO_x) differs from total NO_x in several important ways. First, NO_2 concentrations tended to increase over the period from around 1997 to 2009 (despite concentrations of NO_x decreasing). Second, concentrations of NO_2 have tended to decrease from around 2009 at a time when concentrations of

NO_x have been stable. These changes in concentrations are consistent with the changes calculated for the NO_2/NO_x ratio, shown in Fig. 1.

Spatial analysis of roadside NO_2/NO_x over Europe

The Europe-wide aggregation displayed in Fig. 1 hides the diversity of trends in the NO_2/NO_x ratio across European roadside monitoring sites, urban areas, and countries. When estimates of the NO_2/NO_x ratio were aggregated at an urban level, a peak ratio was observed at or near 2010 in most European urban areas (Fig. 3). The trends in NO_2/NO_x ratio are shown for two periods 2005 to 2010 and 2010 to 2015. Over the first period most urban areas showed an increase in NO_2/NO_x, most pronounced in western and central Europe. For the later period the majority of regions showed a declining trend in NO_2/NO_x albeit generally smaller than the earlier increases.

Seven percent of the urban areas however showed opposing trends most likely reflecting unique and localised site or urban area conditions. Some of these urban areas including Amsterdam (Netherlands), Barcelona (Spain), Milan (Italy), and Krakow (Poland) demonstrate a levelling-off of the NO_2/NO_x ratio but had not shown decreasing trends by 2015. Other urban areas such as Dublin (Ireland which had the largest delta), Rotterdam (Netherlands), some urban areas in central United Kingdom, and Helsinki (Finland) showed further increases in NO_2/NO_x by 2015. Some urban areas, most conspicuously in Reykjavík (Iceland), are not shown in the 2010–2015 panel (b) in Fig. 3. This was due to the absence of more-recent observations, usually due to O_3 or NO_x monitoring site closures or when the EU member state stopped reporting NO_x and NO alongside NO_2. It is very difficult to attempt attribute the underlying causes of the 7 % outliers; it may be associated with fleet makeup or indeed other local factors such as changing road layouts, new sources and urban infrastructure. In the absence of consistent information across Europe on these factors we do not speculate further.

The overwhelming consistency seen in the 93 % of urban areas and across the whole of the continent is however strongly suggestive of a European-scale influence on primary NO_2, not that this change in NO_2/NO_x is a result of a series of uncoordinated local factors. These changes are consistent with a steady evolution of the European fleet as a whole, for example, the effect of Euro standards and technologies, rather than trends driven by city or country specific interventions such as changes to local urban public transport fleets, introduction of congestion zones, and so on.

Potential factors controlling recent declines in NO_2/NO_x

Whilst the periods of increase in the NO_2/NO_x ratio can be rationalised based on previous evidence, the recent declines in ratio from around 2010 are more difficult to understand because diesel vehicles continue to use DOC with DPF. We raise here some potential factors that could explain this result. Remote sensing measurement of selected vehicles has showed that selective catalytic reduction (SCR) control systems introduced on heavy duty vehicles have improved, resulting in both lower overall emissions of NO_x and a better control of NO_2.[16] Although the numbers of heavy duty vehicles passing each monitor is unknown across Europe, this technology working on part of the fleet may have contributed to the ratio declining. A second potential factor is the ageing of exhaust control systems themselves, and an engineering shift towards 'catalytic thrifting'. This refers to vehicle manufacturers and catalyst developers progressively reducing the amount of platinum group metals used in exhaust systems which in turn has a consequence of reducing the amount of NO_2 generated. Finally, evidence from vehicle emission remote sensing shows that as light duty diesel vehicles age, the NO_2/NO_x ratio does decrease over time although the extent of this is uncertain.[16] It would seem plausible that all of these poorly understood factors could, in combination, contribute to the stabilisation and decline seen in NO_2/NO_x ratio since 2010. However, with ambient data alone, it is impossible to quantify the individual contributions robustly.

Comparisons to emissions inventories

The Europe-wide primary NO_2/NO_x estimated by the observational filtering method here differs substantially from previous works which report roadside NO_2/NO_x ratio trends. Other inventories estimate higher NO_2/NO_x than what we see in the real world. A modelled estimate of traffic emissions at a national and European level in five year intervals between 2000 and 2030[15] predicted NO_2/NO_x to increase ≈ 25 % by 2020 and stay at this level until 2030 (Fig. 4). Using these model estimates of NO_2/NO_x around 30 monitoring areas were then forecast to still be in breach of the European NO_2 air quality standard in 2030. The current United Kingdom (UK) vehicular primary NO_2 emission factors are also predicted up to 2030 in the National Atmospheric Emissions Inventory (NAEI).[34] The UK emission factors are derived from the COPERT database with modelling of predicted fleet changes in the future. The UK primary NO_2 emission factors for all UK urban areas are currently predicted to reach a peak NO_2/NO_x ratio in 2015 at 23 % (Fig. 4). After 2015, the UK emission factors decrease until 2030 to a minimum ratio of 17 %.

Both emission estimates appear to substantially overstate the current fraction of emissions that is directly released as NO_2, in one case by nearly a factor two for the year 2015, and the measured vs. modelled trends are currently diverging further from one another. If primary NO_2 emissions remain similar or even further decreases as the current analysis suggests, the use of these inventory estimates for air quality modelling purposes would result in overly pessimistic future predictions of compliance with European NO_2 ambient air quality standards.

Impact on the attainment of air quality standards

Policy projections of air quality that use too high a value for the NO_2/NO_x ratio will predict higher concentrations of roadside NO_2 than may actually occur for the same total amount of NO_x emitted. As an example of the potential changes brought about by using different NO_2/NO_x ratios, we compare how ambient concentrations would vary based on the current range of estimates. The most recent ratio reported here by the filtering method was 14.5 % in 2015 while the other reported estimates ranged from 25 to 22 % (Fig. 4). To estimate the influence of differing primary NO_2 assumptions on roadside annual mean NO_2 concentrations, we have considered the roadside increment of NO_x concentration at each measurement site *i.e.* the increment in NO_x concentration above urban background values of NO_2. Two scenarios have been considered: first, that the roadside NO_x increment is associated with a NO_2/NO_x ratio of 14.5 % and second, that it is associated with a ratio of 23 %. Considering all European roadside sites, the mean difference in NO_2 concentration between these two scenarios is $6.6\,\mu g\,m^{-3}$. The current analysis, which applies data filtering techniques, is not strictly consistent with the changes expected to annual mean NO_2 concentrations because only a subset of data have been analysed. However, the changes in the NO_2/NO_x ratio identified will have a strong influence on annual mean NO_2 concentrations close to roads.

The impact of differing primary NO_2 assumptions will clearly vary depending on individual sites. However, for the most polluted NO_2 sites in Europe, examples being Brixton

Road and Farringdon Street in London, the annual mean difference in NO_2 from the traffic contribution could be as much as $19\,\mu g\,m^{-3}$. Differences in projected NO_2 of this kind of magnitude are highly significant when compared against targets for compliance with the European annual NO_2 ambient standard which is currently $40\,\mu g\,m^{-3}$. In this respect, current air quality modelling of roadside NO_2 that uses these unrealistically high NO_2/NO_x ratios for the future will tend to also be overly pessimistic. Should NO_2/NO_x ratios of the kind now being observed across Europe be projected forward for the next decade then attainment of annual roadside NO_2 standards in many places might be achieved sooner than is currently predicted.

We note however the substantial disconnections that still exist between the legislative controls being placed on reporting vehicle emissions and air quality standards designed to protect public health. By only requiring the reporting of total NO_x from new vehicles, and not NO and NO_2 as separate quantities, the later impacts of those vehicles, and how they influence the regulate pollutant NO_2, cannot be assessed. The continued lack of any systematic collection of information on changes to NO and NO_2 emissions as vehicles age is a further gap in evidence that if filled would greatly improve the reliability of future forecasts of air quality in cities.

Methods

Data

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

The AirBase and AQER data were cleaned and inserted into a single database with a simple data model.[37] The AirBase data are available in well-formatted tabular text files which only required decoding of their file names to be used. However, the AQER XML, documents were a far greater challenge due to the need to parse different observational units to create a coherent and decoded data model. Despite AQER formalising XML schemas, many variations were found across the member states' files which required significant development to ensure that the variations were handled correctly.

The database was also supplemented with other data where available. London for example, has a much larger air quality monitoring network which is not represented by AirBase and the AQER repositories because these monitoring activities are coordinated by other bodies and do not form part of the national network. Therefore, these additional sites and data were accessed using **openair**, which accesses data from King's College London.[38,39] These additional sites follow equivalent quality assurance and quality procedures as the national network. Many countries have not reported the full complement of NO, NO_2, and NO_x presumably due to a lack of a legal obligation and file size concerns. The analysis reported here required both hourly NO_2 and NO_x to be present for a monitoring site and therefore the missing variables were derived from the other components if possible. In the case of Paris, the additional NO_x was accessed through the Airparif web portal.[40] Once the cleaning and tidying was complete, the database contained 2.7×10^9 observations from 8 400 air quality monitoring sites.[37,41]

The data import, transformation, and tidying was conducted with R and the database technology used was PostgreSQL.[42,43] NO_x data spanned from 1973 to 2015, but the analysis focused on years between 1990 and 2015 when the operation of chemiluminescent NO_x instrumentation was wide-spread throughout Europe.

NO_x filtering method

To isolate the primary NO_2 component, a multi-step filtering process was conducted which was similar to past calculation of CO/NO_x ratios by other authors (for example see[44,45]). The first step was to choose urban areas and these were generally identified by the European Commission's Functional Urban Area definition.[46] A Functional Urban Area includes a city and their communing zones, which is approximately equivalent to a metropolitan area. The spatial boundaries (polygons) for these urban areas were obtained from the AQER zones data flow which form the official EU air quality management zones. When the polygons were not available or not suitable for use in the AQER repository, the appropriate administrative boundaries were scraped from OpenStreetMap.[47,48] These polygons were then used as a spatial boundary for an urban area and only monitoring sites within the boundary were selected and used. Seventy-six urban areas were identified and used but after the filtering process, 61 urban areas had the variables and volume of data needed for the analysis. An European urban area map can be found in Supplementary Fig. 1.

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

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

NO_2 to NO_x. Varying the absolute value of the threshold between 5 and 30 $\mu g\,m^{-3}$ did not alter the patterns which were determined, only the absolute values of the NO_2/NO_x ratio due to an increase of contamination of non-primary NO_2 (Supplementary Fig. 2). The 10 $\mu g\,m^{-3}$ threshold allowed for more recent years with higher urban O_3 concentrations when compared to earlier time periods to have an adequate number of observations which could be used to estimate the NO_2/NO_x ratio which was not the case for the 5 $\mu g\,m^{-3}$ threshold.

The filtering process removed many of the total NO_2 and NO_x observations but had the goal of isolating the times when the influence of the $NO + O_3$ reaction was negligible. These conditions would therefore represent those when the roadside increment in NO_2 above background would be dominated by primary NO_2 emissions from vehicles using the road. A potential source of uncertainty is the use of chemiluminescent NO_x analysers with molybdenum catalysts in most analysers for compliance monitoring. These instruments are affected by interference due to NO_y species, which are detected as NO_2. However, at roadside locations, and in particular for increments above local background concentrations with very little ageing of the airmass, the influence of NO_y species is expected to be negligible.[49] A potentially more important interferent is the direct emission of nitrous acid (HONO), which would also be detected as NO_2 in these instruments. Measurements of HONO in vehicle exhausts suggests only low amounts are emitted and its effect would be small. For example,[50] measured a $HONO/NO_x$ ratio of $2.9 \pm 0.5 \times 10^{-3}$.

NO_2/NO_x ratio estimation

After the filters had been applied, for each site and year combination, the NO_2/NO_x ratio was calculated with robust linear regression with an MM-estimator. The use of the linear model in this way allowed for the slope to be estimated, which represents an estimate of the the primary NO_2/NO_x ratio. The robust linear regression functions were provided with the **MASS** R package.[51] The robust regression technique is hardened against outliers by a high breakdown point which helped handle noisy observations before 2000 in some locations. When ratios were sequentially aggregated to urban area, country, and European level the arithmetic mean was used as the summary function. For n values, see Supplementary Table 2. After the NO_2/NO_x ratio estimates were aggregated to European level, the trend was non-monotonic. The breakpoints in the trend were identified with the **segmented** R package and three linear least squares regression models were calculated to represent the pieces of the trend.[52,53]

Method validation

The filtering method employed was tested with a total oxidant ($OX = NO_2 + O_3$) method reported by Jenkin[54]. OX can be thought of as the sum of regional and local oxidant contributions at a monitoring site. Like the filtering method, if the OX method is applied to a roadside site, the local oxidant component can provide an estimate of the primary NO_2/NO_x ratio. Therefore the estimates of the filtering and OX methods can be directly compared. The OX method has the limitation of requiring O_3 observations as well as NO_x observations. However, the measurement of O_3 at roadside sites is uncommon. The two methods showed very good agreement and for London Marylebone Road, a monitoring site reported by Jenkin[54], the methods demonstrated near-equivalence for the years 1997–2014 (Supplementary Fig. 3).

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Author contributions

DCC designed the research questions and with SKG developed and evaluated the appropriate methods. SKG processed the European air quality data and with DCC conducted the data analysis. SKG, DCC, ACL and SJM wrote the paper.

Data availability

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

Code availability

The code used to estimate the NO_2/NO_x ratios and to aggregate the ratios are available from the corresponding author on reasonable request. All software used for data storage and analysis is referenced in text and is open-source.

Competing financial interests

The authors declare no competing financial interests.

Figure captions

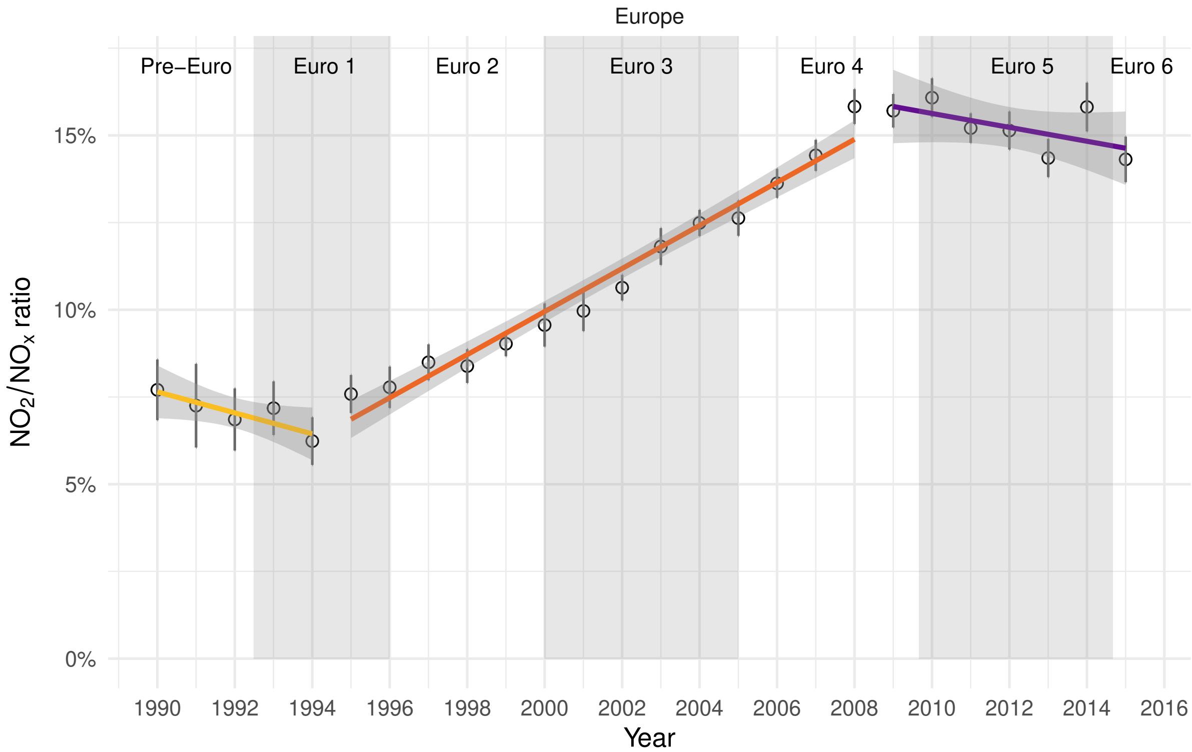

Figure 1: Mean NO_2/NO_x ratio for all roadside monitoring sites for the 61 European urban areas analysed between 1990 and 2015. The error bars represent the 95 % confidence intervals of the slope estimates based on the number of samples (for extra details see Supplementary Table 1). Linear regression models were applied to three separate periods: 1990–1994, 1995–2008, and 2009–2015 identified by segmented regression (see Supplementary Table 2).

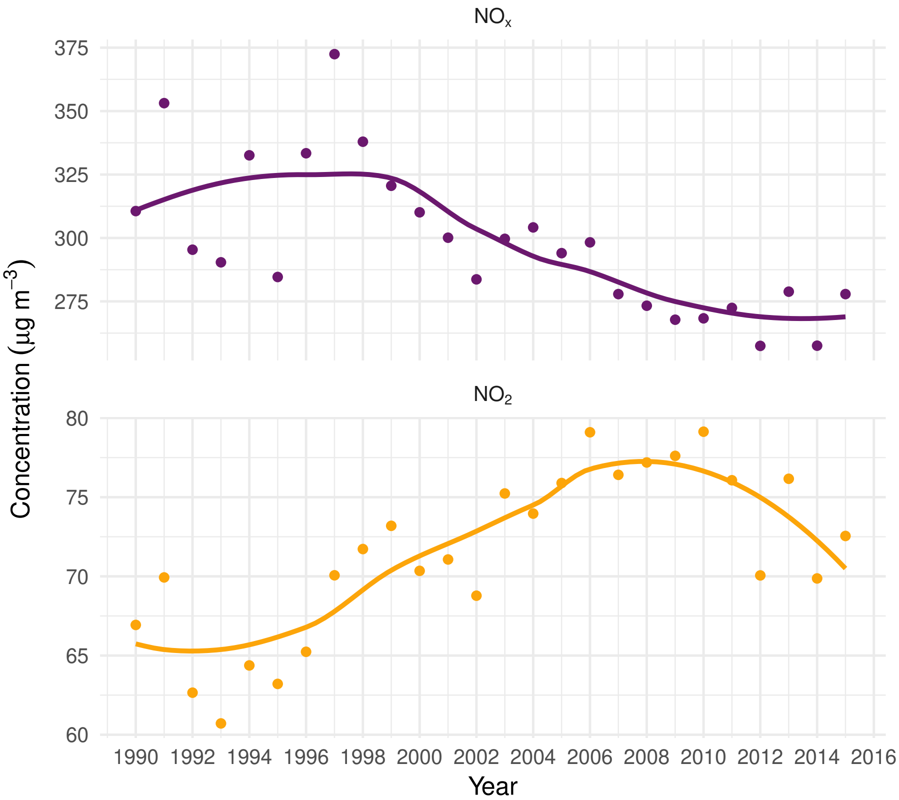

Figure 2: Mean NO_x and NO_2 concentrations after the filtering method was applied (see Methods section) for all roadside monitoring sites for the 61 European urban areas analysed between 1990 and 2015. These concentration data were used for the calculation of the NO_2/NO_x ratio displayed in Fig. 1. The smoothed lines are loess (local regression) fits.

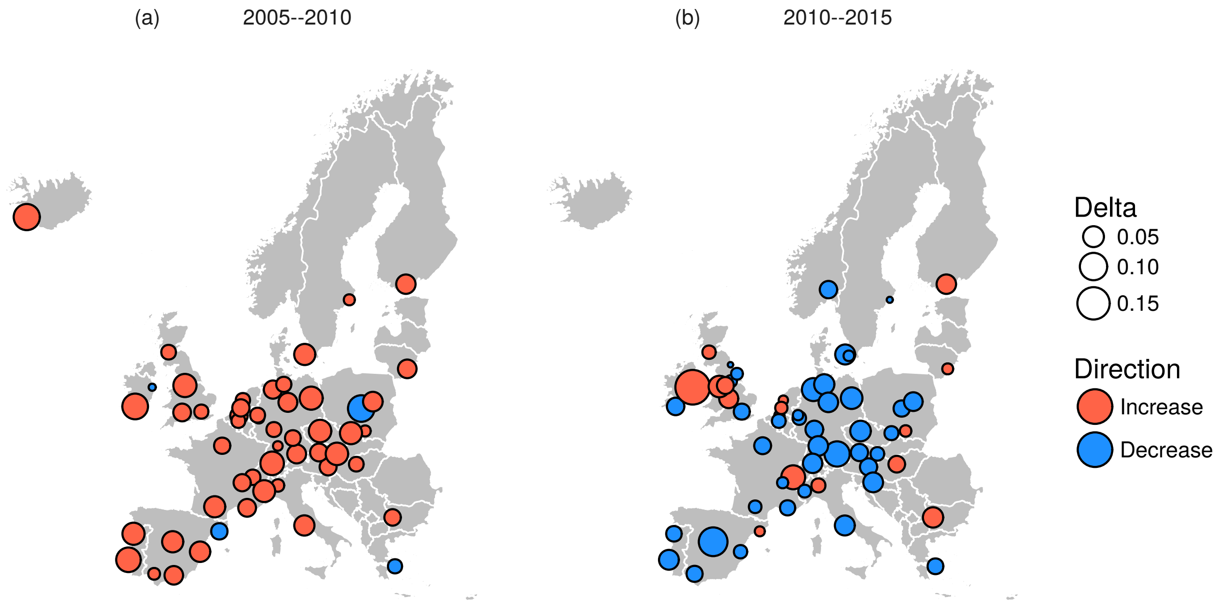

Figure 3: The change in the NO_2/NO_x ratio for each urban area for two time periods, the five years leading up to 2010, and the five years after 2010 (2010 is the year with the highest NO_2/NO_x ratio). Plot (a) shows the change in the NO_2/NO_x ratios from 2005 to 2010 and the plot (b) displays the change in ratio from 2010 to 2015. The size of the dots indicates the magnitude of the change.

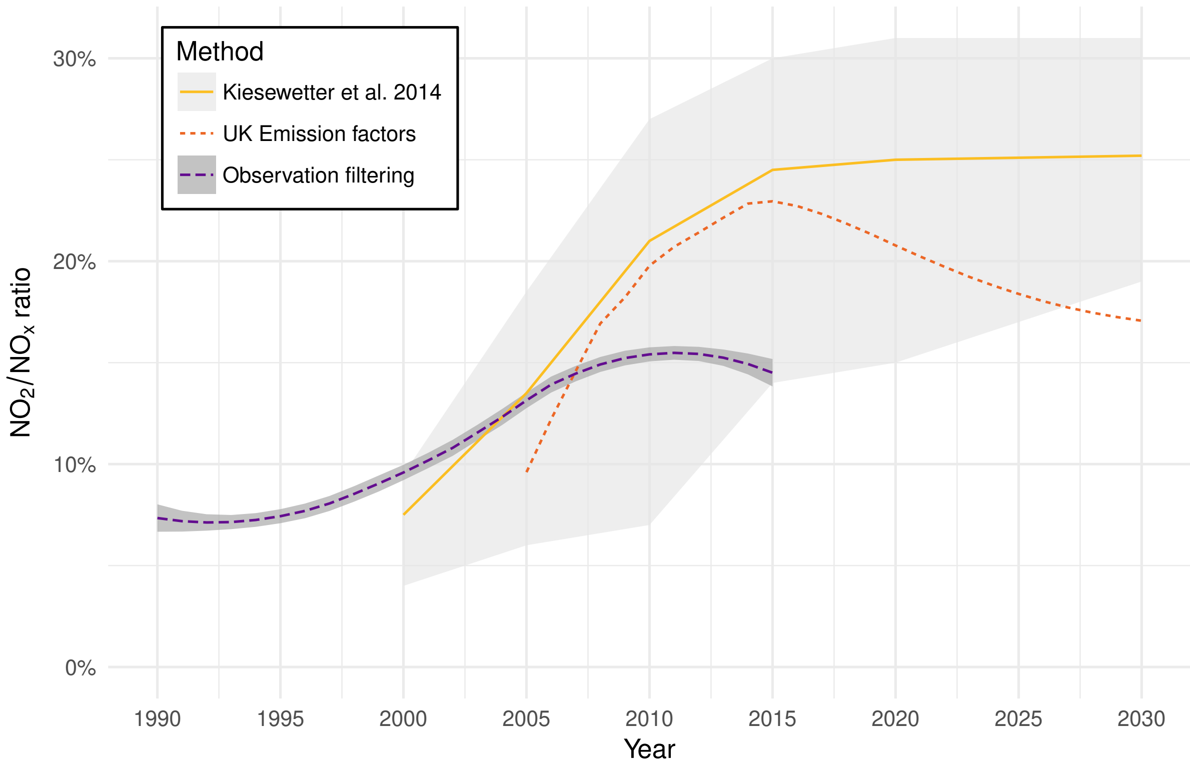

Figure 4: Comparison of three methods which estimate roadside primary NO_2 as a NO_2/NO_x ratio and forecasts from two other sources.[15,34] Shaded zones are the individual EU member state range in Kiesewetter et al. 2014[15] and the 95 % confidence interval of the observation filtering method's loess fit.