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Long-term trends in nitrogen oxides concentrations and on-road vehicle emission factors in Copenhagen, London and Stockholm

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Abstract

Road transport is the main anthropogenic source of NOx in Europe, affecting human health and ecosystems. Thus, mitigation policies have been implemented to reduce on-road vehicle emissions, particularly through the Euro standard limits. To evaluate the effectiveness of these policies, we calculated NO_2 and NOx concentration trends using air quality and meteorological measurements conducted in three European cities over 26 years. These data were also employed to estimate the trends in NOx emission factors (EF_{NOx}, based on inverse dispersion modeling) and NO_2:NOx emission ratios for the vehicle fleets under real-world driving conditions. In the period 1998-2017, Copenhagen and Stockholm showed large reductions in both the urban background NOx concentrations (-2.1 and -2.6 % yr^{-1}, respectively) and EF_{NOx} at curbside sites (68 and 43%, respectively), proving the success of the Euro standards in diminishing NOx emissions. London presented a modest decrease in urban background NOx concentrations (-1.3% yr^{-1}), while EF_{NOx} remained rather constant at the curbside site (Marylebone Road) due to the increase in public bus traffic. NO_2 primary emissions –that are not regulated– increased until 2008-2010, which also reflected in the ambient concentrations. This increase was associated with a strong dieselization process and the introduction of new after-treatment technologies that targeted the emission reduction of other species (e.g., greenhouse gases or particulate matter). Thus, while regulations on ambient concentrations of specific species have positive effects on human health, the overall outcomes should be considered before widely adopting them. Emission inventories for the on-road transportation sector should include EF_{NOx} derived from real-world measurements, particularly in urban settings.

Key words: NOx; air quality in Europe; OSPM model; road transport; dieselization.

1. Introduction

Road transport is the main anthropogenic source of nitrogen oxides (NOx) on a global scale (23% in 2017, McDuffie et al., 2020) and across Europe (39% in 2017, EEA, 2019). In traffic environments, NOx consists mainly of nitric oxide (NO) and nitrogen dioxide (NO_2), with the latter associated with a series of deleterious health effects (Nathan and Cunningham-Bussel, 2013; Brown, 2015; Atkinson et al., 2018). Moreover, NOx affects human health indirectly −through the production of surface ozone (O_3) (Monks et al., 2015) and secondary inorganic aerosol (Fuzzi et al., 2015)− and impacts the environment −through eutrophication and acidification of sensitive ecosystems (Peel et al., 2013).

European countries, in particular those in the northwest, have pioneered strategies to tackle environmental issues, with prominent roles in the international community (Liefferink et al., 2009; Grennfelt et al., 2020). In that context, air pollution has been a major political concern in Europe since the late 1970s, leading to the development of ambient air quality standards and control of the major emissions sources (Crippa et al., 2016). In the case of road transport, new vehicles have had to meet increasingly stringent emission limits since the early 1990s, established by the so-called 'Euro emission standards' (European Commission, 2021). These standards are based on emission factors (EF) measured in laboratories under controlled conditions following regulatory driving cycles.

However, field studies revealed that the EF simulated with traffic emission models (COmputer Programme to calculate Emissions from Road Transport COPERT, and Handbook Emission Factors for Road Transport HBEFA), and validated with laboratory-based EF, largely underestimated the real exhaust emissions (Carslaw et al., 2011; Carslaw and Rhys-Tyler, 2013; Krecl et al., 2017). Because laboratory-based EF are used to compile the official national inventories for the road transport sector, it is of utmost importance to conduct real-world EF measurements to identify mismatches in the emission models (Franco et al., 2013). In light of this, the European Union through the Real Driving Emissions

mandates that laboratory tests be complemented with real driving condition tests for new passenger cars (PC) and light-commercial vehicles (LCV) since September 2019 (European Commission, 2021). On the other hand, to assess how EF has responded to policies on emission reduction and its long-term trend, we need to consider approaches based on continuous measurements over a long period. In that context, extended datasets of ambient air pollutant concentrations at roadside sites available in several European cities can be used.

In the case of nitrogen species, only NOx emissions are regulated for on-road vehicles in Europe, despite NO_2 being also directly emitted by vehicle exhausts (Carslaw et al., 2011). The NO_2:NOx emission ratios largely increased in Europe in the period 1995-2010 (Grange et al., 2017), and the annual air quality standard for NO_2 was still exceeded at 10% of the European stations (329 out of 3260), mainly near roads (European Environmental Agency, 2019). This is particularly worrying since roadside stations are located in densely populated areas where population exposure can be large.

Based on unique long-term datasets, this study analyzed the trends of NO_2 and NOx concentrations at three curbside sites in three European cities: Copenhagen, London and Stockholm. Then, EF_{NOx} for the vehicle fleet were determined based on the street increment of the NOx concentrations and inverse modeling techniques. The NO_2:NOx vehicles emission ratios were estimated using their respective ambient concentrations as proxies. We compare our EF_{NOx} values for the mixed fleet with EF extracted from databases and remote sensing studies. Finally, the temporal evolutions of EF_{NOx} and primary NO_2 emissions are discussed in relation to regional and local policies applied to mitigate the road transport emissions.

2. Methods

2.1 Sampling sites and instrumentation

We selected paired street canyon and urban background sites in Copenhagen, London and Stockholm, where long-term hourly NOx ($NO+NO_2$), O_3 and traffic measurements were available. Another criterion was the availability of meteorological data at stations representative of winds above the corresponding street canyons (Table 1, and Supplementary Material). NOx and O_3 concentrations were measured using chemiluminescence and ultraviolet photometry analyzers, respectively, complying with European reference methods (EN14211, 2012; EN14625, 2012). Note that the measurements conducted at the air pollution and meteorological sites are subject to rigorous quality assurance procedures since they belong to national networks.

Hourly traffic data consisted of traffic volume (TR) and vehicle speed (VS). Traffic measurements were continuously recorded on Hornsgatan St. (Stockholm) (Krecl et al., 2017) and Marylebone Road (London) (Harrison et al., 2011) by using loop-profilers embedded in the surface. In the case of Jagtvej St. (Copenhagen), pre-defined traffic data profiles provided by the Danish Operational Street Pollution model (OSPM) were scaled up by the annual average daily traffic (AADT) and mean vehicle speed as described in the Supplementary Material, together with details of traffic data validation.

2.2 Data processing

2.2.1 Trend analysis of atmospheric concentrations

Trends in air pollutant concentrations can be driven by changes in meteorological conditions, emissions, atmospheric chemistry or the built environment (Grange and Carslaw, 2019; Malley et al., 2018). When trend analysis is conducted for assessing the success of certain air quality management strategies, the influence of the weather conditions on ambient concentrations should be removed. Thus, we applied the

116 *rmweather* R package (version 0.1.51; Grange and Carslaw, 2019) on hourly concentrations measured at
117 all sites to remove this influence. The package builds Random Forest models that predict hourly NOx (or
118 NO_2) concentrations based on several independent variables, and then estimates the meteorologically
119 normalized series. We used the following explanatory variables: Unix date (number of seconds elapsed
120 since Jan. 1, 1970) representing the trend term, Julian day (day of the year) as the seasonal trend, day of
121 the week, hour of the day, and meteorological variables (Table 1). The importance of the predictor
122 variables on the air pollutant concentrations was also assessed with the *rmweather* package. Further
123 details on the model development and normalization technique are given in the Supplementary Material.
124 The normalized hourly ambient concentrations were aggregated to mean monthly values, which were
125 subsequently used to estimate linear trends by the non-parametric Theil-Sen method (Snell et al., 1996)
126 for each pollutant and site over the common period (1998-2017). The Theil-Sen trend is a median slope
127 trend line resistant to outliers. It was calculated with the *TheilSen* function available in the *openair* R
128 package (Carslaw and Ropkins, 2012), which also computed the confidence intervals at 95% and *p*-
129 values by bootstrap resampling.
130
131 **2.2.2 Calculation of NO_2:NOx emission ratios**
132 We estimated the NO_2:NOx vehicle emission ratios by filtering ambient concentrations of NO_2 and NOx
133 measured at curbside sites following Grange et al. (2017). This technique isolates the primary NO_2
134 component by selecting measurements conducted in periods when the production of NO_2 via the $NO+O_3$
135 reaction is negligible. Thus, we chose only NO_2 and NOx concentrations corresponding to traffic-
136 dominated periods (06:00-18:00 on weekdays), with low O_3 background concentrations. An O_3 threshold
137 of 10 µg m^{-3} was found appropriate to minimize the NO_2 secondary production and still have enough
138 measurements for the emission ratio calculation (more details are provided in the Supplementary
139 Material). For each curbside site and year combination, we calculated the slope of the robust linear

140 regression between the filtered NOx and NO_2 atmospheric concentrations, which is a proxy of the
141 primary NO_2:NOx emission ratio.

142

143 **2.2.3 Determination of EF_{NOx}**

144 For each street canyon and year, hourly EF_{NOx} [g veh^{-1} m^{-1}] were determined for the mixed fleet as
145 follows (Ketzel et al., 2003; Krecl et al., 2018):

146

147 $$EF_{NOx} = \frac{\Delta NOx(t)\, D(t)}{TR(t)}, \quad (1)$$

148

149 where ΔNOx [g m^{-3}] is the measured increment concentration (curbside minus urban background
150 concentrations) due to the emissions of vehicles driving on that street, TR [veh s^{-1}] is the total traffic
151 volume on that street, *D* [m^2 s^{-1}] is the dilution rate and *t* is the time [s]. The dilution rate depends on
152 wind conditions, traffic characteristics (TR and VS) and street canyon geometry, and was computed by
153 inverse dispersion modeling using the OSPM (Berkowicz, 2000). Details on the inverse modeling
154 technique can be found elsewhere (Palmgren et al., 1999; Ketzel et al., 2003).

155 The OSPM has been extensively tested (Kakosimos et al., 2010) and successfully simulates the NOx
156 concentrations at regular street canyons, such as Jagtvej and Hornsgatan (Ottosen et al., 2015). However,
157 an initial screening of our OSPM results revealed abnormally high *D* values (> 24 m^2 s^{-1}) at Marylebone
158 Road site associated with northerly winds with WS > 2.0 m s^{-1}, which we attributed to the more complex
159 street canyon geometry. This wind condition was not very frequent (12%), but may lead to the
160 overestimation of both the dilution and the mean EF_{NOx} values if it prevails for certain hours. Thus, these
161 occurrences were excluded from further analysis.

Only hourly EF_{NOx} values for the period 07:00-23:00 on weekdays were considered for the analysis because (i) the fleet composition is rather similar between weekdays, and (ii) it avoids the large uncertainties in EF_{NOx} calculations associated with the small street increments and low TR, typically observed in the early hours on weekdays (Krecl et al., 2018). Then, mean annual values were calculated for the years displayed in Table 1. Further details on EF_{NOx} calculations and OSPM model setup are given in the Supplementary Material.

2.2.4 Validation with other databases

The EF_{NOx} computed by inverse modeling (Eq. 1) was compared with EF_{NOx_w} calculated by aggregating $EF_{NOx\,i,j,k}$ per vehicle category and weighted according to each category share *n* within the fleet, as follows:

$$EF_{NOx\_w} = \sum_{i,j,k} EF_{NOx\,i,j,k} \cdot n_{i,j,k}\,, \quad (2)$$

where the category is a combination of vehicle class *i*, fuel *j* and Euro standard stage *k*.

$EF_{NOx\,i,j,k}$ were extracted from three sources: (i) the European Monitoring and Evaluation Program (EMEP) guidebook (EMEP/EEA, 2019), (ii) HBEFA V.3.3 handbook processed for typical site-specific traffic conditions by Burman et al. (2019), and (iii) remote sensing studies conducted under urban driving conditions in Europe (UK: Carslaw et al., 2011; Carslaw and Rhys-Tyler, 2013; Carslaw et al., 2019; Ghaffarpasand et al., 2020, and Sweden: Liu et al., 2019; Zhou et al., 2020) (Table 2). We used the HBEFA EF_{NOx} for ethanol and biogas since the other two sources do not include these fuels.

Individual EF_{NOx} largely depends on the vehicle category, and the vehicle category share at national and municipal levels can largely differ from the typical share of the actual fleet driving on the canyon street

for the same year (Burman et al., 2019). Thus, we profited from the detailed in situ surveys of the vehicle fleet on Hornsgatan St. for the years 2009 and 2017 to validate our EF_{NOx} against the EMEP, HBEFA and remote sensing estimates. These surveys analyzed automatic number plate recordings of four million vehicles, and subsequent inquiry of vehicle information from the city municipality provided detailed composition of the fleet in terms of vehicle class, fuel and Euro standard stage (Burman et al., 2019).

3. Results and Discussion

3.1 Trends in ambient concentrations

The most polluted street canyon was Marylebone Road (mean of NOx and NO_2 in 2017: 286.3 and 83.9 µg m^{-3}), followed by Hornsgatan (79.9 and 35.3 µg m^{-3}) and Jagtvej (55.2 and 27.5 µg m^{-3}). The urban background air was cleanest in Stockholm (mean of NOx and NO_2 in 2017: 13.3 and 10.7 µg m^{-3}) followed by Copenhagen (18.4 and 15.3 µg m^{-3}) and London (50.4 and 32.3 µg m^{-3}).

Figure 1 shows the monthly mean NO_x and NO_2 concentrations measured at the street canyon and urban background sites in Copenhagen (1994-2017), London (1998-2017) and Stockholm (1992-2017), together with the street increments of NOx and NO_2 (ΔNOx and ΔNO_2, respectively) and the normalized concentrations. Note that the mean NO_2 annual limit of the EU air quality directive (40 µg m^{-3}) was exceeded every year at the street canyon sites in Copenhagen (1994-2009), London (1998-2017) and Stockholm (1992-2016), and the urban background site in London (1998-2003). The meteorologically normalized series show a decreasing trend in NOx, ΔNOx and (to a lesser extent) NO_2 in Stockholm and Copenhagen over the years, but London presented either modest improvements or increase in concentrations at Marylebone Road (Figs. 1a-f). Over the period 1998-2017, Copenhagen and Stockholm showed similar patterns in concentration reductions: (i) NOx decreased more at curbside (55-60%) than at urban background sites (41-52%), and (ii) NO_2 reductions were smaller than NOx, and declined more at urban background (35-46%) than at street canyon sites (27-35%). London exhibited a different

behavior, with the largest NOx reduction recorded at the urban background site (36%), and no reductions in NO_2 concentrations at the curbside site (Figs. 1b,e).

Although road transport dominates the total NOx emissions in Europe (EEA, 2019), other local and non-local sources might have contributed to ambient NOx concentrations at specific sites. Hence, by calculating the NOx increment at the street canyon sites the non-local contributions are filtered out, leaving only the traffic-related contributions from vehicles driving on that street. Street increments for NO_2 and NOx were higher for London compared to Stockholm and Copenhagen (Figs. 1g-i), which is consistent with the ADDT values recorded at the canyon streets in the period 1998-2017: 78300, 27500 and 18900 respectively.

In general, the monthly mean concentrations at all sites showed a sawtooth pattern due to meteorologically driven effects on atmospheric mixing and transport and temperature-driven effects on emissions, which were removed after normalization (Fig. 1, orange lines). The analysis of the importance of the explanatory variables of the Random Forest models revealed that the nitrogen oxide concentrations within the street canyons were largely influenced by rooftop-level wind (WD and WS, Fig. S2a, Supplementary Material). This result agrees with Krecl et al. (2015), who reported that recirculation patterns governed the air pollution concentrations within Hornsgatan street canyon (Fig. S2a, Supplementary Material). For example, the site-dependent Random Forest model run in our study was able to capture the recirculation pattern at that site. The meteorologically normalized concentrations showed non-linear associations with WS, with dilution increasing with WS (e.g., Fig. S2b,d, Supplementary Material). The main predictor for the urban background sites was WS, with high NOx concentrations associated with low WS, as also reported by Krecl et al. (2011), while WD had negligible influence. This confirms that the sites can be taken as representative of urban background environment. Kamińska (2019) and Laña et al. (2016) found similar results at other European sites.

In general, seasonal trends played a modest role on NOx concentrations, with lower NOx values observed in summertime. This is most likely due to improved dispersion and reduced emissions, since summer presents lower traffic volume (long holidays) and higher ambient temperatures might decrease NOx emissions for the diesel fleet (Grange et al., 2019).

The trend analysis is very sensitive to the chosen period, as reported by several studies (Grange and Carslaw, 2019; Olstrup et al., 2018). Hence, we focused on the overlapping period 1998-2017 to avoid the influence of site-specific conditions outside these years. Overall, there was a significant downward trend in concentrations (Fig. 2), with NOx decreasing faster than NO_2 in the three cities. At the curbside sites, this pattern is explained by the higher NO_2:NOx emission ratios due to the introduction of some exhaust treatments for diesel vehicles (that convert NO to NO_2) and the accelerated penetration of diesel PC (Grange et al., 2017). At urban background sites, the NO_2 concentrations are mainly controlled by the photochemical conversion of locally emitted NO to NO_2 rather than direct NO_2 emissions (Keuken et al., 2009; Anttila and Tuovinen, 2010). In urban atmospheres highly impacted by NOx emissions, a reduction in NO concentrations reduces the consumption of O_3 by titration (Monks et al., 2015) and, specifically for Europe, the regional background O_3 has been increasing (0.20–0.59 $\mu g\ m^{-3}\ yr^{-1}$ for the annual mean in 1995-2014, Yan et al., 2018). As a consequence, more O_3 is available to oxidize NO to NO_2, causing a steeper downward trend of NO concentrations than NO_2 at the urban background sites.

To facilitate the comparison of the concentration trends among sites with different pollution levels, changes were also expressed as percentage of variation per year over the period 1998-2017 (Fig. 2). The reductions in NOx concentrations in the urban background atmosphere were comparable in Copenhagen and Stockholm (-2.1 and -2.6 % yr^{-1}, respectively). In Denmark, the reduction in NOx emissions is due to the increasing use of catalysts in vehicles, and installation of low-NO_x burners and denitrifying units in power plants and district heating plants (Nielsen et al., 2019). In Sweden, the total decline in NOx emissions is linked to more stringent road transport emission standards, increased use of district heating

and introduction of a NOx fee in 1992 for reducing industrial emissions (Swedish Environmental Protection Agency, 2020). Particularly, the former might be more relevant for Stockholm where road traffic is the dominant NOx source (Johansson et al., 2008). Note that changes in the urban atmosphere can be also affected by variations in the regional concentrations since they have non-negligible contributions (Ellermann et al., 2017; Krecl et al., 2011). The reduction in NOx concentrations in the urban background atmosphere of London was modest (-1.3 % yr^{-1}) compared to the other two cities.

Figure 2 also shows that the negative trends of the NOx street increments in Copenhagen and Stockholm were even larger (-2.6 and -3.0 % yr^{-1}, respectively) than at the urban background sites. These large drops were attributed to variations in the traffic emissions over time, since neither the street canyons nor the adjacent areas underwent any changes in their configuration, and concentrations were already meteorologically normalized. In Denmark, the largest source of NOx emissions is road transport (30% in 2017), with a 65% decrease in the period 1998-2017 (mean of -3.2 % yr^{-1}) (Nielsen et al., 2019). Based on the emission inventories for Sweden in 1998 and 2017 (SCB, 2021), road traffic emissions were the main NOx sources and decreased 48.5% over the 20-year period, which corresponds to -2.4 % yr^{-1}. Thus, this national reduction in traffic emissions is in the same order of the reduction in concentrations found at the street canyon (-3.0% yr^{-1}). In the case of London, the main emission source for NOx was road transport (49%) in the year 2016 (Transport for London, 2016). Road transport also dominates the NOx emissions at national level in the UK (33% in 2017), with a reduction of 67% in the period 1998-2017 (DEFRA, 2020). This represents a reduction of -3.3 % yr^{-1} at UK level, which is far from the small street increment trend at Marylebone Road site (-0.2 % yr^{-1}). This large discrepancy could be explained by the use of emission inventories built with EF_{NOx} that largely underestimate the real emissions in the UK (Carslaw et al., 2011; Carslaw and Rhys-Tyler, 2013) and/or changes in the vehicle fleet composition for certain streets.

In relation to the NO_2 concentration trends, both urban background and curbside sites showed long-term improvements, but smaller for the latter where traffic emissions dominate. London presented the smallest decreases in concentration, with slight positive NO_2 street increment but not statistically significant for the study period (1998-2017). The discussion on the NO_2:NOx emission ratios is further developed in Section 3.2.

3.2 Trends in EF for the vehicle fleet

The annual evolutions of the EF_{NOx} for the vehicle fleet at the three curbside sites over the study period are displayed in Figs. 3a-c. The grey shadows represent the 95% confidence interval of the mean, calculated using the monthly mean values for each year and site. In general, the decreasing trends observed at Jagtvej and Hornsgatan sites for the mixed fleet (Fig. 3 a,c) match the temporal reduction in EF_{NOx} for different vehicle categories/fuel, as reported by remote sensing studies conducted in European urban areas (Tables 2). These results agree with the introduction of new technologies in the vehicle fleet to reduce air pollution emissions. However, the EF_{NOx} pattern was rather constant at Marylebone Road over the period (Fig. 3b), and showed a larger monthly variability.

Inspecting the normalized ΔNOx trends (Figs. 3d-f), we can observe a clear resemblance between the EF_{NOx} trends for Copenhagen and Stockholm (Figs. 3a, c). However, note that the EF_{NOx} value was reported as the mean of the mixed fleet per vehicle whereas the normalized ΔNOx does not consider variations in traffic patterns (volume, speed, or vehicle type share). For example, the "bump" observed in the EF_{NOx} time series at Hornsgatan site in the period 2011-2017 (Fig. 3c) coincided with the reduction in the total TR observed since January 2010, when a ban on studded tires was introduced for the wintertime and which remained over the years (Norman et al., 2016). The normalized ΔNOx was flat for the same period (Fig. 3f), suggesting that total NOx emissions might have not changed, but increased per vehicle. We hypothesize that this increase in EF_{NOx} for the mixed fleet at Hornsgatan site could have

been caused by the introduction of buses fueled with 100% Rapeseed Methyl Ester (RME) in 2011, as part of the city of Stockholm's strategy for running the entire bus fleet on renewable fuels and to comply with the Clean Vehicles Directive (2009/33/EC). Note that RME buses emit on average 2.5 times more NOx than the diesel ones with similar engine and after-treatment technology (Table S2, E5 and Selective Catalytic Reduction SCR). In the year 2011, 10% of the public bus fleet was fueled with 100% RME (Johan Böhlin, personal communication, Feb. 2021), and the RME bus consumption doubled in 2014 (Clean Fleets, 2014). This information is consistent with the fast increase in RME sales in the Stockholm county in the period 2011-2017 (Stockholms stad, 2021). The reduction observed in EF_{NOx} after the year 2015 might be mainly associated with the introduction of newer bus engines and/or cleaner exhaust after-treatment technologies for NOx emissions.

The ΔNO_x trend at Marylebone Road demonstrates that, despite all the measures implemented for NOx control, the total emission remained stable since 2002. According to Font and Fuller (2016), the ΔNOx trends in London showed a large spatial heterogeneity in the period 2005-2014. They found that increasing ΔNOx trends were experienced on streets with increasing number of buses per day, such as Marylebone Road in 2010-2014. Conversely, ΔNOx reductions were associated with a lower traffic volume of buses and/or retrofitted buses with cleaner technologies (such as SCR + Diesel Particulate Filter DPF, Carslaw et al., 2015).

The time evolution of the NO_2:NOx emission ratios for the vehicle fleet is displayed in Figs. 3g-i for the three canyon sites. The interpretation is complex because the mean emission ratio for the whole fleet is influenced by the large variation observed with vehicle category/fuel and Euro standard stage (Tables 2). The fraction of primary NO_2 emissions also depends on the exhaust after-treatment (particularly for buses, Table S2, Supplementary Material), vehicle mileage (Carslaw et al., 2019), mean VS (Grice et al., 2009), ambient temperature (Grange et al., 2019), and engine load (Carslaw et al., 2011; Carslaw and Rhys-Tyler, 2013). Moreover, differences in emission ratios vary considerably from manufacturer to

manufacturer even for the same Euro standard stage and model year (Bernard et al., 2018; Carslaw et al., 2019).

Grange et al. (2017) showed a clear positive trend in annual mean NO_2:NOx emission ratios for 61 European cities between 1995 and 2010. This trend can be attributed to the wide use of diesel oxidation catalysts (DOC) on PC −that target CO and hydrocarbons, but intentionally convert NO into NO_2 (Fiebig et al., 2014; Russell and Epling, 2011). Remote sensing studies confirm the increase of the NO_2:NOx emission ratios with the introduction of DOC in E3 diesel PC (Table 2). The overall impact of these primary NO_2 emissions became important due to the dieselization of the European PC fleet, driven by improvements in fuel economy and supposed CO_2 emission reduction (Cames and Helmers, 2013).

This dieselization process was strong in the three countries (Figs. 3j-l) with the help of government incentives (Cames and Helmers, 2013). Even though the emission ratios are slightly higher for diesel LCV than for diesel PC for certain Euro stages (Table 2), diesel PC have become abundant at national and urban street levels in more recent times. For example, the shares of diesel PC and LCV in relation to the total fleet on Hornsgatan St. were 33 and 13% in 2017 vs. 17 and 11% in 2009. Note that when the shift towards the use of diesel fuel in PC at the expense of gasoline occurred, increasing NO_2:NOx emission ratios were clearly observed at Jagtvej and Hornsgatan sites until 2008 and 2010, respectively (Figs. 3g,i). The decay in primary NO_2 emissions observed afterwards might be explained by the development of more efficient DOC systems by the car manufacturers (Carslaw et al., 2016; Carslaw et al., 2019). E6 standards introduced tighter limits for NOx emissions, and diesel PC were also equipped with NOx after-treatment systems that increased the NO_2:NOx emission ratios again (Table 2, E6). Jagtvej and Hornsgatan experienced this increase in emission ratios but differences in time and magnitude might be explained by the composition of the diesel PC fleet per manufacturer group, given the large variations reported by Carslaw et al. (2019). Finally, the absolute NOx and NO_2 emissions remained low

in the period matching the E6 stage, and reductions in ΔNOx and ΔNO_2 were found at Jagtvej (Figs. 2g,j) and Hornsgatan sites (Figs. 2i,l).

Note that certain particular characteristics of the vehicle fleet might arise when analyzing the behavior of NO_2:NOx emission ratios for individual cities and sites. Notably, Marylebone Road showed the maximum peak value (23 vol. %) in 2005 and dropped thereafter (Fig. 3h). This site was largely affected by changes in the urban bus engines and exhaust after-treatment technologies, since the number of buses operating on that street is high (e.g., 1473 buses per weekday in 2003). For example, the steep increase in ratios observed between 2002 and 2003 was attributed to the retrofitting program of London urban buses (E3 stage) with continuously regenerating particle traps (formed by a combination of DOC and DPF, Grange and Carslaw, 2019) and an increase in buses as part of the London congestion charge scheme (Givoni, 2012). The decline in ratios after 2008 was linked to the introduction of buses with newer and cleaner technologies and removal of old buses (Grange and Carslaw, 2019). The peak and decay of NO_2:NOx at Marylebone Road were observed earlier than those in inner London (Carslaw et al., 2016) and we hypothesize that this shift might be due to the different implementation stages in the bus retrofitting programs and bus fleet renewal, depending on the analyzed street. Even though buses largely influence the emissions at Marylebone Road, the contribution of the diesel PC to the emission ratios cannot be ruled out because of their large number (Fig. 3k).

3.3 Comparison of EF_{NOx} at Hornsgatan with literature data

Figure 4 shows the mean EF_{NOx} for the mixed fleet at Hornsgatan site in the years 2009 and 2017 extracted from the EMEP and HBEFA databases, urban remote sensing studies (Table 2), and the results based on inverse modeling. Regardless of the method, lower EF_{NOx} values were found in 2017 than in 2009, following the general trend of decreasing NOx emissions with the introduction of new engines and after-treatment systems.

For both years, the EMEP-based EF_{NOx} presented the lowest values (0.73 and 0.51 g km^{-1} veh^{-1} in 2009 and 2017, respectively), whereas the results based on HBEFA and remote sensing studies were very similar (1.13 and 1.19 g km^{-1} veh^{-1} in 2009; 0.92 and 0.98 g km^{-1} veh^{-1} in 2017). This similarity might be explained by the update of the HBEFA database (V.3.3) with EF_{NOx} of diesel PC for E4-E6 stages, considering new laboratory and real-world measurements (portable emission monitoring systems and remote sensing data), after compelling evidence that these EF were lower than in-use vehicles studies (Carslaw et al., 2011; Carslaw and Rhys-Tyler, 2013). The EF_{NOx} presented in the EMEP guidebook were developed with the COPERT model, which has been reported to predict lower NOx emissions than the HBEFA database under stop-and-go traffic conditions in cities, particularly for diesel vehicles (Borge et al., 2012). A recent UK study (Davison et al., 2021) also found that the national inventory –that heavily relies on the COPERT database– underestimates the NOx emissions from PC and LCV up to 47% in urban areas compared with emissions calculated with real-world EF_{NOx} from remote sensing studies.

The inverse modeling results presented the highest mean values for both years (1.72 and 1.35 g km^{-1} veh^{-1} in 2009 and 2017, respectively). The weighted EF_{NOx} calculations at Hornsgatan street using mean values per vehicle category from remote sensing data (Table 2) was a conservative approach. Considering the upper 95% confidence interval of EF_{NOx} for each vehicle category yielded weighted EF_{NOx} values much closer to those obtained with inverse modeling (1.69 and 1.23 g km^{-1} veh^{-1} in 2009 and 2017, respectively). Moreover, most of the remote sensing studies were conducted in the UK (Table 2), where ambient conditions and the mix of on-road vehicle manufacturers and engine sizes might be different from Hornsgatan St. Thus, all these factors could have contributed to the EF_{NOx} differences between inverse modeling and remote sensing methods.

3.4 Study strengths and limitations

As far as we know, this is the first study to analyze the trends of real-world EF_{NOx} for the vehicle fleet at the same locations over two decades. Previous studies analyzed NOx emission trends using only street increment concentrations as a proxy, or remote sensing measurements. Our approach (inverse modeling) presents advantageous features since: (i) we delivered EF_{NOx} rather than NOx street increments; this means that we addressed variations in traffic patterns that can largely influence emissions, and (ii) we assessed the overall effectiveness of policies for reducing the fleet emissions over a long time period. Although remote sensing studies provide individual EF_{NOx} for a large vehicle sample, they might not cover the entire fleet particularly on busy roads with several lanes. Moreover, remote sensing field campaigns are short and traffic and ambient conditions might not be representative of the entire year.

This study was limited to the analysis of three paired sites because of the reduced availability of long-term measurements. Hence the transferability of the results to other streets in the same cities should be done cautiously, considering site-specific features and local traffic policies.

4. Conclusions

The Euro standard limits for new road vehicles have been successful in reducing NOx vehicle emissions in the studied sites and the ambient concentrations over time, except for Marylebone Road. This busy street canyon –which experienced an increase in bus traffic since 2003– masked the modest effects of the Euro standard limits on citywide road traffic emissions in London, as shown by the reduction in NOx concentrations in the urban background atmosphere. The NO_2:NOx emission ratios showed a positive trend until 2008-2010, which was also reflected in the NO_2 ambient concentrations. This increase was associated with a strong dieselization process and the introduction of new after-treatment technologies that targeted the emission reduction of other species (greenhouse gases, carbon monoxide or particulate matter). Thus, while regulations on ambient concentrations of specific species have positive effects on human health, the overall outcomes should be considered before widely adopting them.

Our results suggest revising the low EF_{NOx} values presented in the EMEP guidebook for vehicle emissions, since they are used to compile official national inventories in Europe, estimate the exposures of population to air pollutants and of ecosystems to acidification and eutrophication. Finally, this work showed the relevance of long-term observations combined with dispersion modeling to detect trends, to assess the effectiveness of programs aimed at improving the urban air quality, and to validate emission estimates based on models and laboratory tests.

Supplementary Material

Details of air pollution sampling sites, traffic data, meteorological normalization of ambient concentrations, calculation of NO_2:NOx ratios, determination of EF_{NOx} for the mixed fleet, partial dependence plots, and review of real-world EF_{NOx} for urban buses are available.

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Tables

Table 1. Details of the sites and datasets used in this study.

City	Site	Type	Variables	Period
Copenhagen	Jagtvej	Street canyon	NOx, NO_2, TR, VS	1994-2017
	H.C. Ørsted	Urban background	NOx, NO_2, O_3	
	H.C. Ørsted	Meteorology	T, RH, WS, WD	
London	Marylebone Road	Street canyon	NOx, NO_2, TR, VS	1998-2017
	North Kensington	Urban background	NOx, NO_2, O_3	
	Heathrow	Meteorology	T, RH, P, WS, WD	
Stockholm	Hornsgatan	Street canyon	NOx, NO_2, TR, VS	1992-2017
	Torkel	Urban background	NOx, NO_2, O_3	
	Högdalen	Meteorology	T, P, WS, WD	

T: air temperature, RH: relative humidity, WS: wind speed, WD: wind direction, P: atmospheric pressure

Table 2. Mean EF_{NOx} and NO_2:NOx emission ratios for several vehicle categories, taken from remote sensing studies conducted in European cities (UK: Carslaw et al., 2011; Carslaw and Rhys-Tyler, 2013; Carslaw et al., 2019; Ghaffarpasand et al., 2020, and Sweden: Liu et al., 2019; Zhou et al., 2020).

Variable	Euro stage	PC gasoline	PC diesel	LCV diesel	Truck (<12 t) diesel	Truck (>12 t) diesel	[a]Urban bus diesel
EF_{NOx}	E0	2.38	1.22	1.46	5.36	[b]n.a.	n.a.
[g km^{-1} veh^{-1}]	E1	1.59	1.24	2.27	3.44	n.a.	11.13
	E2	1.05	1.30	2.01	5.95	13.01	12.35
	E3	0.41	1.23	1.83	5.33	10.61	15.58
	E4	0.23	1.00	1.57	5.09	7.75	16.93
	E5	0.14	1.02	1.86	5.33	7.59	12.78
	E6	0.19	0.51	0.67	2.64	0.74	2.40
NO_2:NOx	E0	3.2	10.8	7.6	6.2	n.a.	n.a.
[vol. %]	E1	2.8	16.8	12.5	11.0	n.a.	11.0
	E2	3.1	8.1	8.4	21.0	11.7	15.4
	E3	4.1	14.9	13.2	12.3	15.8	8.9
	E4	5.6	22.5	23.0	6.2	2.9	8.0
	E5	8.4	18.8	15.5	6.4	4.9	11.3
	E6	10.5	21.7	24.2	15.2	22.5	17.9

[a]A large variation could be observed within the same Euro stage, depending on the after-treatment system (Table S2, Supplementary Material). [b]Not available.

Figure captions

Figure 1. Monthly mean NOx and NO_2 concentrations at curbside and urban background sites (a-f), together with NOx and NO_2 street increment concentrations (g-l). The orange lines represent the meteorology-normalized concentrations. Note the different y-axis scales adopted to enhance the features in the time series of each site.

Figure 2. Yearly trends (bar plots; in $\mu g\ m^{-3}\ yr^{-1}$) and relative changes (numbers; in $\%\ yr^{-1}$) in NOx (a) and NO_2 (b) concentrations for the three cities over the period 1998-2017, based on monthly mean changes in meteorologically normalized air pollutant concentrations at urban background and curbside sites, together with street increments. The error bars show the 95% confidence intervals of the trends. *Indicates that the trend is not significant.

Figure 3. a-c) Annual mean EF_{NOx} for the vehicle fleet at the curbside sites, with the grey shadows representing the 95% confidence intervals. d-f) Annual mean ΔNOx concentrations (normalized) at curbside, together with the 95% confidence intervals. g-h) Annual NO_2:NOx emission ratios at curbside with 95% confidence intervals. j-l) Diesel PC penetration in the national markets (International Council on Clean Transportation, 2018) expressed as percentages of all PC (thick black line) and new PC (thin black line), together with Euro standard registration dates (E1: Euro 1, E6: Euro 6).

Figure 4. EF_{NOx} for the vehicle fleet at Hornsgatan site in the years 2009 and 2017 calculated using databases (EMEP and HBEFA), remote sensing studies (Table 2) and by inverse modeling. The error bars represent the 95% confidence intervals of the mean.

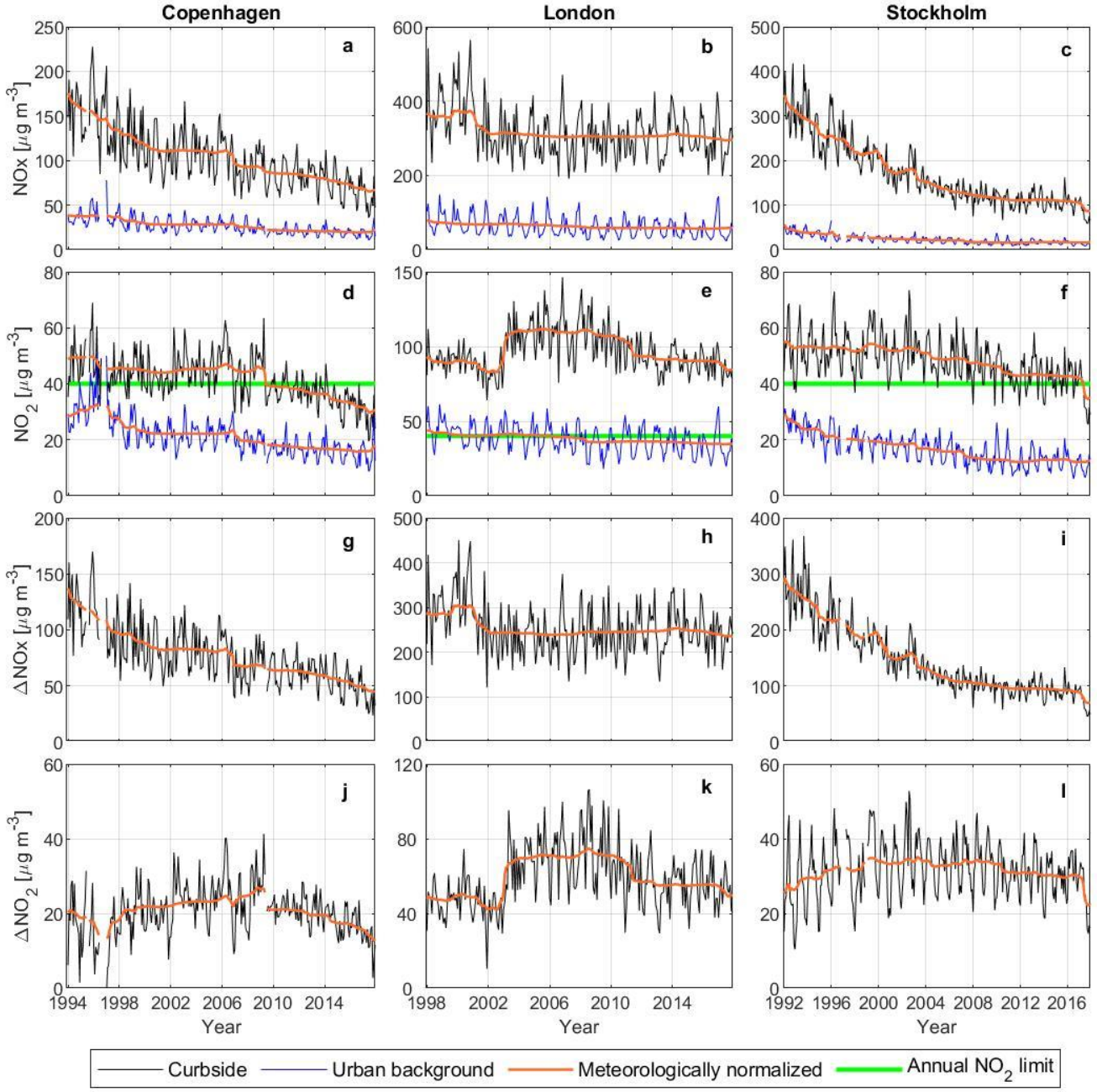
Copenhagen
London
Stockholm
a
b
c
d
e
f
g
h
i
j
k
l
NOx [μg m-3]
NO2 [μg m-3]
ΔNOx [μg m-3]
ΔNO2 [μg m-3]
Year
Curbside
Urban background
Meteorologically normalized
Annual NO2 limit

Figure 1

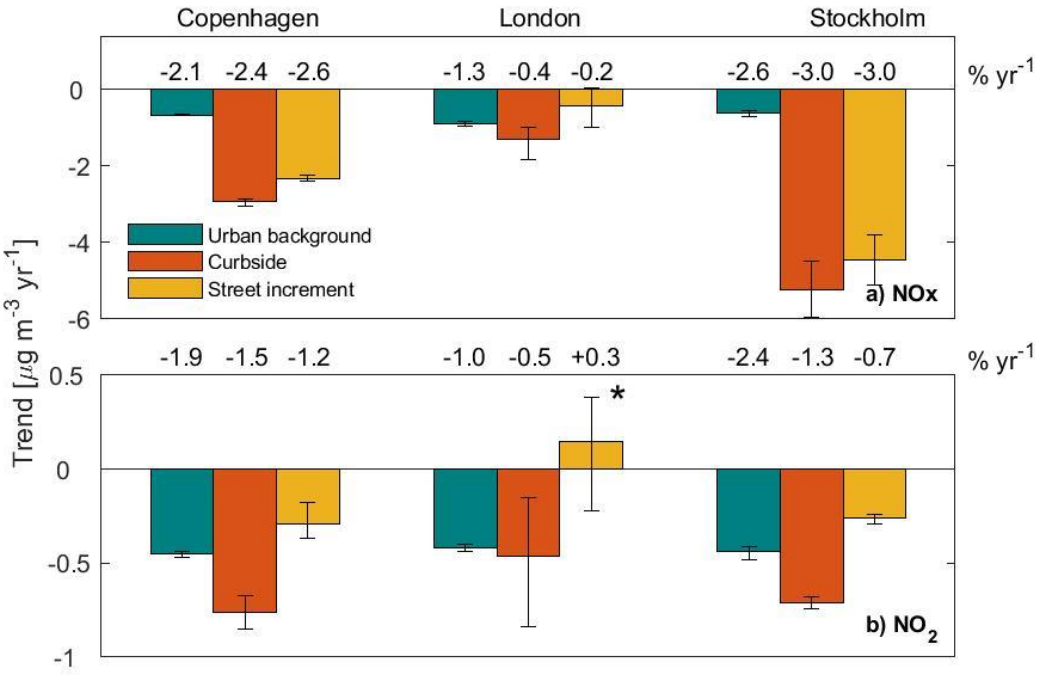
Copenhagen
London
Stockholm
-2.1 -2.4 -2.6
-1.3 -0.4 -0.2
-2.6 -3.0 -3.0
% yr-1
Urban background
Curbside
Street increment
a) NOx
-1.9 -1.5 -1.2
-1.0 -0.5 +0.3
-2.4 -1.3 -0.7
% yr-1
*
b) NO2
Trend [μg m-3 yr-1]

Figure 2

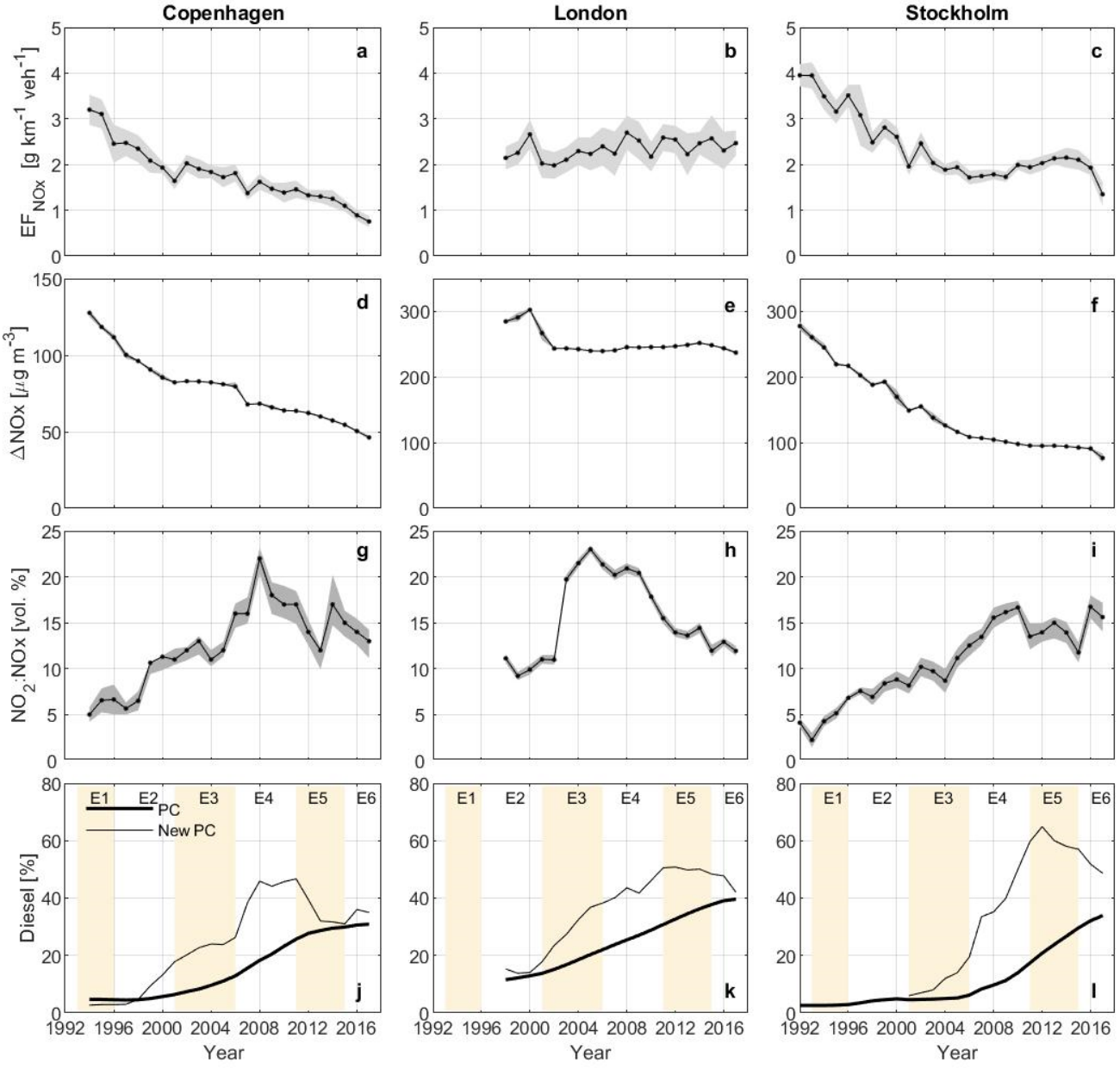
Copenhagen
London
Stockholm
a
b
c
d
e
f
g
h
i
j
k
l
EF NOx [g km-1 veh-1]
ΔNOx [μg m-3]
NO2:NOx [vol. %]
Diesel [%]
PC
New PC
E1
E2
E3
E4
E5
E6
Year

Figure 3

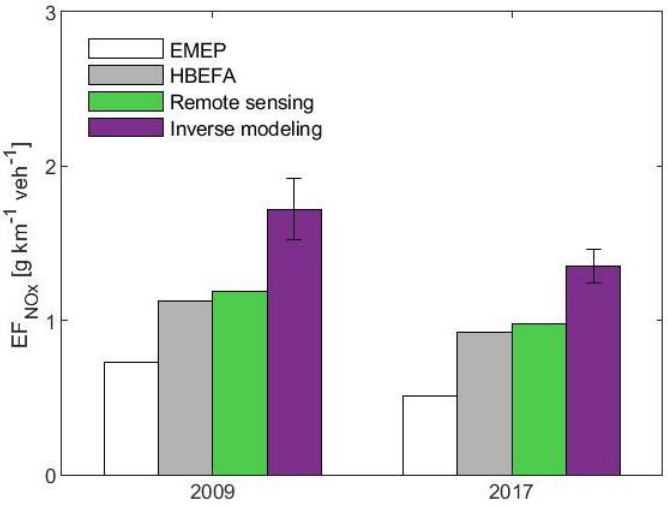
EMEP
HBEFA
Remote sensing
Inverse modeling
EF NOx [g km-1 veh-1]
0
1
2
3
2009
2017

Figure 4