Temporal persistence of intra-urban spatial contrasts in ambient NO2, O3 and Ox in Edinburgh, UK

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Abstract

Ambient NO2, O3 and Ox (the sum of NO2 and O3) are associated with adverse health outcomes. Quantitative assessment of the health burden from these pollutants requires knowledge of small-scale variations in their concentrations in urban environments. In particular, we were interested in the temporal stability of intra-urban spatial contrasts in these pollutants. This was investigated by concurrent measurements of NO2 and O3 by passive samplers at 30 sites in Edinburgh, UK, repeated 12 /2 weeks for NO2 and 6 /2 weeks for O3 in summer and winter. Temporally persistent and large spatial variations in both NO2 and O3 concentrations were observed. Concentrations of NO2 across the sites ranged on average by a factor of 14 between suburban parks and heavily-trafficked roadsides, corresponding to a difference in NO2 on average of ~80 μg m⁻³. Intra-urban O3 concentrations also varied substantially, on average by a factor of 4 (average range 45 μg m⁻³) and with strong anticorrelation to NO2 concentrations across the 30 sites. Consequently intra-urban variability was considerably lower for Ox than for NO2 and O3. The temporal stability in relative NO2 and O3 concentrations indicate potential for deriving intra-urban fields of NO2 and O3 at different times by scaling models of long-term spatial patterns of NO2 and O3 by the measurements at a single site. If Ox is a key determinant of adverse health then the large intra-urban spatial contrasts in NO2 and O3 may be less relevant, with Ox concentrations across an urban area determined at a suitable background site.

1. Introduction

Exposure to the air pollutants nitrogen dioxide (NO2) and ozone (O3) is detrimental to human health (WHO, 2006; WHO, 2013). Quantitative evidence for long-term health effects of NO2 and O3 at the concentrations routinely experienced in ambient air is obtained from epidemiological studies that examine the confidence of spatial correlations between ambient concentrations and adverse health outcomes (WHO, 2006; WHO, 2013). In many cases, these studies assume spatial homogeneity in exposure within relatively large geographical areas around fixed-site monitors (Zanobetti and Schwartz, 2011; Carey et al., 2013; Jerrett et al., 2013). Similarly, when undertaking health impact assessments derived from measurements from fixed-site monitors, spatial homogeneity must again be assumed, which fails to capture variations in health impacts associated with spatial variation in population exposure within that geographical area. However, it is well known that there is substantial spatial variability in NO2 in urban areas (AQEG, 2004; Cyrys et al., 2012). Road traffic and static combustion are major sources of NOx (NO and NO2), and emitted NO reacts rapidly with O3 on the timescale of minutes to yield additional NO2. Since this oxidation of NO to NO2 consumes O3, concentrations of O3 can also exhibit spatial variability in urban areas (Vardoulakis et al., 2005; McConnell et al., 2006; Malmqvist et al., 2014). The chemical inter- conversion between NO2 and O3, coupled with the fact that both are associated with health effects, has also led to recent interest in health effects associated with the entity Ox, the sum of NO2 and O3 (Williams et al., 2014).

Routine measurement of NO2 and O3 (and hence of Ox) at multiple urban sites would be very resource intensive. Thus the aim of this study was to investigate the extent of longer-term temporal stability of patterns of intra-urban spatial variation in NO2 and O3 as a prerequisite for the potential to estimate intra-urban spatial fields.
of NO2 and O3 at different times via scaling models of spatial patterns by routine measurements at a single site. The temporal stability of intra-urban spatial variation was investigated by concurrent measurements of NO2 and O3 by passive samplers across 30 sites in the city of Edinburgh, UK, repeated 12 x 1-weekly for NO2 and 6 x 2-weekly for O3 in summer and winter. Passive diffusion samplers provide a cheap and straightforward approach to undertake simultaneous multi-site measurements of time-averaged concentrations of these pollutants (Lubet et al., 2000). Although deployment of networks of NO2 passive samplers has been undertaken many times previously (Martin et al., 2010; Caballero et al., 2012; Matte et al., 2013), repeated co-deployment of NO2 and O3 in the UK context has been reported only once before (Vardoulakis et al., 2011) and in a substantially smaller network. A further novelty here is the simultaneous investigation of intra-urban Ox.

2. Methodology

The network of 30 passive diffusion tube (PDT) sampling sites was established across an area of ~7 km2 in central and south Edinburgh (Fig. 1), a city of ~490,000 population situated near the east coast of Scotland, UK (55°9’ N, 3°2’ W). The area encompassed a mixture of residences (including streets of 3- and 4-storey terraced flats), local shops, urban and suburban park, and roads with a wide range of traffic flows, but no industry. Sampling sites are described in Table 1 and were selected to span a range of anticipated ambient NO2 and O3 concentrations. Sites adjacent to major roads with UK national classifications were classified as ‘main (A) road’ or ‘secondary (B) road’; sites on less-trafficked roads were classified as ‘minor road’; sites not directly on any roads were classified as ‘off-road’. Site 8 was at the Edinburgh St. Leonard’s ‘real time’ air quality monitoring station (UK-air.defra.gov.uk), providing the opportunity to set the NO2 and O3 concentrations measured at the city’s national network ‘urban background’ site within the range of concentrations measured in the surrounding urban area.

Duplicates NO2 and O3 PDTs were deployed at each site. Wherever possible, tubes were attached to lampposts or traffic signposts at ~2.3 m above ground, a height consistent with UK guidance (Defra WG, 2008). The NO2 tubes were deployed weekly during two six-week blocks in summer (2nd August–13th September 2013) and winter (2nd December 2013–13th January 2014). The O3 tubes were deployed concurrently, but for 2 weeks at a time.

The NO2 PDT measurements followed the protocol established by a UK national working group on behalf of the UK government (Defra WG, 2008). PDTs for NO2 were prepared using standard PDT components (acrylic tubes, rubber caps and stainless steel meshes) from Gradko International Ltd (www.gradko.com). The adsorbent meshes were prepared by soaking in 50% v/v triethanolamine/acetone solution. Tubes were exposed open-ended, in the standard manner. Accumulated nitrite in exposed tubes was determined via the Saltzman reaction and optical absorbance at 540 nm (Heal et al., 1999; Hamilton and Heal, 2004), as per the UK protocol (Defra WG, 2008). PDTs for O3 were obtained prepared from Gradko International Ltd., and returned to their laboratory for analysis by ion chromatography. The analyses undertaken by Gradko International Ltd. are independently verified and accredited by the UK Accreditation Service (UKAS).

3. Results and discussion

The mean (±SD) relative standard deviation (RSD) of PDT duplicates across all NO2 sites and exposures in the summer and in the winter were 8.9 ± 9.7% (n = 162, duplicate data capture 90%) and 11.2 ± 13.0% (n = 164, duplicate data capture 91%), respectively. Mean duplicate RSDs for all O3 PDT measurements in the summer and winter deployments were 13.0 ± 12.2% and 8.1 ± 7.3%, with duplicate data captures of 87% and 94%, respectively. These RSDs are slightly higher than previously reported values of 6.1 ± 5.5% for 1-week duplicate exposures of NO2 PDTs in Edinburgh, UK (Heal et al., 1999), and 7.5 ± 6.1% for 4- or 5-week triplicate exposures for O3 PDTs in Birmingham, UK (Vardoulakis et al., 2009), but are still within normal expectations for duplicate PDT measurements of ambient NO2 concentration (Cape, 2009). The individual site PDT values presented in the rest of this paper are the duplicate means, with no data rejection criteria applied. For 23 measurement periods the value is derived from one tube only because of theft or vandalism of a duplicate. Absence of a PDT value indicates loss of both duplicates.

For O3 PDT measurements at the national network site, correlation r = 0.95 and mean bias = 5 μg m⁻³ (n = 6); for NO2 PDT measurements r = 0.83 and MB = 12 μg m⁻³ (n = 12). Correlation was excellent, indicating the PDT data followed the exposure-averaged concentrations very well, but there was some bias for NO2 measurements at this site. Some bias may arise from the practical constraint that the PDTs were sited a few metres from the network analyser inlet and were therefore not sampling exactly the same air. Although PDTs were deployed as per standard protocol it is known that NO2 PDTs can be subject to some positive biases from within-tube chemical reaction between NO and O3 and/or because air turbulence at the mouth of the tube increases uptake rate above that assumed for diffusion only (Heal et al., 2000; Cape, 2009; Martin et al., 2014). This PDT site was in the middle of an open suburban park, particularly exposed to the wind. However, as shown in Fig. 2a, and discussed below, the inter-site variability in NO2 concentrations exceeded an order of magnitude, far more than the maximum uncertainty of a few 10s % potentially introduced by variation in any biases between different sites and measurement periods. An analysis of the impact of potential bias on inter-site concentration ranges is presented later.

The NO2 concentrations varied substantially across the network of sites in each measurement period (Fig. 2a). However, the trend in the network mean between measurement periods followed very closely the trend in the reference NO2 analyser concentrations measured at site 8. The trend in the network mean O3 concentrations across measurement periods also followed very closely the trend in the reference O3 analyser concentrations at site 8 (Fig. 2b). These consistencies provide confidence in the trends provided by the PDT network, and are consistent with urban-wide background NO2 and O3 concentrations (determined by upwind concentrations and meteorology) superimposed with local NO2 and O3 spatial variability.

In this study there was no significant difference in inter-site mean (and analyser) NO2 concentration between summer and winter (mean ± 1 SD of the six one-week site-averaged concentrations in summer and winter of 37 ± 5 and 34 ± 5 μg m⁻³, respectively) (Fig. 2a). NO2 concentrations are often observed to be lower in summer (Lozano et al., 2011; Caballero et al., 2012; Matte et al., 2013; Dominguez-Lopez et al., 2014), but most of the summer measurements in this work coincided with the annual Edinburgh arts festivals, the biggest collection of festival events in the world, which bring in large number of visitors and corresponding elevations in traffic. The general trend for a small decline in NO2 in winter periods W3 (16–23 Dec) and W4 (23–30 Dec) and rebound in weeks W5 (30 Dec–6 Jan) and W6 (6–13 Jan) is presumed associated with reduced vehicle movements over the Christmas and New Year extended holiday season and a return to normal urban commuting activity thereafter. In contrast to NO2, inter-site mean (and analyser) O3 concentrations differed significantly
Table 1
Sampling locations and site descriptions.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Fixing</th>
<th>Site type</th>
<th>Other observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Esslemont Rd/Mayfield Rd</td>
<td>Fence(^a)</td>
<td>Minor road</td>
<td>Light-controlled junction</td>
</tr>
<tr>
<td>2</td>
<td>Liberton Rd (A701)</td>
<td>Fence(^a)</td>
<td>Main (A) road</td>
<td>Crossing island on light-controlled junction; slope</td>
</tr>
<tr>
<td>3</td>
<td>Cameron Toll Shopping Centre</td>
<td>Lamppost</td>
<td>Off-road</td>
<td>Shopping centre pedestrian entrance</td>
</tr>
<tr>
<td>4</td>
<td>Dalkeith Rd (A7)</td>
<td>Fence</td>
<td>Main (A) road</td>
<td>Crossing island on light-controlled junction</td>
</tr>
<tr>
<td>5</td>
<td>Dalkeith Rd (A7)</td>
<td>Lamppost</td>
<td>Main (A) road</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Dalkeith Rd (A7)</td>
<td>Lamppost</td>
<td>Main (A) road</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>St. Leonard's Hill</td>
<td>Fence(^a)</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>AURN Edinburgh St. Leonard's air quality monitoring station</td>
<td>Fence(^a)</td>
<td>Off-road</td>
<td>UK national urban background station</td>
</tr>
<tr>
<td>9</td>
<td>Cowgate</td>
<td>Lamppost</td>
<td>Secondary (B) road</td>
<td>Tall buildings beside narrow road</td>
</tr>
<tr>
<td>10</td>
<td>Grassmarket</td>
<td>Lamppost</td>
<td>Secondary (B) road</td>
<td>Tall buildings beside narrow road</td>
</tr>
<tr>
<td>11</td>
<td>West Port</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Near bus stop, tall buildings beside narrow road</td>
</tr>
<tr>
<td>12</td>
<td>Thornybank/Home St (A702)</td>
<td>Lamppost</td>
<td>Main (A) road</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Warrender Park Rd/Marchmont St</td>
<td>Signpost</td>
<td>Minor road</td>
<td>Uncontrolled junction</td>
</tr>
<tr>
<td>14</td>
<td>George Square Lane</td>
<td>Signpost</td>
<td>Minor road</td>
<td>Light-controlled pedestrian crossing</td>
</tr>
<tr>
<td>15</td>
<td>Potterow</td>
<td>Fence(^a)</td>
<td>Secondary (B) road</td>
<td>Trees beside road</td>
</tr>
<tr>
<td>16</td>
<td>Melville Drive (A700)</td>
<td>Signpost</td>
<td>Minor road</td>
<td>Nearby bus stop</td>
</tr>
<tr>
<td>17</td>
<td>Marchmont Crescent</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Uncontrolled junction</td>
</tr>
<tr>
<td>18</td>
<td>Beaufort Rd</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Uncontrolled junction</td>
</tr>
<tr>
<td>19</td>
<td>Whitehouse Terrace</td>
<td>Lamppost</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Grange Loan/Blackford Avenue</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Uncontrolled junction</td>
</tr>
<tr>
<td>21</td>
<td>Lauder Rd/Grange Loan</td>
<td>Signpost</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Sciennes</td>
<td>Signpost</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Summerhall Crescent (A700)</td>
<td>Signpost</td>
<td>Main (A) road</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Minto St (A701)</td>
<td>Signpost</td>
<td>Main (A) road</td>
<td>Light-controlled junction</td>
</tr>
<tr>
<td>25</td>
<td>Mayfield Rd/Mentone Terrace</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>W Saville Terrace</td>
<td>Fence(^a)</td>
<td>Secondary (B) road</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>W Saville Terrace/Blackford Avenue</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Crossing island on light-controlled junction</td>
</tr>
<tr>
<td>28</td>
<td>Observatory Rd</td>
<td>Signpost</td>
<td>Off-road</td>
<td>Open area</td>
</tr>
<tr>
<td>29</td>
<td>Max Born Crescent</td>
<td>Lamppost</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Dinmont Drive</td>
<td>Porch pillar(^a)</td>
<td>Off-road</td>
<td>Suburban residence</td>
</tr>
</tbody>
</table>

\(^a\) Tubes at these locations were deployed at a lower height (~1.5 m) than at the other locations (~2.3 m).

Fig. 2. Box plots of the distributions of (a) NO\(_2\) weekly, and (b) O\(_3\) two-weekly, PDT concentrations measured across all sampling sites in summer and winter. The indentations on the boxes indicate the 95% confidence intervals for the median. The whiskers extend to the highest (lowest) data values that are within 1.5 times the inter-quartile range above (below) the upper (lower) quartiles. The markers within each box connected with solid lines are the inter-site mean PDT concentrations each exposure. The open triangles connected with dashed lines are the exposure means of the hourly concentrations measured by the reference analysers at the Edinburgh St. Leonard's national air quality monitoring station. The notation Sx and Wx refers to summer week x and winter week x, respectively, whilst the notation Sxy and Wxy refers to the summer and winter 2-week periods of weeks x and y together.

Fig. 1. Locations of the sampling sites in central-south Edinburgh; inset shows position of Edinburgh within the UK. Site numbers correspond to the descriptions in Table 1. Edinburgh Waverley railway station towards the top of the map is in the centre of the city and is surrounded by shops and commercial premises. The major 'A-road' transport network is coloured in pink. Non-shaded areas indicates areas of parkland. Site 8 is the Edinburgh St. Leonard's national air quality monitoring station.
between season (p < 0.05), with the mean ± 1 SD of the three 2-week site-averaged PDT concentrations in winter (61 ± 8 μg m⁻³) about 1.6 times higher than in summer (37 ± 1 μg m⁻³). Higher O₃ in winter than in late summer in south-east Scotland is expected; the same observation was reported from analyses of O₃ measurements for 2007–10 from the EMEP monitoring sites at Bush, about 10 km south of Edinburgh, and Auchencorth, about 18 km south of Edinburgh (Malley et al., 2014), and reflects the predominance of hemispheric O₃ contributions to O₃ levels in north-west Europe (Derwent et al., 2013; Parrish et al., 2013). The causes are multiple and include longer lifetime of O₃ in westerly air masses and in winter (lower surface deposition to water and to vegetation, and less reactive removal), and substantial recent declines in wintertime NOₓ emissions.

The relative magnitudes and temporal stabilities of the inter-site variations in NO₂ and O₃ between measurement periods were compared by normalising the concentration at each site relative to the variations in the measurement period inter-site mean (xᵢ/ξ). The normalised inter-site variations are shown in Fig. 3, grouped into the four categories of site type. Since the quantity xᵢ/ξ cannot be <0, the log₁₀ values are plotted to reduce asymmetry in the visual presentation of values less than unity. To aid quantitative interpretation of Fig. 3, y-axis values of 0.4, 0.2, −0.2 and −0.4 correspond to xᵢ/ξ ratios of 2.51, 1.58, 0.63 and 0.40, respectively. Four observations are apparent from the figure:

(i) a very large variation in NO₂ across the 30 sites in this network;
(ii) a large variation in O₃ across the 30 sites in this network;
(iii) a strong temporal consistency in the spatial variability of both NO₂ and O₃ concentrations between measurement periods in summer and winter;
(iv) an anti-correlation between NO₂ and O₃ concentrations across the sites.

The spread in NO₂ concentrations across the sites spanned log (xᵢ/ξ) values from about −0.7 to 0.5 (xᵢ/ξ ratios from −0.2 to −3.1) (Fig. 3), i.e. well over an order of magnitude ratio in NO₂ concentrations between sites with highest and lowest concentrations. The average value of this ratio across all exposures was 14. These variations corresponded to a range in NO₂ concentration of ~45 μg m⁻³ on average across all exposures. There is an obvious trend that NO₂ concentrations are lowest at sites close to roads and greatest at the off-road sites. Lowest NO₂ concentrations were in the range 10 μg m⁻³ (summer) to 45 μg m⁻³ (winter) whilst highest O₃ concentrations were in the range 53 μg m⁻³ (summer) to 88 μg m⁻³ (winter) (Fig. 2b). The O₃ concentration measured at the national network urban background site (site 8) was consistently at the higher end of the spread in intra-urban O₃ concentrations measured in this study (Fig. 3).

The scatter plots in Fig. 4 illustrate the anti-correlation in spatial distribution of NO₂ and O₃. The NO₂ PDT concentrations were first averaged over the two one-week periods corresponding to each two-week period of the O₃ PDT measurements, and, for both NO₂ and O₃, the ‘background’ concentration for that period (the mean of the concentrations at the two off-road sites 28 & 30) was subtracted. The latter adjustment removes the effect of variation in background concentration between the measurement periods. Highly significant inverse correlations are revealed (r range of −0.62 to −0.81, p < 10⁻⁶). Although this is expected from the inverse relationship of the two species in the chemical reaction NO + O₃ → NO₂ + O₂, driven particularly by traffic-emitted NO, and has been noted before (Martin et al., 2010; Vardoulakis et al., 2011; Ahmad and Aziz, 2013), these data illustrate the persistence of this relationship over (i) a large network of 30 sites, (ii) a wide range in NO₂ and O₃ concentrations, and (iii) several different time periods.

Recent attention has been given to the potential health associations with concentrations of O₃ (≡ NO₂ + O₃) and the basis that NO₂ and O₃ are both associated with adverse health effects and their concentrations are closely chemically coupled (Williams et al., 2014). Fig. 3 compares the relative inter-site spatial variability in this study of the concentrations of O₃ (the NO₂ and O₃ concentrations were first converted to volume mixing ratio) with those of NO₂ and O₃ individually. The inter-site variability in O₃ is clearly lower than for NO₂ and O₃ individually; mean inter-site RSDs for O₃ in summer and winter exposures were 21% and 15%, respectively, compared with summer and winter RSDs of 66% and 66% for NO₂, and 26% and 21% for O₃. Higher O₃ levels at some individual sites,
particularly sites 2 & 11, can be attributed to strong sources of primary NO\textsubscript{2} from bus emissions at these locations. Additional variability in Ox between sites will also reflect variability in primary NO\textsubscript{2} emissions from nearby sources, but also be a consequence of variability in particular dispersion characteristics that facilitate the NO + O\textsubscript{3} reaction (and variability in individual measurements). Alongside the greater spatial homogeneity in Ox, a key observation is that Ox at site 8, the Edinburgh St. Leonard’s national network urban background site, is in the middle of the distribution of Ox concentrations across all 30 sites, in contrast to the situations for NO\textsubscript{2} and O\textsubscript{3} individually.

The substantial urban spatial gradients in O\textsubscript{3} as well as in NO\textsubscript{2} — reported also in other studies (Lozano et al., 2011; Matte et al., 2013; Malmqvist et al., 2014) — are clearly not captured by sparsely distributed fixed-site monitoring locations. The spatial heterogeneity in exposure to NO\textsubscript{2} and O\textsubscript{3} clearly leads to an underestimate in urban NO\textsubscript{2} exposure and an overestimate in urban O\textsubscript{3} exposure compared with values measured at the urban background site.
However, the strong temporal stability in the patterns of NO$_2$ and O$_3$ concentrations suggest good prospect for ‘imprinting’ relatively straight-forward models of the temporally-averaged spatial patterns of NO$_2$ and O$_3$ onto the data measured at a single network site. This temporal stability of spatial contrasts in NO$_2$ is useful in the context of developing land-use regression models (Eeftens et al., 2011; Wang et al., 2013; Cesaroni et al., 2012) but has not been noted previously for O$_3$. Intra-urban variability was considerably lower for O$_3$ and the concentration at the national network site was in the middle of the range of inter-site O$_3$ concentrations. Therefore, should O$_3$ be further demonstrated to be a key metric of adverse health associated with (long-term) exposure to NO$_2$ and O$_3$, then population exposure to O$_3$ is much better estimated over an urban area by the measurement at a single urban background site than is NO$_2$ and O$_3$.

This study was carried out during a single year in a single urban area, so caution is needed in extrapolation of the findings to other years and locations. The fact that persistence in intra-urban spatial variation in NO$_2$ and O$_3$ is observed over a number of months is evidence that this persistence is maintained over this timescale. There are reasons why the persistence will not hold over extended, year-on-year timescales, such as differential changes in emissions strengths from different sources/sectors. However, the point of this study was to investigate the temporal persistence on intermediate, inter-seasonal timescales as a potential route to estimating subannual temporal changes in spatial pollution. In respect of extrapolation to other urban areas there is no reason to expect that Edinburgh is particularly special, i.e. different, from other comparable urban areas. This work forms a comparator for future studies of whether observations here are representative elsewhere.

4. Conclusions

Temporally persistent variations in NO$_2$ and O$_3$ concentrations were observed in simultaneous measurements of NO$_2$ and O$_3$ by passive samplers at 30 locations in the city of Edinburgh, UK, repeated 12 times (for NO$_2$) and 6 times (for O$_3$) between summer and winter. Concentrations of NO$_2$ ranged by a factor of 14 on average across the locations, or to an average absolute difference in NO$_2$ concentrations of ~80 µg m$^{-3}$, with a clear NO$_2$ concentration gradient from heavily-trafficked main road sites to quieter minor roads to suburban parks. Concentrations of O$_3$ also varied substantially, with a 4-fold range on average, equivalent to an average difference in ambient O$_3$ concentrations of ~45 µg m$^{-3}$. The NO$_2$ and O$_3$ concentrations were strongly anti-correlated across the 30 sites, consistent with the reaction between NO and O$_3$ being important in determining local concentrations. Although many locations had considerably higher NO$_2$ and lower O$_3$ than recorded at the national network monitoring site in this study area, the strong temporal stability in the relative patterns of NO$_2$ and O$_3$ concentrations indicates good prospect to estimate intra-urban spatial fields of NO$_2$ and O$_3$ at different times via scaling of models of spatial patterns to routine measurements at a single site. On the other hand, if Ox (the sum of NO$_2$ and O$_3$) turns out to be an important determinant of adverse health associated with exposure to NO$_2$ and O$_3$ then the greater spatial homogeneity in Ox means that the large intra-urban spatial gradients in NO$_2$ and O$_3$ may be less relevant.

Conflict of interest

We, the authors, hereby certify that we have NO affiliations with or involvement in any organisation or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this paper.

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