Temporal persistence of intra-urban spatial contrasts in ambient NO\textsubscript{2}, O\textsubscript{3} and Ox in Edinburgh, UK

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Abstract

Ambient NO\textsubscript{2}, O\textsubscript{3} and Ox (the sum of NO\textsubscript{2} and O\textsubscript{3}) 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 NO\textsubscript{2} and O\textsubscript{3} by passive samplers at 30 sites in Edinburgh, UK, repeated 12/2-weekly for NO\textsubscript{2} and 6/2-weekly for O\textsubscript{3} in summer and winter. Temporally persistent and large spatial variations in both NO\textsubscript{2} and O\textsubscript{3} concentrations were observed. Concentrations of NO\textsubscript{2} across the sites ranged on average by a factor of 14 between suburban parks and heavily-trafficked roadsides, corresponding to a difference in NO\textsubscript{2} on average of ~80 \textgamma\textpercm\textsuperscript{3}. Intra-urban O\textsubscript{3} concentrations also varied substantially, on average by a factor of 4 (average range 45 \textgamma\textpercm\textsuperscript{3}) and with strong anticorrelation to NO\textsubscript{2} concentrations across the 30 sites. Consequently intra-urban variability was considerably lower for Ox than for NO\textsubscript{2} and O\textsubscript{3}. The temporal stability in relative NO\textsubscript{2} and O\textsubscript{3} concentrations indicate potential for deriving intra-urban spatial fields of NO\textsubscript{2} and O\textsubscript{3} at different times by scaling models of long-term spatial patterns of NO\textsubscript{2} and O\textsubscript{3} by the measurements at a single site. If Ox is a key determinant of adverse health then the large intra-urban spatial contrasts in NO\textsubscript{2} and O\textsubscript{3} 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 (NO\textsubscript{2}) and ozone (O\textsubscript{3}) is detrimental to human health (WHO, 2006; WHO, 2013). Quantitative evidence for long-term health effects of NO\textsubscript{2} and O\textsubscript{3} 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 NO\textsubscript{2} in urban areas (AQEG, 2004; Cyrys et al., 2012). Road traffic and static combustion are major sources of NO\textsubscript{x} (NO and NO\textsubscript{2}), and emitted NO reacts rapidly with O\textsubscript{3} on the timescale of minutes to yield additional NO\textsubscript{2}. Since this oxidation of NO to NO\textsubscript{2} consumes O\textsubscript{3}, concentrations of O\textsubscript{3} 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 NO\textsubscript{2} and O\textsubscript{3}, 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 NO\textsubscript{2} and O\textsubscript{3} (Williams et al., 2014).

Routine measurement of NO\textsubscript{2} and O\textsubscript{3} (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 NO\textsubscript{2} and O\textsubscript{3} as a prerequisite for the potential to estimate intra-urban spatial fields...
of NO$_2$ and O$_3$ 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 NO$_2$ and O$_3$ by passive samplers across 30 sites in the city of Edinburgh, UK, repeated 12 × 1-weekly for NO$_2$ and 6 × 2-weekly for O$_3$ 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 (Lebret et al., 2000). Although deployment of networks of NO$_2$ passive samplers has been undertaken many times previously (Martin et al., 2010; Caballero et al., 2012; Matte et al., 2013), repeated co-deployment of NO$_2$ and O$_3$ 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 km$^2$ 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 NO$_2$ and O$_3$ 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 NO$_2$ and O$_3$ concentrations measured at the city’s national network ‘urban background’ site within the range of concentrations measured in the surrounding urban area.

Duplicate NO$_2$ and O$_3$ 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 NO$_2$ 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 O$_3$ tubes were deployed concurrently, but for 2 weeks at a time.

The NO$_2$ PDT measurements followed the protocol established by a UK national working group on behalf of the UK government (Defra WG, 2008). PDTs for NO$_2$ 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 O$_3$ 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 ($\pm$SD) relative standard deviation (RSD) of PDT duplicates across all NO$_2$ 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 O$_3$ 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 NO$_2$ PDTs in Edinburgh, UK (Heal et al., 1999), and 7.5 ± 6.1% for 4- or 5-week triplicate exposures for O$_3$ PDTs in Birmingham, UK (Vardoulakis et al., 2009), but are still within normal expectations for duplicate PDT measurements of ambient NO$_2$ 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 O$_3$ PDT measurements at the national network site, correlation $r = 0.95$ and mean bias $= 5 \mu g m^{-3}$ ($n = 6$); for NO$_2$ PDT measurements $r = 0.83$ and MB = 12 $\mu g m^{-3}$ ($n = 12$). Correlation was excellent, indicating the PDT data followed the exposure-average concentrations very well, but there was some bias for NO$_2$ 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 NO$_2$ PDTs can be subject to some positive biases from within-tube chemical reaction between NO and O$_3$ 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 NO$_2$ 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 NO$_2$ 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 NO$_2$ analyser concentrations measured at site 8. The trend in the network mean O$_3$ concentrations across measurement periods also followed very closely the trend in the reference O$_3$ 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 NO$_2$ and O$_3$ concentrations (determined by upwind concentrations and meteorology) superimposed with local NO$_2$ and O$_3$ spatial variability.

In this study there was no significant difference in inter-site mean (and analyser) NO$_2$ concentration between summer and winter (mean $\pm 1$ SD of the six one-week site-averaged concentrations in summer and winter of 37 ± 5 and 34 ± 5 $\mu g m^{-3}$, respectively) (Fig. 2a). NO$_2$ 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 NO$_2$ 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 NO$_2$, inter-site mean (and analyser) O$_3$ 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†</td>
<td>Minor road</td>
<td>Light-controlled junction; slope</td>
</tr>
<tr>
<td>2</td>
<td>Liberton Rd (A701)</td>
<td>Fence†</td>
<td>Main (A) road</td>
<td>Crossing island on light-controlled junction</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†</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†</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></td>
</tr>
<tr>
<td>14</td>
<td>George Square Lane</td>
<td>Signpost</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Potterow</td>
<td>Fence†</td>
<td>Secondary (B) road</td>
<td>Light-controlled pedestrian crossing</td>
</tr>
<tr>
<td>16</td>
<td>Melville Drive (A700)</td>
<td>Signpost</td>
<td>Main (A) road</td>
<td>Trees beside road</td>
</tr>
<tr>
<td>17</td>
<td>Marchmont Crescent</td>
<td>Signpost</td>
<td>Minor road</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Beaufort Rd</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Near bus stop</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†</td>
<td>Secondary (B) road</td>
<td>Crossing island on light-controlled junction</td>
</tr>
<tr>
<td>27</td>
<td>W Saville Terrace/Blackford Avenue</td>
<td>Signpost</td>
<td>Secondary (B) road</td>
<td>Open area</td>
</tr>
<tr>
<td>28</td>
<td>Observatory Rd</td>
<td>Signpost</td>
<td>Off-road</td>
<td></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†</td>
<td>Off-road</td>
<td>Suburban residence</td>
</tr>
</tbody>
</table>

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

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**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.

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**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 \(\pm 1\ SD\) of the three 2-week site-averaged PDT concentrations in winter \((61 \pm 8 \mu g \text{ m}^{-3})\) about 1.6 times higher than in summer \((37 \pm 1 \mu g \text{ m}^{-3})\). Higher \(O_3\) in winter than in late summer in south-east Scotland is expected; the same observation was reported from analyses of \(O_3\) 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 \(O_3\) contributions to \(O_3\) levels in north-west Europe (Derwent et al., 2013; Parrish et al., 2013). The causes are multiple and include longer lifetime of \(O_3\) in westerly air masses and in winter (lower surface deposition to water and to vegetation, and less reactive removal), and substantial recent declines in winter-time \(NO_x\) emissions.

The relative magnitudes and temporal stabilities of the inter-site variations in \(NO_2\) and \(O_3\) between measurement periods were compared by normalising the concentration at each site relative to the variation in the measurement period inter-site mean \((x_i/\bar{X})\). The normalised inter-site variations are shown in Fig. 3, grouped into the four categories of site type. Since the quantity \(x_i/\bar{X}\) cannot be \(<0\), the \(\log_{10}\) 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 \(x_i/\bar{X}\) 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 \(NO_2\) across the 30 sites in this network;

(ii) a large variation in \(O_3\) across the 30 sites in this network;

(iii) a strong temporal consistency in the spatial variability of both \(NO_2\) and \(O_3\) concentrations between measurement periods in summer and winter;

(iv) an anti-correlation between \(NO_2\) and \(O_3\) concentrations across the sites.

The spread in \(NO_2\) concentrations across the sites spanned \(\log (x_i/\bar{X})\) values from about \(-0.7\) to \(0.5\) \((x_i/\bar{X}\) ratios from \(-0.2\) to \(-3.1\) \((\text{Fig. 3})\), i.e. well over an order of magnitude ratio in \(NO_2\) 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 \(NO_2\) concentration of \(100 \mu g \text{ m}^{-3}\) on average across all exposures; highest \(NO_2\) concentrations routinely exceeded \(100 \mu g \text{ m}^{-3}\), whilst lowest \(NO_2\) concentrations varied in the range \(5–16 \mu g \text{ m}^{-3}\) (Fig. 2a). As noted above, there is possible positive bias in \(NO_2\) PDT measurements. A constant bias does not affect ratios of \(NO_2\) concentrations, but does affect the values and ranges of \(NO_2\) concentrations. Sensitivity calculations show that if all PDT concentrations were positively biased by \(20\%\) then the average of the range in \(NO_2\) concentration across all exposures would decrease from \(100 \mu g \text{ m}^{-3}\) to \(85 \mu g \text{ m}^{-3}\); if all PDT concentrations were positively biased by \(50\%\) the average range would be \(68 \mu g \text{ m}^{-3}\). Further sensitivity calculations randomly assigning different positive biases in the range \(0–80\%\) across the PDT measurements indicate that a reasonable value to assign for the average inter-site ratio in \(NO_2\) concentrations remains \(14\), and for the average inter-site range in \(NO_2\) concentrations is \(-80 \mu g \text{ m}^{-3}\). The uncertainties in the \(NO_2\) concentrations do not alter the key observations from Figs. 2a and 3 of substantial spatial variation in ambient \(NO_2\) within a relatively small urban area, and of its temporal persistence across exposures.

As expected, there was a strong association between \(NO_2\) concentration and assigned site category. Concentrations at minor-road and off-road sites were consistently at the lower end of the \(NO_2\) inter-site distribution, including site 8, the location in a suburban park of the city’s national network air pollution monitors. Site 2, a pedestrian crossing at the junction of two heavily-trafficked roads, and site 28, an open area outside the Royal Observatory on Blackford Hill, were almost without exception the sites with highest and lowest \(NO_2\) concentrations, respectively, in each exposure, in both summer and winter. Aside from traffic volume, site-specific topographic and other conditions also influenced the local \(NO_2\) concentrations. For example, \(NO_2\) concentrations were exacerbated at those sites adjacent to light-controlled junctions with regular instances of idling traffic (sites 1, 2, 4, 15 & 27) and in street canyons (sites 9, 10 & 11). Site 2, which had the highest concentrations, as well as being at a major light-controlled intersection along one of the busiest roads (annual average daily flow, AADF, of \(-18,000\)) was also adjacent to a short stretch of uphill start from the junction. The reduced dispersion in the narrow street canyon containing sites 9, 10 & 11 led to higher \(NO_2\) concentrations along this secondary road compared with sites 5 & 6 on a main road with greater volume of traffic. Concentrations were particularly enhanced at site 11 presumed due to its proximity to a bus stop.

The spread in \(O_3\) concentrations across the same network spanned \(\log (x_i/\bar{X})\) values from about \(-0.4\) to \(0.2\), i.e. \(x_i/\bar{X}\) ratios from \(-0.4\) to \(-1.5\) \((\text{Fig. 3})\), and again there was temporal consistency to the spatial pattern of \(O_3\) concentrations between measurement periods. The average value of the ratio of max/min \(O_3\) concentrations across all measurement periods was 4. Although the average variation in ambient \(O_3\) across this network was smaller than for \(NO_2\), this range in \(O_3\) concentration is still substantial and corresponded to differences in absolute \(O_3\) concentration across the network of \(-45 \mu g \text{ m}^{-3}\) on average, across the measurement periods. There is an obvious trend that \(O_3\) concentrations are lowest at sites close to roads and greatest at the off-road sites. Lowest \(O_3\) concentrations were in the range \(10 \mu g \text{ m}^{-3}\) (summer) to \(45 \mu g \text{ m}^{-3}\) (winter) whilst highest \(O_3\) concentrations were in the range \(53 \mu g \text{ m}^{-3}\) (summer) to \(88 \mu g \text{ m}^{-3}\) (winter) \((\text{Fig. 2b})\). The \(O_3\) concentration measured at the national network urban background site (site 8) was consistently at the higher end of the spread in intra-urban \(O_3\) concentrations measured in this study \((\text{Fig. 3})\).

The scatter plots in Fig. 4 illustrate the anti-correlation in spatial distribution of \(NO_2\) and \(O_3\). The \(NO_2\) PDT concentrations were first averaged over the two one-week periods corresponding to each two-week period of the \(O_3\) PDT measurements, and, for both \(NO_2\) and \(O_3\), 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 \((r = -0.62\) to \(-0.81, p < 10^{-6})\). Although this is expected from the inverse relationship of the two species in the chemical reaction \(NO + O_3 \rightarrow NO_2 + O_2\), driven particularly by traffic-emitted \(NO\), and has been noted before \((\text{Martin et al., 2010; Vardoulakis et al., 2011; Ahmad and Aziz, 2013})\), these data illustrate the persistence of this relationship over (i) a large network of 30 sites, (ii) a wide range in \(NO_2\) and \(O_3\) concentrations, and (iii) several different time periods.

Recent attention has been given to the potential health associations with concentrations of \(O_3\) (= \(NO_2 + O_3\)), on the basis that \(NO_2\) and \(O_3\) are both associated with adverse health effects and their concentrations are closely chemically coupled \((\text{Williams et al., 2014})\). Fig. 3 compares the relative inter-site spatial variability in this study of the concentrations of \(O_3\) (the \(NO_2\) and \(O_3\) concentrations were first converted to volume mixing ratio) with those of \(NO_2\) and \(O_3\) individually. The inter-site variability in \(O_3\) is clearly lower than for \(NO_2\) and \(O_3\) individually; mean inter-site RSDs for \(O_3\) in summer and winter exposures were 21% and 15%, respectively, compared with summer and winter RSDs of 66% and 66% for \(NO_2\), and 26% and 21% for \(O_3\). Higher \(O_3\) levels at some individual sites,
particularly sites 2 & 11, can be attributed to strong sources of primary NO$_2$ from bus emissions at these locations. Additional variability in Ox between sites will also reflect variability in primary NO$_2$ emissions from nearby sources, but also be a consequence of variability in particular dispersion characteristics that facilitate the NO + O$_3$ 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$_2$ and O$_3$ individually.

The substantial urban spatial gradients in O$_3$ as well as in NO$_2$ — 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$_2$ and O$_3$ clearly leads to an underestimate in urban NO$_2$ exposure and an overestimate in urban O$_3$ exposure compared with values measured at the urban background site.
concentrations at each site for O3 exposure periods 1–3 in summer (S) and winter (W). The notation Sxy and Wxy refers to the summer and winter 2-week periods of weeks x and y together.

However, the strong temporal stability in the patterns of NO2 and O3 concentrations suggest good prospect for ‘imprinting’ relatively straight-forward models of the temporally-averaged spatial patterns of NO2 and O3 onto the data measured at a single network site. This temporal stability of spatial contrasts in NO2 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 O3. Intra-urban variability was considerably lower for O3 and the concentration at the national network site was in the middle of the range of inter-site Ox concentrations. Therefore, should Ox be further demonstrated to be a key metric of adverse health associated with (long-term) exposure to NO2 and O3, then population exposure to Ox is much better estimated over an urban area by the measurement at a single urban background site than is NO2 and O3.

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 NO2 and O3 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 sub-annual 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 NO2 and O3 concentrations were observed in simultaneous measurements of NO2 and O3 by passive samplers at 30 locations in the city of Edinburgh, UK, repeated 12 times (for NO2) and 6 times for (O3) between summer and winter. Concentrations of NO2 ranged by a factor of 14 on average across the locations, or to an average absolute difference in NO2 concentrations of ~80 μg m⁻³, with a clear NO2 concentration gradient from heavily-trafficked main road sites to quieter minor roads to suburban parks. Concentrations of O3 also varied substantially, with a 4-fold range on average, equivalent to an average difference in ambient O3 concentrations of ~45 μg m⁻³. The NO2 and O3 concentrations were strongly anti-correlated across the 30 sites, consistent with the reaction between NO and O3 being important in determining local concentrations. Although many locations had considerably higher NO2 and lower O3 than recorded at the national network monitoring site in this study area, the strong temporal stability in the relative patterns of NO2 and O3 concentrations indicates good prospect to estimate intra-urban spatial fields of NO2 and O3 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 NO2 and O3) turns out to be an important determinant of adverse health associated with exposure to NO2 and O3 then the greater spatial homogeneity in Ox means that the large intra-urban spatial gradients in NO2 and O3 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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