Atmospheric Pollution Research 7 (2016) 734–741

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Atmospheric Pollution Research

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Original article

Temporal persistence of intra-urban spatial contrasts in ambient NO_2, O_3 and Ox in Edinburgh, UK

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ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form
25 March 2016
Accepted 25 March 2016
Available online 19 April 2016

Keywords:
Air quality
NO_2
O_3
Oxidant Ox
Passive diffusion tube

ABSTRACT

Ambient NO_2, O_3 and O_x (the sum of NO_2 and O_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_2 and O_3 by passive samplers at 30 sites in Edinburgh, UK, repeated 12 × 1-weekly for NO_2 and 6 × 2-weekly for O_3 in summer and winter. Temporally persistent and large spatial variations in both NO_2 and O_3 concentrations were observed. Concentrations of NO_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_2 on average of ~80 μg m^{-3}. Intra-urban O_3 concentrations also varied substantially, on average by a factor of 4 (average range 45 μg m^{-3}) and with strong anticorrelation to NO_2 concentrations across the 30 sites. Consequently intra-urban variability was considerably lower for Ox than for NO_2 and O_3. The temporal stability in relative NO_2 and O_3 concentrations indicate potential for deriving intra-urban spatial fields of NO_2 and O_3 at different times by scaling models of long-term spatial patterns of NO_2 and O_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_2 and O_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_2) and ozone (O_3) is detrimental to human health (WHO, 2006; WHO, 2013). Quantitative evidence for long-term health effects of NO_2 and O_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_2 in urban areas (AQEG, 2004; Cyrys et al., 2012). Road traffic and static combustion are major sources of NO_x (NO and NO_2), and emitted NO reacts rapidly with O_3 on the timescale of minutes to yield additional NO_2. Since this oxidation of NO to NO_2 consumes O_3, concentrations of O_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_2 and O_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_2 and O_3 (Williams et al., 2014).

Routine measurement of NO_2 and O_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_2 and O_3 as a prerequisite for the potential to estimate intra-urban spatial fields

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control (TUNCAP).

http://dx.doi.org/10.1016/j.apr.2016.03.008

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 (±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 μg m^{-3} ($n = 6$); for NO_2 PDT measurements $r = 0.83$ and MB = 12 μg 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 ± 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). 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

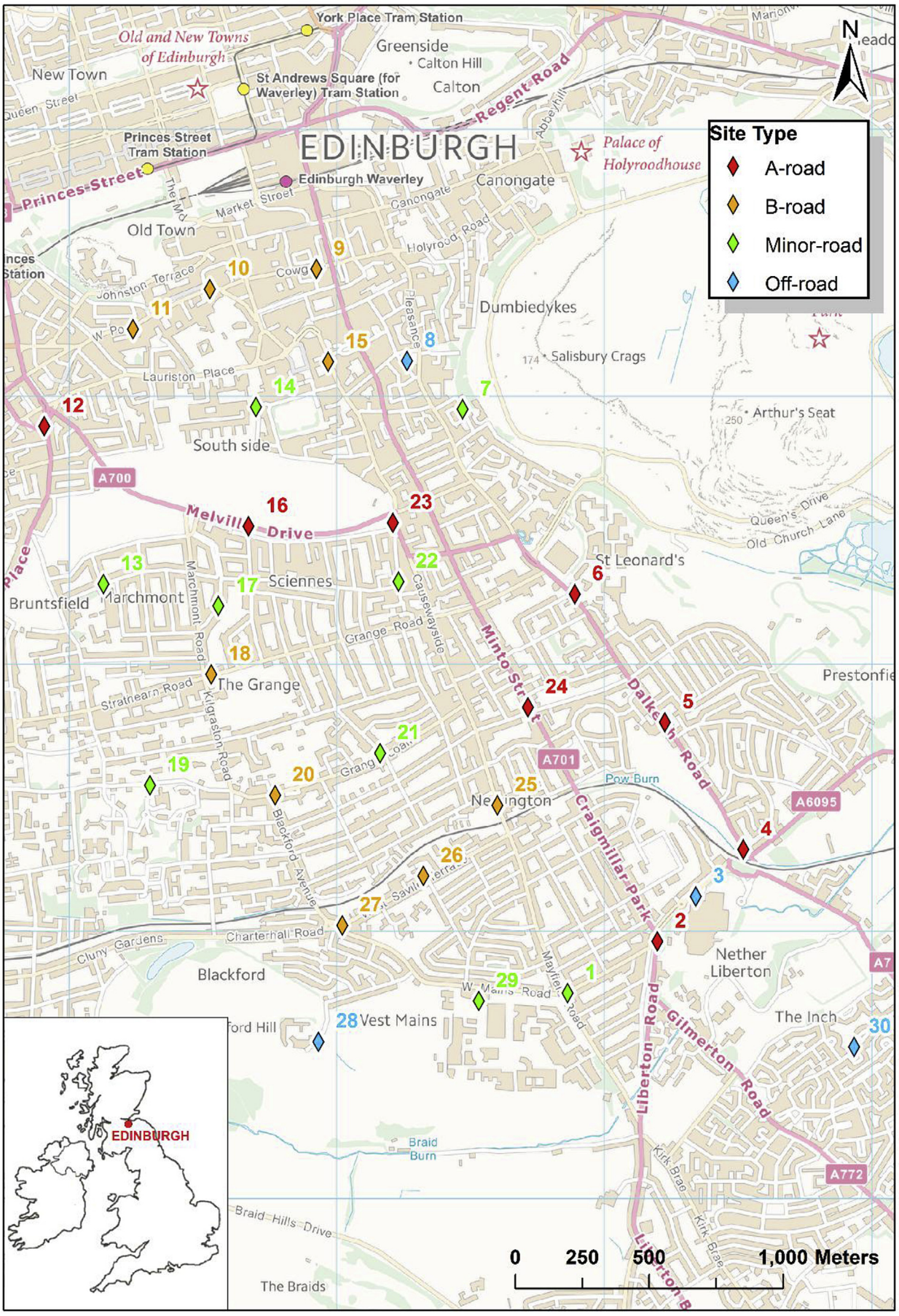
York Place Tram Station
Old and New Towns of Edinburgh
Greenside
Calton Hill
New Town
St Andrews Square (for Waverley) Tram Station
Calton
Regent Road
Princes Street Tram Station
EDINBURGH
Palace of Holyroodhouse
Princes Street
Edinburgh Waverley
Canongate
Market Street
Old Town
Holyrood Road
Dumbiedykes
Salisbury Crags
Arthur's Seat
Lauriston Place
South side
A700
Melville Drive
Queen's Drive
Old Church Lane
St Leonard's
Bruntsfield
Marchmont
Sciennes
Causewayside
Grange Road
Minto Street
Dalkeith Road
Prestonfield
Stratnearn Road
The Grange
Kilgraston Road
A701
Pow Burn
A6095
Craigmillar Park
Blackford Avenue
Charterhall Road
Cluny Gardens
Blackford
Nether Liberton
The Inch
Liberton Road
Gilmerton Road
A772
Braid Burn
Braid Hills Drive
The Braids
Site Type
A-road
B-road
Minor-road
Off-road
N
0 250 500 1,000 Meters
EDINBURGH

Table 1
Sampling locations and site descriptions.

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

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

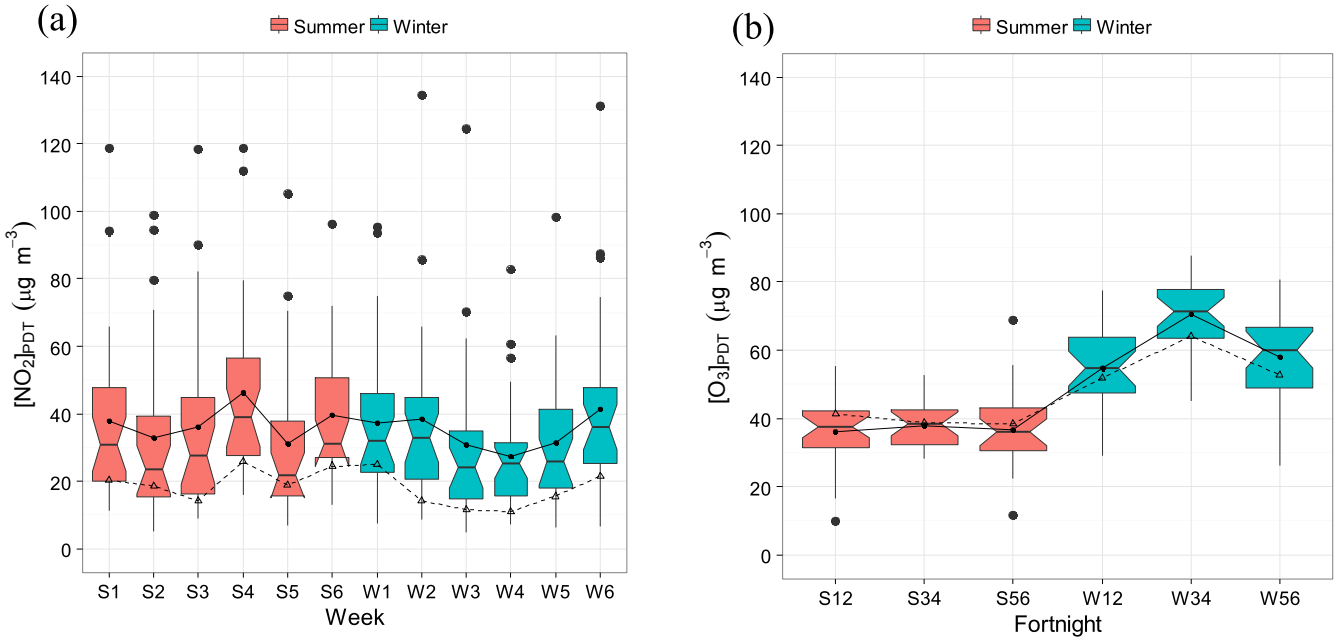

Fig. 2. Box plots of the distributions of (a) NO_2 weekly, and (b) O_3 two-weekly, PDT concentrations measured across all sampling sites in summer and winter. The indentations on the boxes indicate the 95% confidence intervals for the median. The whiskers extend to the highest (lowest) data values that 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 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 wintertime 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 measurement period inter-site mean ($x_i/\overline{x}$). The normalised inter-site variations are shown in Fig. 3, grouped into the four categories of site type. Since the quantity $x_i/\overline{x}$ 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 $x_i/\overline{x}$ 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 ($x_i/\overline{x}$) values from about −0.7 to 0.5 ($x_i/\overline{x}$ ratios from ~0.2 to ~3.1) (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 μg m^{-3} on average across all exposures; highest NO_2 concentrations routinely exceeded 100 μg m^{-3}, whilst lowest NO_2 concentrations varied in the range 5–16 μg 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 μg m^{-3} to 85 μg m^{-3}; if all PDT concentrations were positively biased by 50% the average range would be 68 μg 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 μg 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 ($x_i/\overline{x}$) values from about −0.4 to 0.2, i.e. $x_i/\overline{x}$ ratios from ~0.4 to ~1.5 (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 μg 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 μg m^{-3} (summer) to 45 μg m^{-3} (winter) whilst highest O_3 concentrations were in the range 53 μg m^{-3} (summer) to 88 μg m^{-3} (winter) (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 (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 (range in *r* 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 $NO + O_3 \rightarrow NO_2 + O_2$, 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 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 Ox (= 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 (Williams et al., 2014). Fig. 3 compares the relative inter-site spatial variability in this study of the concentrations of Ox (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 Ox is clearly lower than for NO_2 and O_3 individually; mean inter-site RSDs for Ox 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 Ox levels at some individual sites,

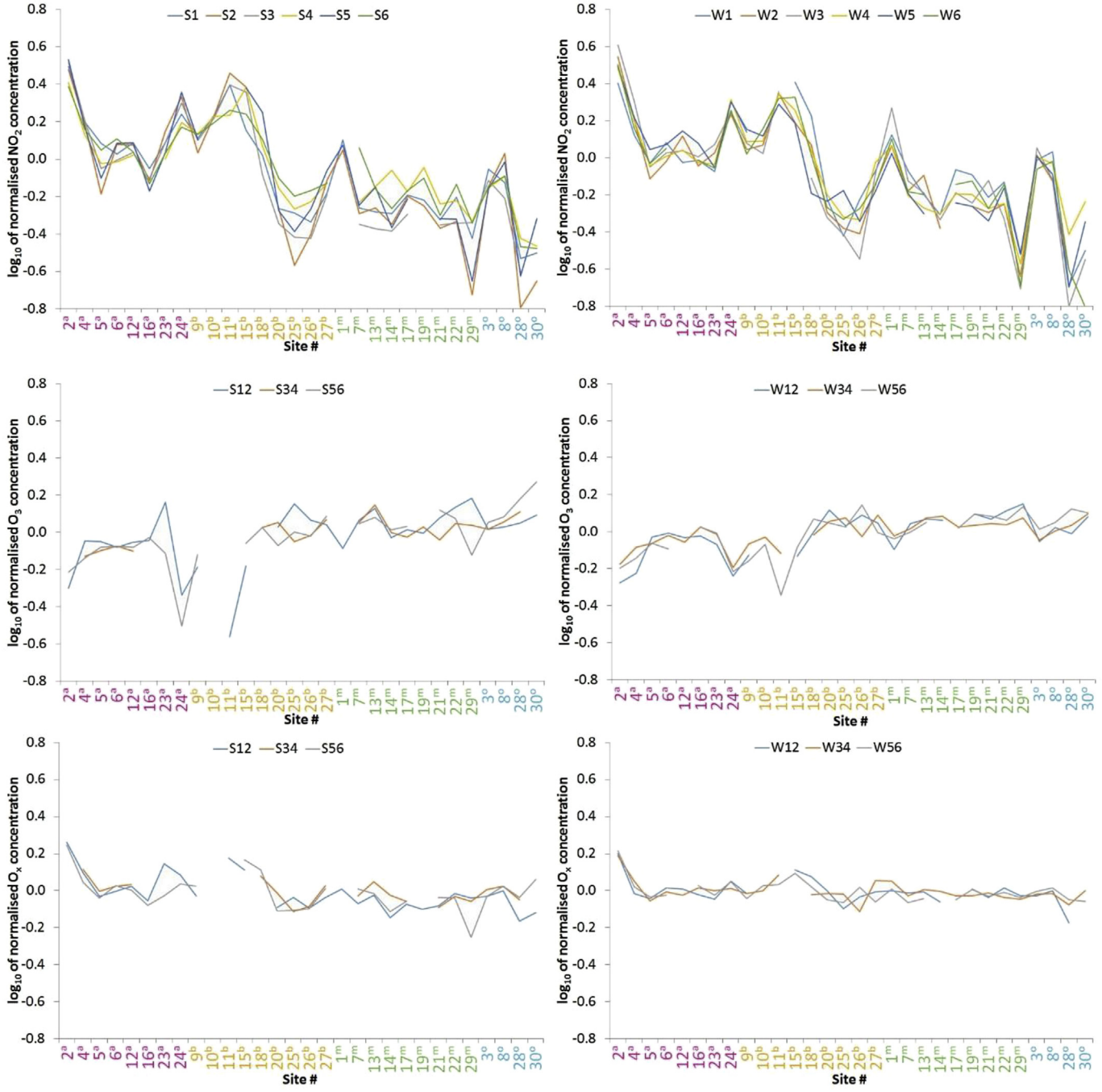

Fig. 3. Log_{10} values of the ratios of NO_2, O_3 and Ox concentrations at each site relative to the exposure period mean. Site numbers correspond to the descriptions in Table 1 and have been grouped according to the four designated site types in the order 'A-road' ([a]), 'B-road' ([b]), 'minor road' ([m]) and 'off-road' (°). Site 8 is the Edinburgh St. Leonard's national air quality monitoring station. Disconnections in lines indicate missing data for that exposure period. Data for Ox are derived after conversion of mass concentrations to mixing ratios. The explanation of the notation for the exposure periods is given in the caption of Fig. 2.

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.

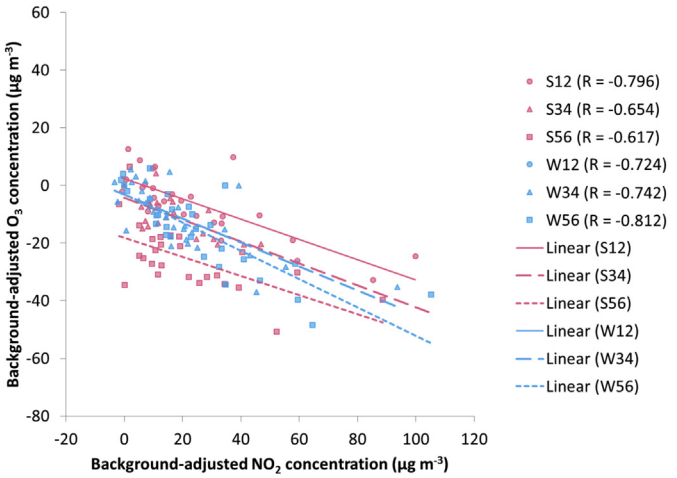

Fig. 4. Relationships between background-adjusted O_3 and NO_2 two-weekly average concentrations at each site for O_3 exposure periods 1–3 in summer (S) and winter (W). The notation Sxy and Wxy refers to the summer and winter 2-week periods of weeks x and y together.

However, the strong temporal stability in the patterns of 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 Ox 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 NO_2 and O_3, then population exposure to Ox 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 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 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.

Acknowledgements

The authors acknowledge the UK Natural Environment Research Council grant NE/I008063/1 for funding, and thank Anthony Newton (University of Edinburgh) for loan of a GPS unit and Wesley Duberstein (Carroll University, USA) for assistance with PDT placement in the summer measurements. Use of data from Defra's Automatic Urban and Rural Network, obtained from uk-air.defra.gov.uk and subject to Crown 2014 copyright licenced under the Open Government Licence (OGL), is also acknowledged.

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