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RESEARCH ARTICLE

Enhancements in nocturnal surface ozone at urban sites in the UK

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Abstract Analysis of diurnal patterns of surface ozone (O_3) at multiple urban sites in the UK shows the occurrence of prominent nocturnal enhancements during the winter months (November–March). Whilst nocturnal surface ozone (NSO) enhancement events have been observed at other locations, this is the first time that such features have been demonstrated to occur in the UK and the second location globally. The observed NSO enhancement events in the UK were found to be so prevalent that they are clearly discernible in monthly diurnal cycles averaged over several years of data. Long-term (2000–2010) analysis of hourly surface ozone data from 18 urban background stations shows a bimodal diurnal variation during the winter months with a secondary nighttime peak around 0300 hours along with the primary daytime peak. For all but one site, the daily maxima NSO concentrations during the winter months exceeded 60 μg/m^3 on >20 % of the nights. The highest NSO value recorded was 118 μg/m^3. During the months of November, December, and January, the monthly averaged O_3 concentrations observed at night (0300 h) even exceeded those observed in the daytime (1300 h). The analysis also shows that these NSO enhancements can last for several hours and were regional in scale, extending across several stations simultaneously. Interestingly, the urban sites in the north of the UK exhibited higher NSO than the sites in the south of the UK, despite their daily maxima being similar. In part, this seems to be related to the sites in the north typically having lower concentrations of nitrogen oxides.

Keywords Nocturnal surface ozone · Urban background stations · Bimodal diurnal variation · UK

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Introduction

Ozone is a highly reactive volatile secondary photochemical air pollutant found in trace concentrations and is an important greenhouse gas (Mickley et al. 2001) which contributes to global warming and climate change (Unger et al. 2006). The precursors of ozone are nitrogen oxides (NO_X) and non-methane volatile organic compounds (NMVOCs), which are short-lived gases, as well as methane (CH_4) and carbon monoxide (CO), which are long-lived gases. Increase in NO_X emissions from preindustrial times to the present day explains about 57 % of the direct rise in the global tropospheric ozone production (Wang and Jacob 1998). Further, increasing emission of CH_4, CO, and NMHCs accounts for the remaining 43 % of the rise in the global tropospheric ozone production through indirectly increasing the ozone production efficiency of NO_X. It is now well known that NO_X, along with volatile organic compounds (VOCs), play a crucial role in controlling the distribution and variability of tropospheric ozone (Jena et al. 2015). The increase of ozone precursor emissions from traffic and industrial activities leads to increased production of

surface ozone (O_3) over polluted regions (Ghude et al. 2008; Kulkarni et al. 2010). The ozone produced near the surface can get lifted into the free troposphere where it has a longer lifetime [~22 days (Stevenson et al. 2006)]) compared to near the surface [~1 day (Royal Society 2008)]; however, lifetime of ozone is highly variable in terms of time of the year and location of measurement. This is of great importance since O_3 formed over source regions can then be transported over large distances affecting areas far from the sources (Li et al. 2002; Doherty et al. 2005; Fehsenfeld et al. 2006; Kulkarni et al. 2009, 2011). High concentrations of O_3 are harmful for humans and plants (Finnan et al. 1997; Ghude et al. 2014). As per the European directive on ambient air quality (Directive 2008) for the protection of human health, the maximum daily 8-h mean O_3 concentration should not exceed 120 μg/m^3 on more than 25 days per calendar year averaged over 3 years and for the protection of vegetation, the value of AOT40 (accumulated amount of ozone over the threshold value of 80 μg/m^3 (Directive 2008)) calculated during May to July should not exceed 18,000 μg/m^3/h averaged over 5 years.

At urban sites, under clear sky conditions, O_3 concentrations exhibit a marked diurnal variation (Zhang et al. 2004) with a maximum during the afternoon and minimum from the late evening until early morning (Aneja et al. 2000). The observed diurnal pattern of O_3 is primarily controlled by changes in the boundary layer height and to some extent by photochemical production during the day and dry deposition (Pio et al. 2002), all of which are influenced by the geographical location of the measurement site. Typically, a shallow and stable nocturnal boundary layer (NBL) is formed during the evening, and with no sunlight, there is no source of O_3 production. Furthermore, nitrogen oxide (NO) emitted from local urban sources reacts with O_3 producing nitrogen dioxide (NO_2) and destroying O_3. This, combined with efficient loss of O_3 through surface deposition, results in minimum O_3 concentrations during the late evening/early night. Above the NBL, there is the residual layer (RL), which acts as a reservoir of O_3-rich air (Kuang et al. 2011), as it is not subject to the same loss processes as the NBL. After sunrise, the NBL and RL merge to give a well-mixed, deep boundary layer (BL). This, along with photochemical production of O_3, leads to increasing surface O_3 concentrations which maximize in the afternoon (Aneja et al. 2000). The diurnal pattern of O_3 at suburban and rural sites is almost the same, but the differences between daytime and nighttime concentrations are less pronounced.

On calm nights, O_3 generally has a positive gradient from the surface to the top of the NBL (Stutz et al. 2004; Geyer and Stutz 2004). This is due to insufficient downward mixing caused by the nocturnal capping of the boundary layer (Kuang et al. 2011) and due to the trapping of O_3 produced during the daytime in the RL aloft.

However, sporadic nocturnal surface ozone (NSO) enhancements have been observed in different parts of Europe, North and South America, and Asia by various researchers (Coulter 1990; Corsmeier et al. 1997; Löffler-Mang et al. 1997; Zhang et al. 1998; Kalthoff et al. 2000 ; Jain et al. 2005; Tong et al. 2011). These are prominent, well-defined phenomena and appear as secondary maxima during the nighttime, with NSO concentrations at times exceeding 100 μg/m^3. In the absence of any known sources of O_3 in the NBL and due to the termination of the photochemical production of O_3 during nighttime, NSO enhancement can likely be attributed to meteorological processes (Salmond and McKendry 2002). Various possible atmospheric mechanisms for the NSO enhancement are proposed by various researchers, some of which are mountain-valley wind system and vertical mixing (Sanchez et al. 2005), sea-land-breeze (Nair et al. 2002), titration of urban O_3 in the late afternoon/early evening followed by vertical mixing (Chan et al. 1998; Leung and Zhang 2001), and transport due to downward vertical wind from the residual layer (Sanchez et al. 2007).

At Essen, Germany, Reitebuch et al. (2000) noted an increased NSO concentration ranging from 26 to 182 μg/m^3 during 29 individual summer measurement campaigns between May 1995 and September 1997. Salmond and McKendry (2002) analyzed O_3 data obtained from multiple surface monitoring sites during a field campaign conducted during the summer 1998 in the Lower Fraser Valley (LFV), British Columbia, Canada, to study the spatial extent of the NSO enhancement. They observed 57 nocturnal spikes in O_3 concentration at different stations within the LFV with NSO concentration as high as 93 μg/m^3. In Jerusalem, Asaf et al. (2009) observed 21 events of NSO concentrations during July 2005–September 2007 with maximum concentration of 120 μg/m^3 in July 2007. One of the various reasons for NSO enhancement is reported as horizontal advection and land breeze circulation. Sousa et al. (2011) studied the effect of horizontal transport on the NSO enhancement and reported the influence of land breeze on NSO at four different costal sites in the North of Portugal during 2005–2007.

WRF-Chem Model studies have also been performed by Wang et al. (2007) over The Pearl River Delta (PRD) and the Yangtze River Delta (YRD) in China, Hu et al. (2012) over Maryland, USA, and Klein et al. (2014) over Oklahoma metropolitan area, USA, to understand the atmospheric mechanisms responsible for the NSO enhancement. Wang et al. (2007) concluded that urbanization and related temperature, wind speed, and the planetary boundary layer (PBL) mixing-layer depth and stability change as the causes for the NSO enhancement, whereas Hu et al. (2012) and Klein et al. (2014) reported the role of low level jets on vertical mixing and downward transport of O_3 as the responsible factor. Depending on the geographical location, boundary layer dynamics, topography, type of environment (urban, suburban,

and rural), and climatic features, or a combination of the aforementioned atmospheric mechanisms and transport processes can contribute to NSO enhancements.

Musselman and Massman (1999) reported that an increased level of NSO plays an important role in determining the negative response of vegetation to O_3. In the majority of the plant species, incomplete stomatal closure is observed during nighttime, leading to high leaf conductance (Caird et al. 2007), exposing plants to nighttime air pollution (Segschneider et al. 1995; Musselman and Minnick 2000; Takahashi et al. 2005). During high O_3 concentrations, stomatal responsiveness may be reduced (Keller and Hasler 1984; Skarby et al. 1987) resulting in water loss and whole-plant production (Matyssek et al. 1995).

NSO enhancements are thought to be isolated, unusual events which are considered to be highly variable in time and space (Löffler-Mang et al. 1997) and, as such, are not expected to be discernible in data averaged over several days (Salmond and McKendry 2002). However, this study for the first time demonstrates the frequent occurrences of NSO in the UK and second time globally [first being Portugal (Kulkarni et al. 2013)] during the study period. The NSO enhancement events occur sufficiently frequently at urban background sites in the UK that they are clearly discernible in monthly diurnal cycles averaged over several years of data. RoTAP (2012) has already analyzed long-term hourly surface ozone data for 11 rural sites in the UK irrespective of day and night. In the current study, surface ozone data from across 18 urban background sites in the UK are analyzed and found to exhibit enhanced NSO concentrations during winter months (November–March) over the period 2000–2010.

Study area and data

The UK is an island nation located in Western Europe. The UK has a total area of 243,610 km^2 and lies between latitudes 49° to 61° N and longitudes 9° W to 2° E. The UK has a coastline 17,820 km long and is surrounded by the North Atlantic Ocean and Irish Sea to the west, with the North Sea in the east, and the English Channel in the south. The UK has a temperate climate and receives rainfall almost all around the year. The UK predominantly experiences south westerly air flow, often in low pressure systems, coming across the Atlantic. The spatial and temporal patterns of O_3 distribution in the UK are reported in detail by the Royal Society (2008) and Air Quality Expert Group-Ozone in the United Kingdom (AQEG-OUK) (2009). As stated in the Royal Society (2008) and AQEG-OUK (2009) reports, the O_3 trends in the UK are basically a combined function of (a) the global scale increase in hemispheric background ozone, (b) regional and local scale photochemical production from ozone precursors emitted across Europe, and (c) reduced removal of O_3 by freshly emitted NO, particularly in urban areas, as a result of reduced NO_X emissions due to the strict policies adopted by the UK for emission control. The peak O_3 concentrations occur under warm and sunny conditions. In the UK, peak O_3 concentrations are observed from April to September and show an overall decreasing trend (Jenkin 2008; Fowler et al. 2008) and in fact have reduced by approximately 60 $\mu g/m^3$ in the last 20–30 years due to the reduction in ozone precursors (NO_X and VOCs) in the UK and Europe (RoTAP 2012). However, the annual mean O_3 concentrations show an increasing trend over the last 20 years: At urban sites, this is due to the reduction in local sources of NO resulting in reduced titration of O_3; in rural areas, this is due to the increase in the concentration of hemispheric background O_3 (AQEG-OUK 2009), which is about 8 $\mu g/m^3$ (RoTAP 2012). The increase in the background concentration of ozone is the result of increased shipping, aircraft, vehicle, and industrial emissions in developing economies (Ghude et al. 2008). As per the AQEG-OUK report (2009), of the 18 urban sites used in this study, 14 sites show a positive trend in the annual mean O_3 concentration (8 statistically significant), one site shows no trend, one a negative trend (not statistically significant), and trends are not available for 2 sites.

Hourly records of O_3 and daily mean surface NO_X (hereafter "daily mean surface NO_X" as NO_X) concentrations are obtained from the 18 air quality monitoring stations representing the urban background environment (defined by EU (Directive 2008/50/EC) and classified by the Department for Environment Food & Rural Affairs (Defra) (http://uk-air.defra.gov.uk/networks/site-types)). Only stations with >85 % data coverage during the period 2000–2010 are used in this study. The monitoring stations are reasonably well spread all over the UK as shown in Fig. 1 (and identified in Table 1), although four stations (LT, LHi, LNK, and LB) are clustered in London, the biggest metropolitan area in the UK, and two stations (Th and SoS) are close to London. The northernmost monitoring station used in this study is located at 55° N, and southernmost is located at 50.9° N. All of these stations are part of the UK-AIR (UK-Air Information Resource), Defra air quality network. The detailed list of stations with information such as name of the stations, latitude-longitude-altitude coordinates, and percentage of data availability is outlined in Table 1. In this study, as per the EU air quality reporting procedures, the unit of the O_3 concentration used is micrograms per cubic meter. In order to facilitate the data analysis and interpretation, the study area (part of the UK shown in Fig. 1, covering 50° N to 55° N) is broadly categorized into two regions, (i) north of UK (NoUK) including all the stations north of 52° N latitude and (II) south of UK (SoUK): including all the stations south of 52° N latitude. Following the categorization of the UK in two regions, 10 of the 18 monitoring stations are located in the NoUK and the remaining 8 in the SoUK. The topography of the northern region tends to be

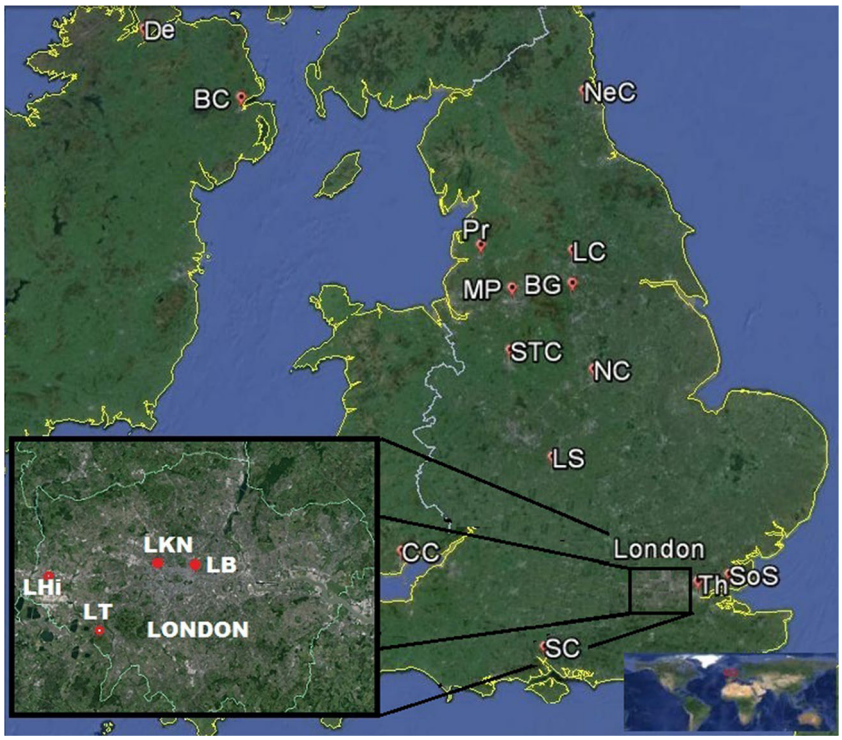

Fig. 1 Map of the UK showing the 18 locations of the urban background monitoring stations considered in the present analysis (Table 1). The *inset* shows five background monitoring stations in the metropolitan city—London

Table 1 Main features of the selected O_3 and NO_X urban background monitoring stations over the UK

Code	Site name[a] (NoUK/SoUK)	UK-AIR ID	Lat	Long	Alt. (m)	A[b]	A (%)	B[c] (μg/m^3)
	NoUK sites							
SC	Southampton Centre	UKA00235	50.908	−1.395	7	3695	91.9	**68.9**
LT	London Teddington	UKA00267	51.420	−0.339	29	3722	92.6	*40.9*
Th	Thurrock	UKA00272	51.477	0.317	8	3744	93.1	**61.9**
CC	Cardiff Centre	UKA00217	51.481	−3.176	12	3673	91.4	*52*
LHi	London Hillingdon	UKA00266	51.496	−0.460	34	3738	93.0	**115.9**
LNK	London N. Kensington	UKA00253	51.521	−0.213	5	3512	87.4	58.6[d]
LB	London Bloomsbury	UKA00211	51.522	−0.125	20	3553	88.4	**103.3**
SoS	Southend-on-Sea	UKA00409	51.544	0.678	37	3482	86.6	*35.7*
	SoUK sites							
LS	Leamington Spa	UKA00265	52.288	−1.533	175	3691	91.8	*41.9*
NC	Nottingham Centre	UKA00274	52.954	−1.146	41	3876	96.4	*65*
STC	Stoke-on-Trent Centre	UKA00337	53.028	−2.175	172	3757	93.5	*58.5*
MP	Manchester Piccadilly	UKA00248	53.481	−2.237	45	3673	91.4	**86.5**
BG	Barnsley Gawber	UKA00353	53.562	−1.510	100	3735	92.9	*37.3*
Pr	Preston	UKA00408	53.765	−2.680	40	3625	90.2	*43.8*
LC	Leeds Centre	UKA00222	53.803	−1.546	78	3770	93.8	**70.8**
BC	Belfast Centre	UKA00212	54.599	−5.928	10	3685	91.7	*58.4*
NeC	Newcastle Centre	UKA00213	54.978	−1.610	45	3790	94.3	*55.7*
De	Derry	UKA00343	55.001	−7.329	32	3701	92.1	31.8[d]

NoUK North of UK, *SoUK* South of UK

[a] Urban background sites

[b] No. of days of surface ozone observation used (only days with ≥75 % [≥1800 h] of data used for diurnal variation study).

[c] Decadal mean surface NO_X concentration (values in bold represents sites with high surface NO_X stations (HSNS) with decadal mean NO_X concentration >60 μg/m^3 and values in italics represents sites with low surface NO_X stations (LSNS) with decadal mean NO_X concentration <60 μg/m^3)

[d] Annual mean surface NO_X concentration for the year 2010 instead of decadal mean

more hilly/mountainous than the south, which is generally quite flat. The climate of the south, particularly the south east is influenced more by the continent, whereas the north typically has a more maritime climate. The sites in the south tend to be in more densely populated urban regions, although there are some exceptions (see Table S1 in Supplementary Material). The urban background NO_X concentration in the SoUK (average of seven urban NO_X monitoring stations collocated with ozone monitoring) is higher than NoUK (average of nine urban NO_X monitoring stations collocated with ozone monitoring) (see Figs. S1, S2, and S3 in Supplementary Material). Similarly, the monitoring stations used in the study are also categorized into two groups: (i) high surface NO_X stations (HSNS), stations with decadal mean NO_X concentration>60 μg/m^3, and (ii) low surface NO_X stations (LSNS), stations with decadal mean NO_X concentration<60 μg/m^3. Following the categorization of the monitoring stations used in the study in two groups, 7 of the 16 monitoring stations are HSNS (4 stations in NoUK and 3 in SoUK), and the remaining 9 are LSNS (2 stations in NoUK and 7 in SoUK). Decadal mean NO_X concentrations for each station are given in Table 1. The analysis of NSO based on the categorization of the monitoring stations in two groups considered 16 stations instead of 18 stations, since at 2 stations (LNK and De), NO_X monitoring only started in 2010.

Result and discussion

Annual diurnal variation of surface ozone

The monthly average diurnal variations (MADV) of O_3 concentration averaged over the 18 urban background stations for the period 2000–2010 are depicted in Fig. 2. It reflects the overall seasonal variation of O_3 concentration in the UK, which exhibits a spring maximum and an autumn minimum at all the UK urban background sites (Jenkin 2008). During the summer months, the diurnal cycles exhibit daytime maxima and nighttime minima, with a slight "shoulder" close to midnight in the decline from the maxima to the minima. During the autumn, this shoulder develops into a peak, such that by the winter, there is a clear bimodal structure with a nighttime maxima that even exceeds the daytime maxima. The highest concentration of daily maximum NSO during the study period was observed at Stoke-on-Trent Centre (118 μg/m^3). In the transition from spring to summer, the nighttime maxima diminish. Kulkarni et al. (2013) observed similar seasonal variations in annual diurnal variation of MADV of O_3 concentration in Portugal with prominent nighttime maxima during winter months but never exceeded the daytime maxima. Similarly, Chung (1977) observed a bimodal structure in the MADV of O_3 concentration at Toronto (~120 μg/m^3) and Montreal (~55 μg/m^3), Canada, during

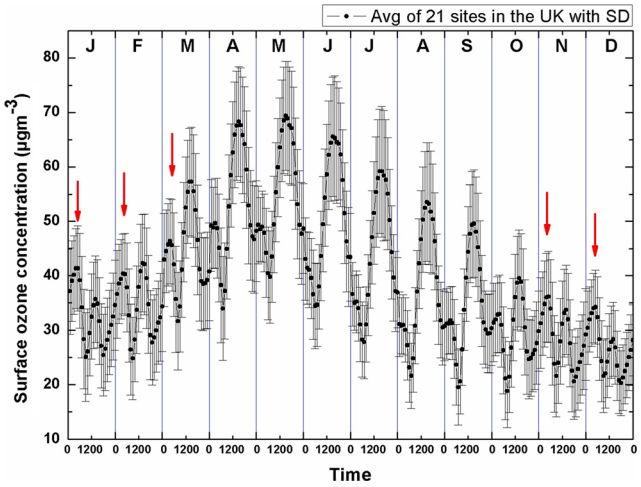

Fig. 2 Average of the monthly averaged diurnal variation of ozone for the period 2000–2010 from 18 urban background monitoring stations from January to December. Each 24-h period represents the monthly averaged diurnal variation for the respective month labeled *J* (Jan) to *D* (Dec). *Vertical bars* are 2σ standard deviation for the spatial variability of 18 sites. The *red arrows* indicate the NSO enhancement in the respective months

summer 1973–1975, Leung and Zhang (2001) and Wang et al. (2001) at Hong Kong (~68 μg/m^3), China, during November–December 1996–1997, Saliba et al. (2006) at Beirut (~50 μg/m^3), Lebanon, during November 2004–February 2005 and Asaf et al. (2010) at Jerusalem (~65 μg/m^3) during winter 2005–2007. The detailed analysis of the winter-time bimodal structure of O_3 concentration is presented in the following subsection ("Bimodal diurnal variation of O3 during winter months").

Over the UK, the highest daytime maximum is observed during April and May with the monthly average (MA) daytime maximum O_3 concentration of 69±10 μg/m^3 in May. Similarly, the lowest MA daytime maximum is observed in December (28±7 μg/m^3). Further, Fig. 3 shows the annual variation of MA O_3 concentrations for specific hours, i.e., 0300, 0800, 1300, and 1800 hours, averaged across all sites in the UK. It shows that during the winter, the MA at 0300 hours is much higher than at 1800 and at 0800 hours. Moreover, the O_3 concentrations at 0300 hours even exceed those at 1300 hours during the months of November, December, and January.

Bimodal diurnal variation of O_3 during winter months

As briefly mentioned in the previous subsection ("Annual diurnal variation of surface ozone"), a bimodal structure is exhibited in the MADV of O_3 concentration during winter, with a daytime maxima during typically around 1300 hours and nighttime maxima typically around 0300 hours. The nocturnal peak is particular prominent during November to January when the nocturnal maxima exhibit higher

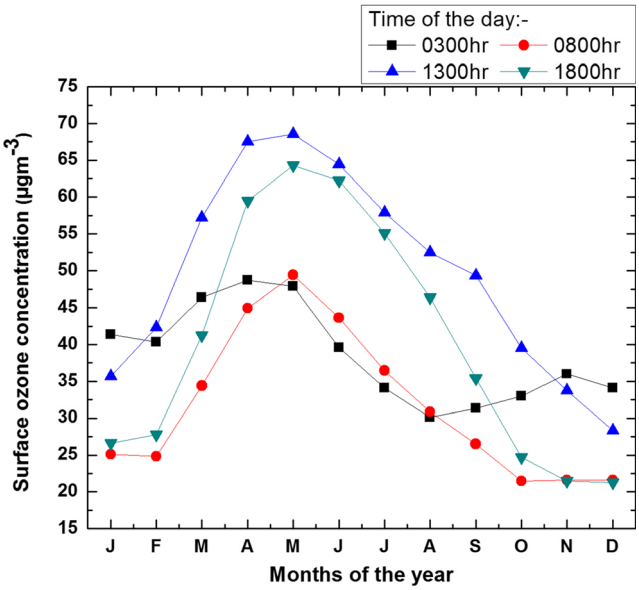

Fig. 3 Annual variation of the average of the monthly averaged ozone for the period 2000–2010 from 18 urban background monitoring stations at (a) 0300 hours (*black*), (b) 0800 hours (*red*), (c) 1300 hours (*blue*), and (d) 1800 hours (*green*)

concentrations than the daytime maxima. The highest nocturnal maximum in the MADV occurs in March (46±7 µg/m^3). Globally, there are very few studies focused on NSO enhancement and almost no studies on a decadal time scale except the one by Kulkarni et al. 2013. Kulkarni et al. (2013) analyzed winter time NSO enhancement on a decadal time scale at three urban background sites in Portugal similar to the urban background sites in the UK; the highest nocturnal maximum in the MADV of O_3 concentration is observed in March with almost the same concentrations (~49 µg/m^3). The appearance of a bimodal structure in the O_3 diurnal cycle when averaged over a month and over several stations (in this case 18 urban background monitoring stations) is only possible if the frequency and magnitude of the enhanced NSO are high and observed at almost all the stations.

To further understand the bimodal diurnal variation of O_3 during winter months, detailed analyses were performed based on (1) regional division of monitoring stations in UK (NoUK vs. SoUK) and (2) division of monitoring stations depending on NO_X concentration in UK (HSNS vs. LSNS) as described in the section "Study area and data". In Fig. 4, the MADV of surface ozone concentrations for NoUK and SoUK regions are depicted (Figs. S4 and S5 [in Supplementary Material] shows MADV of surface ozone concentration for each site in SoUK and NoUK respectively). Interestingly, in the regional division, the nighttime maxima differ significantly between the two regions with the NoUK average NSO being higher for each month compared to SoUK, despite the daytime maxima being very similar for both regions (mean and standard deviations). This pattern is the same for all the winter months. As it can be seen in Fig. 4, the differences

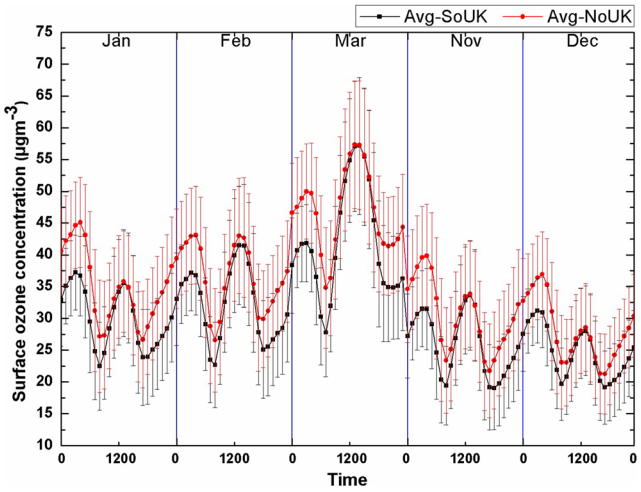

Fig. 4 Average of the monthly averaged diurnal variations of ozone for 8 (black) and 10 (red) urban background monitoring stations from the south and north of the UK for the winter months (November to March) during the period 2000–2010. *Vertical bars* are 2σ standard deviation for the 18 sites

between the two regions in the nighttime peak concentrations are of the order of 9 µg/m^3 in January and November, 7 µg/m^3 in February and December, and 10 µg/m^3 in March. From November to January, the nighttime maxima exceed the daytime maxima for the NoUK region, but this only occurs in December and January for the SoUK.

Similarly, in Fig. 5, the MADV of surface ozone concentration for HSNS and LSNS groups is depicted. As it can be seen in Fig. 5, the MADV of O_3 concentrations in the HSNS are lower than LSNS throughout day and night. On close comparison between Figs. 4 and 5, the monthly averaged daytime O_3 peak concentrations in both NoUK and SoUK regions are closer to LSNS daytime peak concentrations, whereas the

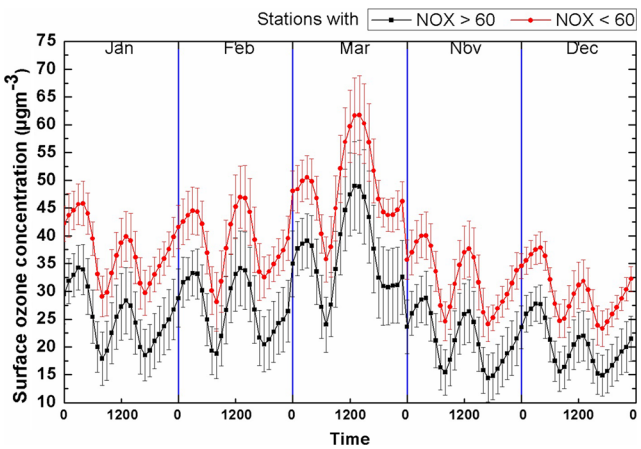

Fig. 5 Average of the monthly averaged diurnal variations of ozone for urban background monitoring stations with decadal mean urban background surface NO_X concentration >60 µg/m^3 [seven stations (*black*)] and <60 µg/m^3 [nine stations (*red*)] for the winter months (November to March) during the period 2000–2010. *Vertical bars* are 2σ standard deviation for the 16 sites

monthly averaged nighttime O_3 peak concentrations in NoUK get closer to LSNS nighttime O_3 peak concentrations and SoUK gets closer to HSNS nighttime O_3 peak concentrations in all the winter months. This is due to higher concentration of NO_X in SoUK favoring higher rate of O_3 titration compared to NoUK, particularly during the night.

The detailed spatial distribution of monitoring stations within regions and groups shows that, out of eight monitoring sites in the SoUK, four sites (LT, LHi, LNK, and LB) are in the London metropolitan area, with a population of more than eight million, high vehicular density and anthropogenic activity leading to high urban background NO_X concentration (particularly LHi and LB [decadal mean NO_X concentration greater than 100 μg/m^3] see Fig. S2 in Supplementary Material). The remaining four sites in SoUK, each with population less than 400 thousand, have lower urban background NO_X concentration (decadal mean NO_X concentration of ~55 μg/m^3). In the NoUK region, 2 out of 10 stations (LC and MP) are in major urban centers (with population≥500 thousand) and have high urban background NO_X concentration (decadal mean NO_X concentration of ~75 μg/m^3). The remaining eight sites in NoUK, each with population less than 400 thousand, have lower urban background NO_X concentration (decadal mean NO_X concentration of ~49 μg/m^3) (see Fig. S3 in Supplementary Material). In general, urban background sites in SoUK have higher NO_X concentrations than urban background sites in NoUK. This along with other reasons, such as topography, meteorological conditions, and the site-specific local chemistry, may explain the observed differences in the nighttime maxima of NSO concentration. However, these findings are still unclear and warrant further investigation.

Frequency distribution analysis for the winter months

The frequency distribution of daily maximum values of NSO observed between 2100 and 0500 hours at 18 urban background sites in the UK during the winter months for the period 2000–2010 is shown in Fig. 6. The frequency distribution shows that on more than 50 % of the days, the daily maximum NSO concentrations were above 40 μg/m^3, except at London Bloomsbury and London Hillingdon, and for more than 20 % of the days, these were above 60 μg/m^3, except at London Bloomsbury. For almost all sites, the frequency distributions indicate that on more than 20 % of the days, the NSO concentrations exceeded the Avg-MA daytime maximum O_3 concentration for all sites observed for the month of March (57 μg/m^3), except at London Bloomsbury and Manchester Piccadilly which only exceeded this on more than 11 and 19 % of the days, respectively.

Each of the 18 urban background sites exceeded the daily maximum NSO concentrations of 80 μg/m^3 from 0.2 to 21 % of the days of observation used in this analysis (Fig. 6). At Derry, the most northwestern site, the daily maximum NSO

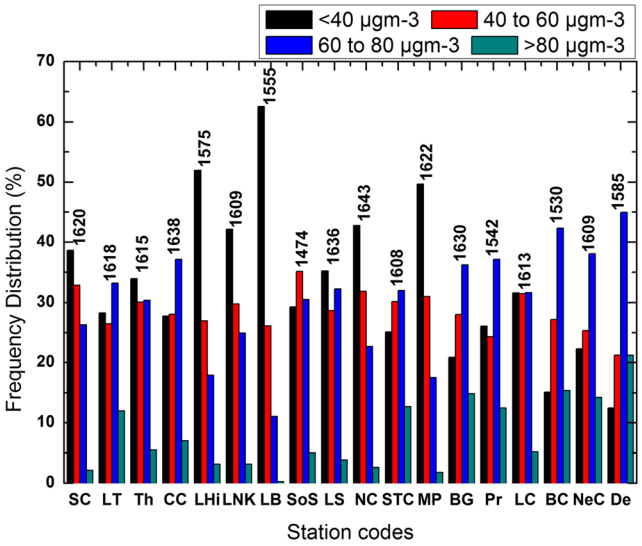

Fig. 6 The frequency distribution (%) of daily maximum NSO concentration at each station with respect to the total number of days of observations used (number specified on top of each set of bar graph for each station) for winter period during the study period 2000–2010

concentrations exceeded 80 μg/m^3 on the most number of days (21 %). As the UK predominantly experiences south-westerly air flow from the Atlantic and Derry that is the westernmost site, it is not expected to be affected greatly by regional UK or continental ozone. Also, Derry is a small city with a low population and limited industrial and traffic activities which leads to relatively low NO_X environment (annual mean NO_X concentration for the year 2010 was ~31 μg/m^3). Therefore, the frequent high daily maximum NSO concentrations observed at Derry are likely to be due to the greater influence of background tropospheric ozone than at other sites in this study. Furthermore, at only one (London Teddington) out of eight sites in the SoUK did the daily maximum NSO concentration exceeded 80 μg/m^3 on more than 11 % of the days, whereas at 6 out of 10 sites in the NoUK, the daily maximum NSO concentration exceeded 80 μg/m^3 on more than 12 % of the days.

AQEG-OUK (2009) in its report observed between the years 1991 and 1998 a marked shift in the frequency of occurrence of lower values of hourly O_3 concentration to higher values of hourly O_3 concentration at an urban background site in central London. The report concluded that the observed changes were due to the reduction in the NO_X emission resulting in a decreased titration of O_3 and an increase in the background ozone, particularly during winter.

Kulkarni et al. (2013) analyzed long-term (2000–2010) hourly O_3 data for the Porto and Lisbon regions in Portugal and reported that NSO concentration exceeded 40, 60, and 80 μg/m^3, respectively, on more than 50, 20, and 2 % of winter days. Of the nine sites analyzed by Kulkarni et al. (2013), only three are urban background sites, with Alfragide having the highest frequency of NSO occurrences

(i.e., concentrations exceeded 80 μg/m^3 during 13 % of winter nights). During the same study period (2000–2010), many stations in UK (BG, NeC, BC) observed much higher frequencies of NSO events exceeding 80 μg/m^3, with the highest frequency being 21 % observed at Derry. Sousa et al. (2011) studied the frequency of occurrence of NSO at four different sites (two urban traffic sites and two rural background sites) in Portugal during 2005–2007 and observed around 40 to 50 % of the days with NSO enhancement with an average concentration of 52±19 μg/m^3. Eliasson et al. (2003) observed high values of NSO concentration at Göteborg, Sweden, and reported the occurrence of NSO enhancement (>80 μg/m^3) on 33 % of the nights during the May–August period.

Temporal extent of the high NSO enhancements

For this analysis, an NSO concentration of 80 μg/m^3 is considered as a threshold, and values higher than the threshold are termed as high concentrations of NSO (HNSO) (RoTAP 2012). The hourly NSO concentration values observed from 2100 to 0500 hours on the nights when the maximum NSO concentration was observed at each station are given in Table 2. It also gives the number of hours of HNSO that were observed at each station. The temporal coverage was broadly categorized as a short-term, medium-term, or long-term event. If the HNSO were observed for less than 3 h, it is labeled as a short-term event; between 3 and 6 h, it is labeled as a medium-term, and more than 6 h, the HNSO is labeled as long-term. The analysis shows that out of 18 sites, the observed HNSO was short-term at 4 sites, medium-term at 5 sites, and long-term at 9 sites (Table 2).

Spatial extent of the high NSO enhancements

Table 3 contains the maximum NSO concentration values observed at all stations during the nights of the maximum NSO occurrences presented in Table 2. This overview of the NSO dataset allows for the evaluation of the spatial coverage of the HNSO events, considering the number of stations with HNSO values during the same night. The spatial coverage was broadly divided into three categories: (a) local, (b) regional, and (c) national.

1. Local coverage: If the HNSO values were observed at less than 6 sites
2. Regional coverage: If the HNSO values were observed from 6 up to 12 sites
3. National coverage: If the HNSO values were observed at more than 12 sites

This analysis was performed using NSO measurements made on 15 nights (instead of 18 nights), as there are 3 nights,

Table 2 Hourly NSO concentration observed at each station on the night when the maximum NSO concentration was observed during the study period 2000–2010 with number of hours exceeding 80 μg/m^3/h

Station code	Max. NSO	Date (after midnight)	NSO concentration (at specific time of the night)									A[a]
			2100	2200	2300	0000	0100	0200	0300	0400	0500	
SC	92	6-Mar-05	44	42	46	64	76	90	88	90	92	4
LT	108	6-Mar-05	42	74	90	104	100	106	108	102	102	7
Th	108	31-Mar-07	108	106	100	96	94	94	94	88	84	9
CC	100	26-Feb-02	72	62	48	64	72	74	68	100	100	2
LHi	114	31-Mar-07	110	110	114	112	112	112	108	106	102	9
LK	100	10-Feb-00	36	54	54	64	82	90	98	100	98	5
LB	82	12-Mar-08	56	60	64	64	64	82	80	80	78	1
SoS	110	11-Mar-06	70	60	56	70	86	88	96	108	110	5
LS	100	30-Mar-08	88	90	90	90	94	98	100	90	80	8
NC	100	2-Mar-08	64	54	50	56	54	72	80	90	100	2
STC	118	8-Nov-01	38	46	56	62	86	86	94	114	118	5
MP	114	22-Feb-08	4	20	114	56	44	22	24	34	48	1
BG	112	3-Mar-00	78	78	76	76	78	104	112	104	98	4
Pr	108	21-Mar-08	92	96	98	102	106	108	102	98	100	9
LC	112	21-Mar-08	104	108	110	110	110	108	112	106	102	9
BC	106	24-Mar-00	48	78	92	98	106	104	106	104	104	7
NeC	110	17-Mar-06	86	88	94	96	104	106	108	110	108	9
De	112	7-Mar-02	96	98	100	104	100	110	112	110	108	9

[a] No. of hours with NSO ≥80 μg/m^3

Table 3 Daily maximum NSO concentration observed at all the station used in this study on the night when the maximum NSO concentration was observed at the specific station during the study period 2000–2010 with number of stations exceeding NSO concentration of 80 μg/m^3

Station code (A)	Max. NSO at (A)	Date	Maximum NSO concentration (at specific station)																	B[a]
			SC	LT	Th	CC	LHi	LK	LB	SoS	LS	NC	STC	MP	BG	Pr	LC	BC	NeC	De	
SC	92	6-M-05	**92**	108	100	68	86	86	70	88	78	72	68	50	70	46		52	44	48	6
LT	108	6-M-05	92	**108**	100	68	86	86	70	88	78	72	68	50	70	46		52	44	48	6
Th	108	31-M-07	86	106	**108**	86	114		64	100	96	82	92	52	76	82	86	92	92	76	13
CC	100	26-F-02	76	82	80	**100**	66	68			84	68	82	78	96	78	54	70	76	94	6
LHi	114	31-M-07	86	106	108	86	**114**		64	100	96	82	92	52	76	82	86	92	92	76	13
LK	100	10-F-00	76	80	78	82	68	**100**	64		84	76	72	68	86		80	90	80	94	6
LB	82	12-M-08	74	92		94	94	88	**82**	88	90	94	68	80	80	98	104		84	102	14
SoS	110	11-M-06	70	70	92	54	64	82	70	**110**	80	74	74		84	70	86	78	92	90	7
LS	100	30-M-08	86	96	90	86	90	94	76	100	**100**	96		74	90	92	100	100	76	94	14
NC	100	2-M-08	66	76	70	82	80	74	66	68	84	**100**	96	92	94	94	90		98	90	10
STC	118	8-N-01	60	64	58	74	66	76	56	58	66	78	**118**	62	70	82	66	90	72	78	3
MP	114	22-F-08	56	68	58	72	60	62	58	62	68	70	70	**114**	82	80	90	94	94	92	6
BG	112	3-M-00	74	72	68	74	56	68	60		92	86	50	44	**112**		94	84	92	94	7
Pr	108	21-M-08	78	90	78	94	100	86	72	96	94	96	70	98	96	**108**	112		86	104	13
LC	112	21-M-08	78	90	78	94	100	86	72	96	94	96	70	98	96	108	**112**		86	104	13
BC	106	24-M-00	36	56	56	72	10	30	26		60	42	72	22	66		20	**106**	86	88	3
NeC	110	17-M-06	78	88	82	94	80	80	72	96	98	86	90		80	104	92	86	**110**	90	13
De	112	7-M-02	64	76	72	78	54	66	54	64	80	88	82	76	106	86	88	104	100	**112**	8

[a] No. of stations with NSO ≥80 μg/m^3

specifically the 6th of March 2005, 31st of March 2007, and 21st of March 2008, on which two stations each observed their highest NSO events (Table 3) on the same night. The analysis showed that, on 2 nights out of 15, the observed NSO enhancement was local, on 9 nights, it was regional, and on 7 nights, it was found to be national.

On 21st of March 2008, high values of O_3 concentrations are observed at almost all the stations during an NSO enhancement event in the UK. Two stations (Pr and LC) experienced maximum NSO concentration of 108 and 112 μg/m^3, respectively, and remained high throughout the night (2100 to 0500 hours) (Table 3). On the same night, 13 out of 17 sites (data is not available for one site "BC") observed NSO concentration>80 μg/m^3, and the remaining four sites observed NSO concentration>70 μg/m^3 (Table 3). The NSO enhancements observed at each urban site in the UK are, on average, comparable with NSO enhancements observed at other urban sites in Europe. At Göteborg, Sweden, Eliasson et al. (2003) observed high values of NSO concentration, with a maximum NSO concentration of 104 μg/m^3 during the summer (May–August) 1994. In Essen, Germany, Strassburger and Kuttler (1998) and Reitebuch et al. (2000) observed high values of NSO concentration during the summer period of 1995–1996 and 1995–1997, respectively. The maximum NSO concentration of 74±14 μg/m^3 was observed by Strassburger and Kuttler (1998), whereas Reitebuch et al. (2000) observed a maximum NSO concentration of 91 μg/m^3. At Segovia, Spain, Sanchez et al. (2005) observed an increase of more than 30 μg/m^3 (from 70 to >100 μg/m^3) from late evening until early morning in June 2004. However, this is the first study of NSO, covering a vast spatial area across the UK (18 stations spread across the UK) exhibiting high NSO concentration values.

Conclusion

In this work, the long-term (2000–2010) diurnal variation of O_3 concentration was analyzed with particular emphasis on the NSO enhancement. The analysis reveals that prominent nocturnal peaks appear regularly in urban centers in the UK during winter months. During the study period, monthly averaged diurnal variations of O_3 concentration show a well-pronounced bimodal distribution with a daytime peak and a nighttime peak. For the months November through to January, the average nighttime peaks actually exceeded the average daytime peaks. Further data analysis highlighted that the NSO enhancement, during the winter season, is more prominent at northern UK sites (42±5 μg/m^3) than at southern UK sites (35±4 μg/m^3). Similarly, the NSO enhancement is less prominent at the sites with the high NO_X concentration than at the sites with the low

NO_X concentration. Frequency distribution analysis of daily maximum NSO concentrations for the winter period shows that >20 % of the daily maximum NSO concentrations are above 60 μg/m^3, and depending on the site, between 0.2 and 21 % of the days have maximum NSO concentration greater than 80 μg/m^3. The analysis of temporal and spatial coverage of high NSO events shows that the NSO enhancements over UK often last for several hours and extend to the regional scale.

Significant research is done on daytime photochemistry and O_3 air quality. Comparatively, less attention is paid to the investigation of nighttime atmospheric chemistry, particularly nighttime enhancement of O_3. Since O_3 production ceases at nighttime, a plausible reasoning for observed bimodal pattern of O_3 with enhanced NSO concentration during nighttime has to be governed by complex combination of atmospheric transport processes, topography, and corresponding meteorological conditions. To fully understand the mechanism of enhancement of NSO at any location, its spatiotemporal extent and severity, in-depth analysis of various meteorological parameters (for example NBL, wind speed and direction, Bulk Richardson Number (BRN), potential temperature, etc.) is essential. The multiple NSO enhancement events may occur over the same geographical location, as demonstrated in this study, but under entirely different atmospheric mechanisms (such as horizontal advection, vertical downdraft and mixing, passing of low level jets, etc.) and warrant further investigation.

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