Environmental Science and Pollution Research

Enhancements in nocturnal surface ozone at urban sites in the United Kingdom

--Manuscript Draft--

Manuscript Number:	ESPR-D-15-02849R2
Full Title:	Enhancements in nocturnal surface ozone at urban sites in the United Kingdom
Article Type:	Research Article
Corresponding Author:	Pavan S Kulkarni, PhD University of Evora Evora, PORTUGAL
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	University of Evora
Corresponding Author's Secondary Institution:	
First Author:	Pavan S Kulkarni, PhD
First Author Secondary Information:	
Order of Authors:	Pavan S Kulkarni, PhD
	Daniele Bortoli, PhD
	Ana Maria Silva, PhD
	Claire Reeves, PhD
Order of Authors Secondary Information:	
Funding Information:	Fundação para a Ciência e a Tecnologia (FCT) (SFRH/BPD/82033/2011) — Dr. Pavan S Kulkarni
Abstract:	Analysis of diurnal patterns of surface ozone (O3) at multiple urban sites in the United Kingdom (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 hr along with the primary daytime peak. For all but one site, the daily maxima NSO concentrations during the winter months exceeded 60 µg/m3 on >20% of the nights. The highest NSO value recorded was 118 µg/m3. During the months of November, December and January, the monthly averaged O3 concentrations observed at night (0300 hr) even exceeded those observed in the daytime (1300 hr). 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.
Response to Reviewers:	Reply to Reviewer's comments (Second revision): We are thankful to the reviewer for reviewing the manuscript and for the helpful and positive comments. In response to the reviewer's comment (second revision), we have replied to the comment in this document and made required changes in the manuscript. As per the reviewer suggestion we have carefully revised the 'conclusion' section of the manuscript and incorporated all the suggestions/corrections. All the changes in the manuscript (second revision) are highlighted in 'Red' colour.

	Reviewers' comments: The manuscript improved against the originally submitted version. The study should be conclusive, which it is not really in the present stage. All repetitions from the results section should be removed from the conclusion section. The only conclusion really made (last paragraph) should be expanded in order to guide further investigation of the topic /phenomena: How can parameters influencing NSO events be addressed, which situations and sites are most promising to elucidate the mechanism (in the light of previous knowledge, referenced in the introduction)? Reply: As per the reviewer suggestion we have carefully revised the 'conclusion' section of the manuscript, deleted repetition and incorporated all the suggestions/corrections. All the changes in the manuscript (second revision) are highlighted in 'Red' colour. We rewrote the last paragraph of the conclusion, which is as follows: 'Significant research is done on daytime photochemistry and O3 air quality. Comparatively less attention is paid to the investigation of nighttime atmospheric chemistry, particularly nighttime enhancement of O3. Since O3 production ceases at nighttime, a plausible reasoning for observed bimodal pattern of O3 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 warrants further investigation.'
Additional Information:	
Question	**Response**
§ Are you submitting to a Special Issue?	No

Enhancements in nocturnal surface ozone at urban sites in the United Kingdom

Pavan S. Kulkarni[1], D. Bortoli[1,2], A. M. Silva[1,3] and C. E. Reeves[4]

1 Geophysics Centre of Evora (CGE), University of Évora, Évora, Portugal

2 Institute for Atmospheric Science and Climate (ISAC-CNR), Bologna, Italy

3 Department of Physics, University of Évora, Évora, Portugal

4 Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK

Abstract

Analysis of diurnal patterns of surface ozone (O_3) at multiple urban sites in the United Kingdom (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 hr 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 hr) even exceeded those observed in the daytime (1300 hr). 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; United Kingdom*

*Corresponding author: Phone: +351-266 740800; Fax: +351-266-745394

E-mail : pavan@uevora.pt; pavannpl@gmail.com

1. 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 pre-industrial 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 lead 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; Kulkarni *et al.,* 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 eight-hour mean O_3 concentration should not exceed 120 µg/m^3 on more than 25 days per calendar year averaged over three 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 18000 µg/m^3·h averaged over five 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 till 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, 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 maximise 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 night-time concentrations are less pronounced.

On calm nights, O_3 generally has a positive gradient from the surface to the top of the NBL (Stutz, 2000; 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; Banta *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 up 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 – Sep. 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 4 different costal sites in the North of Portugal during 2005-07.

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, US and Klein *et al.*, (2014) over Oklahoma metropolitan area, US 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 changes 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 United Kingdom (hereafter 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 (Nov-Mar) over the period 2000-2010.

2. STUDY AREA AND DATA

The UK is an island nation located in Western Europe. The UK has a total area of 243,610 sq. km 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 µg/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 (APEG 2009), which is about 8 µg/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 Figure 1 (and identified in Table 1), although 4 stations (LT, LHi, LNK and LB) are clustered in London, the biggest metropolitan area in the UK and 2 stations (Th and SoS) are close to London. The northern most monitoring station used in this study is located at 55º N and southern most is located at 50.9º 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 co-ordinates and percentage of data availability are outlined in Table 1. In this study, as per the EU air quality reporting procedures, the unit of the O_3 concentration used is $\mu g/m^3$. In order to facilitate the data analysis and interpretation, the study area (part of the UK shown in Figure 1, covering 50º N to 55º N), is be broadly categorized into two regions, (I) North of UK (NoUK) including all the stations north of 52º N latitude and (II) South of UK (SoUK): including all the stations south of 52º 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 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, where as 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 7 urban NO_X monitoring stations collocated with ozone monitoring) is higher than NoUK (average of 9 urban NO_X monitoring stations collocated with ozone monitoring) (See Figures 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 $\mu g/m^3$ and (II) Low Surface NO_X Stations (LSNS): Stations with decadal mean NO_X concentration < 60 $\mu g/m^3$. 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.

3. RESULT AND DISCUSSION

3.1 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 Figure 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 exhibits daytime maxima and night-time 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 night-time 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 night-time maxima diminishes. Kulkarni *et al.*, (2013) observed similar seasonal variations in annual diurnal variation of MADV of O_3 concentration in Portugal with prominent night-time maxima during winter months, but never exceeded the daytime maxima. Similarly, Chung (1977) observed bimodal a structure in the MADV of O_3 concentration at Toronto (~120µg/m^3) and Montreal (~55 µg/m^3), Canada during 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 sub-section (3.2).

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 Figure 3 shows the annual variation of MA O_3 concentrations for specific hours i.e. 0300 hr, 0800 hr, 1300 hr and 1800 hr, averaged across all sites in the UK. It shows that during the winter the MA at 0300 hr are much higher than at 1800 hr and at 0800 hr. Moreover, the O_3 concentrations at 0300 hr even exceed those at 1300 hr during the months of November, December and January.

3.2 Bimodal Diurnal variation of O_3 during winter months:

As briefly mentioned in the previous sub-section (3.1), a bimodal structure is exhibited in the MADV of O_3 concentration during winter, with a daytime maxima during typically around 1300 hr and night-time maxima typically around 0300 hr. The nocturnal peak is particular prominent during November to January when the nocturnal maxima exhibit higher concentrations than the daytime maxima. The highest nocturnal maximum in the MADV occurs in March (46±7µg/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 (~49µg/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 '2. Study area and data'. In Figure 4 the MADV of surface ozone concentrations for NoUK and SoUK regions are depicted (Figure 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 day-time 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 Figure 4, the differences 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 of 10 µg/m^3 in March. From November through to January the night-time maxima exceed the daytime maxima for the NoUK region, but this only occurs in December and January for the SoUK.

Similarly, in Figure 5 the MADV of surface ozone concentration for HSNS and LSNS groups is depicted. As it can be seen in figure 5, the MADV of O_3 concentrations in the HSNS are lower than LSNS throughout day and night. On close comparison between figures 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 monthly averaged nighttime O_3 peak concentrations in NoUK gets 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 8 monitoring sites in the SoUK, 4 sites (LT, LHi, LNK and LB) are in the London metropolitan area, with a population of more than 8 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 Figure S2 in Supplementary Material). The remaining 4 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 centres (with population ≥ 500 thousand) and

have high urban background NO_X concentration (decadal mean NO_X concentration of ~75 µg/m^3). The remaining 8 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 Figure 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.

3.3 Frequency distribution analysis for the winter months:

The frequency distribution of daily maximum values of NSO observed between 2100 hr and 0500 hr at 18 urban background sites in the UK during the winter months for the period 2000-2010 are shown in Figure 6. The frequency distribution shows that on more than 50% of the days the daily maximum NSO concentrations were above 40 µgm^{-3}, except at London Bloomsbury and London Hillingdon; and for more than 20% of the days these were above 60 µgm^{-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 µgm^{-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 µgm^{-3} from 0.2% up to 21% of the days of observation used in this analysis (Figure 6). At Derry, the most north-western site, the daily maximum NSO

concentrations exceeded 80 µgm^{-3} on the most number of days (21%). As the UK predominantly experiences south westerly air flow from the Atlantic and Derry is the most western 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 8 sites in the SoUK, did the daily maximum NSO concentration exceeded 80 µgm^{-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 µgm^{-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 µg/m^3, 60 µg/m^3 and 80 µg/m^3 respectively on more than 50%, 20% and 2% of winter days. Of the 9 sites analyzed by Kulkarni *et al.,* (2013) only 3 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 4 different sites (2 urban traffic sites and 2 rural background sites) in Portugal during 2005-07 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 µgm^{-3}) on 33% of the nights during the May-August period.

3.4 Temporal extent of the high NSO enhancements:

For this analysis an NSO concentration of 80 µgm^{-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 hr 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 hours it is labeled as a short-term event; between 3 to 6 hours it is labeled as a medium-term and more than 6 hours 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).

3.5 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.

(a) Local coverage: If the HNSO values were observed at less than 6 sites;

(b) Regional coverage: If the HNSO values were observed from 6 up to 12 sites;

(c) 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, specifically the 6th of March 2005, 31st March 2007 and 21st March 2008, on which 2 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 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 µg/m^3 and 112 µg/m^3 respectively and remained high throughout the night (2100 hr to 0500 hr) (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 4 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 1995-96 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 till 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.

4. 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±5µg/m^3) than at southern UK sites (35±4µg/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 >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 warrants further investigation.

ACKNOWLEDGEMENT:

The author (Pavan S Kulkarni) is thankful to Fundação para a Ciência e a Tecnologia (FCT) for the grant SFRH/BPD/82033/2011. Thanks are also due to UK-AIR, Defra (http://uk-air.defra.gov.uk/) for the O_3 and NO_X data. The paper was partially funded through FEDER (Programa Operacional Factores de Competitividade – COMPETE) and National funding through FCT – Fundação para a Ciência e a Tecnologia in the framework of project FCOMP-01-0124-FEDER-014024 (Refª. FCT PTDC/AAC-CLI/114031/2009).The author acknowledges the funding provided by the Geophysics

Centre Évora, Portugal, under the contract with FCT (the Portuguese Science and Technology Foundation), PEst-OE/CTE/UI0078/2011.

REFERENCES:

Aneja, V.P., Mathur, R., Arya, S.P., Li, Y., Murray, Jr. G.C. and Manuszak, T.L. (2000). Coupling the Vertical Distribution of Ozone in the Atmospheric Boundary Layer. Environ. Sci. Technol., 34:2324 – 2329.

AQEG-OUK: Air Quality Expert Group – Ozone in the United Kingdom., (2009). Chapter 2. Temporal trends and spatial distributions in ozone concentrations determined from monitoring data. Department for the Environment, Food and Rural Affairs. AQEG-OUK report 5:15-62.

Asaf, D., Pederson, D., Matveev, V., Peleg, M., Kern, C., Zingler, J., Platt, U. and Luria, M. (2009). Long-term measurements of NO3 radical at a semiarid urban site: 1. extreme concentration events and their oxidation capacity. Environ. Sci. Technol., 43:9117–9123.

Asaf, D., Tas, E., Pedersen, D., Peleg, M. and Luria, M. (2010). Long-term measurements of NO3 radical at a semiarid urban site: 2. Seasonal trends and loss mechanisms. Environ. Sci. Technol., 44:5901–5907.

Caird, M.A., Richards, J.H. and Donovan, L.A. (2007). Nighttime Stomatal Conductance and Transpiration in C3 and C4 Plants. Plant Physiology, 143, 4–10.

Chan, L. Y., Chan, C. Y. and Qin, Y., 1998. Surface ozone pattern in Hong Kong. J. App. Meteorology, 37 (10):1153–1165.

Chung, Y.S. (1977). Ground-level ozone and regional transport of air pollutants. J. App. Meteo., 16(11):1127–1136.

Corsmeier, U., Kalthoff, N., Kolle, O., Kotzian, M. and Fiedler, F. (1997). Ozone concentration jump in the stable nocturnal boundary layer during a LLJ-event. Atmos. Environ., 31:1977-1989.

Coulter, R.L. (1990). A case study of turbulence in the stable nocturnal boundary layer. Boundary-Layer Meteorol., 52:75-91.

DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 May 2008 on ambient air quality and cleaner air for Europe (2008). Official Journal of the European Union L152:1-44.

Doherty, R.M., Stevenson, D.S., Collins, W.J. and Sanderson, M.G. (2005). Influence of convective transport on tropospheric O3 and its precursors in a chemistry–climate model. Atmos. Chem. Phys. 5:3205–3218.

Eliasson, I., Thorsson, S. and Andersson-Skolfd, Y. (2003). Summer nocturnal ozone maxima in Goteborg, Sweden. Atmos. Environ., 37:2615–2627.

Fehsenfeld, F.C., Ancellet, G., Bates, T.S., Goldstein, A.H., Hardesty, R.M., Honrath, R., Law, K.S., Lewis, A.C., Leaitch, R., McKeen, S., Meagher, J., Parrish, D.D., Pszenny, A.A.P., Russell, P.B., Schlager, H., Seinfeld, J., Talbot R. and Zbinden, R. (2006). International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America to Europe – Overview of the 2004 summer field study. J. Geophys. Res., 111:D23S01.

Finnan, J.M., Burke, J.I. and Jones, M.B. (1997). An evaluation of indices that describe the impact of ozone on the yield of spring wheat (Triticum aestivum L.). Atmos. Environ., 31:2685–2693.

Geyer, A. and Stutz, J. (2004). Vertical profiles of NO3, N2O5, O3, and NOx in the nocturnal boundary layer: 2. Model studies on the altitude dependence of composition and chemistry. J. Geophys. Res., 109:D12307.

Ghude, S., Fadnavis, S., Beig, G., Polade, S.D. and van der A, R.J. (2008). Detection of surface emission hot spots, trends, and seasonal cycle from satellite-retrived NO2 over India. J. Geophys. Res., 113:D20305.

Ghude, S. D., Jena, C., Chate, D. M., Beig, G., Pfister, G. G., Kumar, R. and Ramanathan, V. (2014). Reductions in India's crop yield due to ozone. Geophys. Res. Lett., 41: 5685-5691.

Hu, X-M., Doughty, D.C., Sanchez, K.J., Joseph, E. and Fuentes, J.D. (2012). Ozone variability in the atmospheric boundary layer in Maryland and its implications for vertical transport model. Atmos. Environ. 46:354-364.

Jain, S.L., Arya, B.C., Kumar, A., Ghude, S.D. and Kulkarni, P.S. (2005). Observational study of surface ozone at New Delhi, India. Int. J. Remote Sensing, 26 (16):3515-3526.

Jena, C, Ghude, S.D., Beig, G., Chate, D.M., Kumar, R., Pfister, G.G., Lal, D.M., Surendran, D.E., Fadnavis, S., van der A, R.J. (2015). Inter-comparison of different NOX emission inventories and associated variation in simulated surface ozone in Indian region. Atmos. Environ., 117, 61-73.

Kalthoff, N., Horlacher, V., Corsmeier, U., Voltz-Thomas, A., Kolahgar, B., Giess, H., Mollmann-Coers, M. and Knaps, A. (2000). Influence of valley winds on transport and dispersion of airborne pollutants in the Freiburg-Schauinsland area. J. Geophys. Res. 105:1585-1597.

Keller, T. and Hasler, R. (1984). The influence of a fall fumigation with ozone on the stomatal behavior of spruce and fir. Oecologia, 64:284–286.

Klein, P.M., Hu. X-M. and Xue, M. (2014). Impacts of Mixing Processes in Nocturnal Atmospheric Boundary Layer on Urban Ozone Concentrations. Boundary-Layer Meteorol., 150:107–130.

Kuang, S., Newchurch, M.J., Burris, J., Wang, L., Buckley, P.I., Johnson, S., Knupp, K., Huang, G., Phillips, D. and Cantrell, W. (2011). Nocturnal ozone

enhancement in the lower troposphere observed by lidar. Atmos. Environ., 45:6078-6084.

Kulkarni, P.S., Bortoli, D. and Silva, A.M. (2013). Nocturnal surface ozone enhancement and trend over urban and suburban sites in Portugal. Atmos. Environ., 71:251-259.

Kulkarni, P.S., Bortoli, D., Salgado, R., Antón, M., Costa, M.J., and Silva, A.M. (2011). Tropospheric ozone variability over the Iberian Peninsula. Atmos. Environ., 45:174-182.

Kulkarni, P.S., Ghude, S.D., and Bortoli, D. (2010). Tropospheric ozone (TOR) trend over three major inland Indian cities: Delhi, Hyderabad and Bangalore. Ann. Geophys., 28:1879–1885.

Kulkarni, P.S., Jain, S.L., Ghude, S.D., Arya, B.C., Dubey, P.K. and Shahnawaz (2009). On some aspects of tropospheric ozone variability over the Indo-Gangetic (IG) basin, India. Int. J. Remote Sensing 30(15-16):4111-4122.

Leung, D.Y.C. and Zhang, D.N. (2001). Characteristics of urban ozone level in Hong Kong. J. Environ. Sci., 13(1):1–7.

Li, Q.B., Jacob, D.J., Bey, I., Palmer, P.I., Duncan, B.N., Field, B.D., Martin, R.V., Fiore, A.M., Yantosca, R.M., Parrish, D.D., Simmonds, P.G. and Oltmans, S.J. (2002). Transatlantic transport of pollution and its effects on surface ozone in Europe and North America. J. Geophys. Res., – Atmos., 107:D13, 4166.

Löffler-Mang, M., Kossmann, M., Vogtlin, R. and Fiedler, F. (1997). Valley wind systems and their influence on nocturnal ozone concentrations. Beitraege zur Physik der Atmosphaere, 70:1–14.

Matyssek, R., Gunthardt-Goerg, M.S., Maurer, S. and Keller, T. (1995). Nighttime exposure to ozone reduces whole-plant production in Betula pendula. Tree Physiol., 15:159–165.

Mickley, L.J., Murti, P.P., Jacob, D.J., Logan, J.A., Koch, D.M., Rind, D. (2001). Radiative forcing from tropospheric ozone calculated with a unified chemistry-climate model. J. Geophys. Res., 104:30153-30172.

Musselman, R.C. and Massman, W.J. (1999). Ozone flux to vegetation and its relationship to plant response and ambient air quality standards. Atmos. Environ., 33:65–73.

Musselman, R.C. and Minnick, T.J. (2000). Nocturnal stomatal conductance and ambient air quality standards for ozone. Atmos. Environ., 34:719–733.

Nair, P.R., Chand, D., Lal, S., Modh, K.S., Naja, M., Parameswaran, K., Ravindran, S. and Venkataramani, S. (2002). Temporal variations in surface ozone at Thumba (8.6ºN, 77ºE)—A tropical coastal site in India. Atmos. Environ., 36:603–610.

Pio, C.A., Feliciano, M.S., Vermeulen, A.T., and Sousa, E.C. (2002). Seasonal variability of ozone dry deposition under southern European climate conditions, in Portugal. Atmos. Environ., 34:195-205.

Reitebuch, O., Strassburger, A., Emeis, S. and Kuttler, W. (2000). Nocturnal secondary ozone concentration maxima analysed by sodar observations and surface measurements. Atmos. Environ., 34:4315-4329.

RoTAP (2012). Review of Transboundary Air Pollution: Acidification, Eutrophication, Ground Level Ozone and Heavy Metals in the UK. Contract Report to the Department for Environment, Food and Rural Affairs. Centre for Ecology & Hydrology.

Royal Society (2008). Ground Level Ozone in the 21st Century: Future Trends, Impacts and Policy Implications, 2008. Science Policy Report 15/08, pp. 132, The Royal Society, London. Available at: http://royalsociety.org/displaypagedoc.asp?id=31506.

Salibaa, N.A., Mousaa, S., Salame, H., and El-Fadel, M. (2006). Variation of selected air quality indicators over the city of Beirut, Lebanon: Assessment of emission sources. Atmos. Environ., 40:3263–3268.

Salmond, J.A. and McKendry, I.G. (2002). Secondary ozone maxima in a very stable nocturnal boundary layer: observations from the Lower Fraser Valley, BC. Atmos. Environ., 36:5771-5782.

Sanchez, M.I., de Torre, B., Garcia, M.A. and Perez, I. (2005). Ozone concentrations at a high altitude station in the Central Massif (Spain). Chemosphere, 60:576–584.

Sanchez, M.I., de Torre, B., Garcia, M.A. and Perez, I. (2007). Ground-level ozone and ozone vertical profile measurements close to the foothills of the Guadarrama mountain range (Spain). Atmos. Environ. 41:1302–1314.

Segschneider, H-J., Wildt, J. and Forstel, H. (1995). Uptake of 15NO2 by sunflower (Helianthus annuus) during exposures in light and darkness: quantities, relationship to stomatal aperture and incorporation into different nitrogen pools within the plant. New Phytol, 131:109–119.

Skarby, L., Troeng, E. and Bostrom, C.A. (1987). Ozone uptake and effects on transpiration, net photosynthesis, and dark respiration in Scots pine. Forest Sci., 33:801–808.

Sousa, S.I.V., Alvim-Ferraz, M.C.M. and Martins, F.G. (2011). Identification and origin of nocturnal ozone maxima at urban and rural areas of Northern Portugal - influence of horizontal transport. Atmos. Environ., 45:942-956.

Stevenson, D.S., Dentener, F.J., Schultz, M.G., Ellingsen, K., van Noije, T.P.C., Wild, O., Zeng, G., Amann, M., Atherton, C.S., Bell, N., Bergmann, D.J., Bey, I., Butler, T., Cofala, J., Collins, W.J., Derwent, R.G., Doherty, R.M., Drevet, J., Eskes, H.J., Fiore, A.M., Gauss, M., Hauglustaine, D.A., Horowitz, L.W., Isaksen, I.S.A., Krol, M.C., Lamarque, J.-F., Lawrence, M.G., Montanaro, V., Müller, J.-F., Pitari, G., Prather, M.J., Pyle, J.A., Rast, S., Rodriguez, J.M., Sanderson, M.G., Savage, N.H., Shindell, D.T., Strahan, S.E., Sudo, K. and Szopa, S. (2006). Multimodel ensemble simulations of present-day and near-future tropospheric ozone. J. Geophys. Res., 111:D08301.

Strassburger, A., and Kuttler, W. (1998). Diurnal courses of ozone in an inner urban park. Meteorologische Zeitschrift- Berliin, N.F., 7:15–18.

Stutz, J., Alicke, B., Ackermann, R., Geyer, A., White, A. and Williams, E. (2004). Vertical profiles of NO3, N2O5, O3, and NOx in the nocturnal boundary layer: 1. Observations during the Texas air quality study 2000. J. Geophys. Res., 109:D12306.

Takahashi, M., Konaka, D., Sakamoto, A. and Morikawa, H. (2005). Nocturnal uptake and assimilation of nitrogen dioxide by C3 and CAM plants. Z Naturforsch Sect C Biosci., 60:279–284.

Tong, N.Y.O., Leung, D.Y.C. and Liu, C.H. (2011). A review on ozone evolution and its relationship with boundary layer characteristics in urban environments. Water, Air, & Soil Pollution 214:13-36.

Unger, N., Shindell, D.T, Koch, D.M., Streets, D.G. (2006). Cross influences of ozone and sulfate precursor emissions changes on air quality and climate. PNAS, 103(12):4377–4380.

Wang, T.,Wu,Y.Y., Cheung, T.F., and Lam, K.S. (2001). A study of surface ozone and the relation to complex wind flow in Hong Kong. Atmos. Environ., 35:3203–3215.

Wang, X.M., Lin, W.S., Yang, L.M., Deng, R.R. and Lin, H. (2007). A numerical study of influences of urban land-use change on ozone distribution over the Pearl River Delta region, China. Tellus, 59B:633-641.

Wang, Y.H. and Jacob, D.J. (1998). Anthropogenic forcing on tropospheric ozone and OH since pre-industrial times. J. Geophys. Res.,103:31123-31135.

Zhang, J., Rao, S.T. and Daggupaty, S.M. (1998). Meteorological Processes and Ozone Exceedances in the Northeastern United staes during the 12-16 July 1995 Episode. Journal of Applied Meteorology, 37:776-789.

Zhang, R., Lei, W., Tie, X. and Hess, P. (2004). Industrial emissions cause extreme urban ozone diurnal variability. PNAS, 101(17):6346–6350.

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

Code	Site name[#] (NoUK/SoUK)[$]	UK-AIR ID	Lat	Long	Alt. (m)	A	A (%)	B (μgm^{-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*
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*

- urban background sites

$ - NoUK : North of UK ; SoUK : South of UK

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

B – 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 $\mu g/m^3$ and values in italics represents sites with Low Surface NO_X Stations (LSNS) with decadal mean NO_X concentration < 60 $\mu g/m^3$)

* - Annual mean surface NO_X concentration for the year 2010 instead of decadal mean

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
			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
			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

B- No. of stations with NSO ≥80 µg/m^3

FIGURE CAPTIONS:

Figure 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 5 background monitoring stations in the metropolitan city – London.

Figure 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 hour 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.

Figure 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 hr [black], (b) 0800 hr [red], (c) 1300 hr [blue] and (d) 1800 hr [green].

Figure 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 (Nov to Mar) during the period 2000-2010. Vertical bars are 2σ standard deviation for the 18 sites.

Figure 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 μgm^{-3} [7 stations (black)] and < 60 μgm^{-3} [9 stations (red)] for the winter months (Nov to Mar) during the period 2000-2010. Vertical bars are 2σ standard deviation for the 16 sites.

Figure 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.

Figure 1
Click here to download Figure: Figure 1 -UK - Site map.jpg

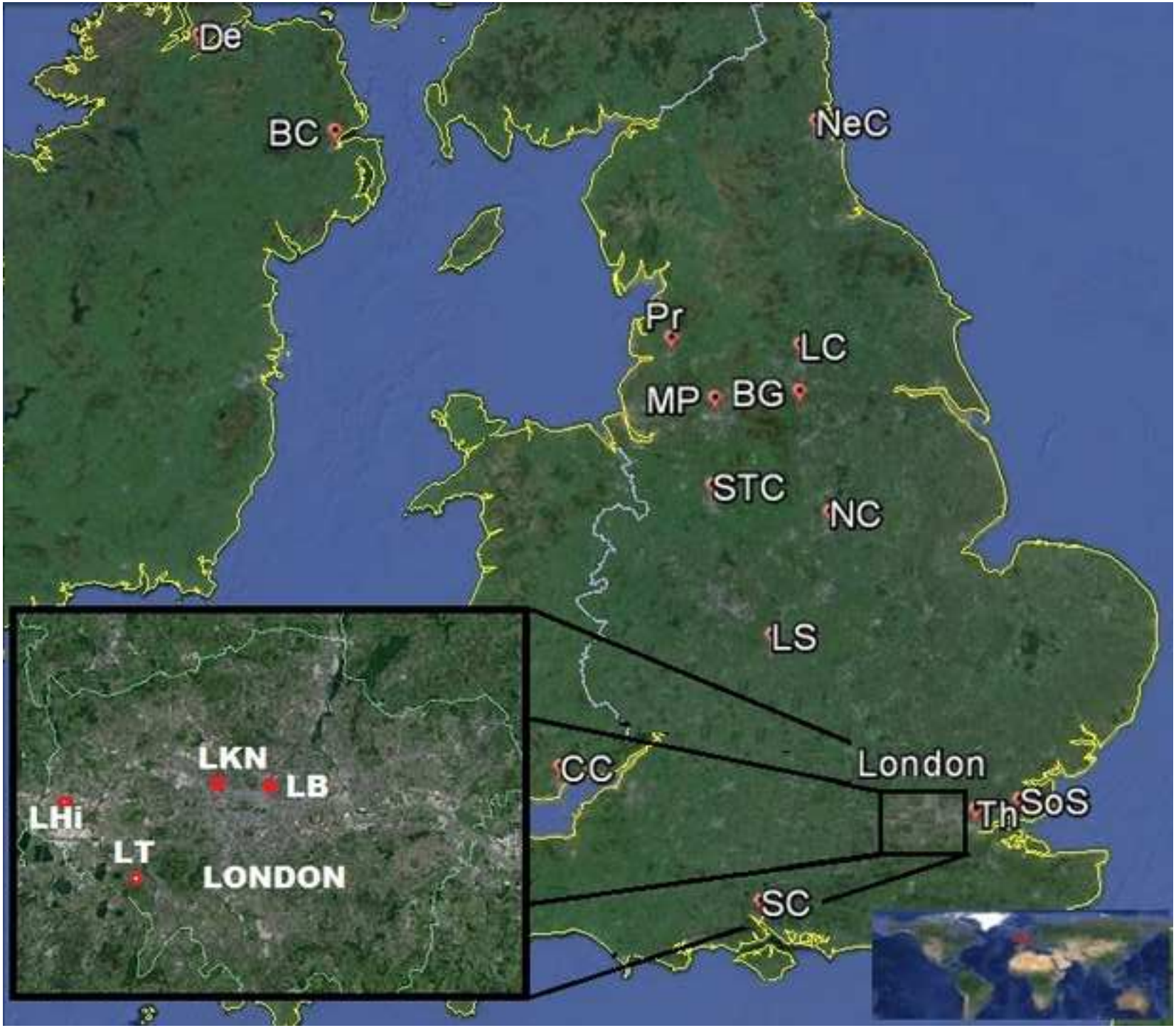

Figure 2
Click here to download Figure: Figure 2 -Annual DV UK.jpg

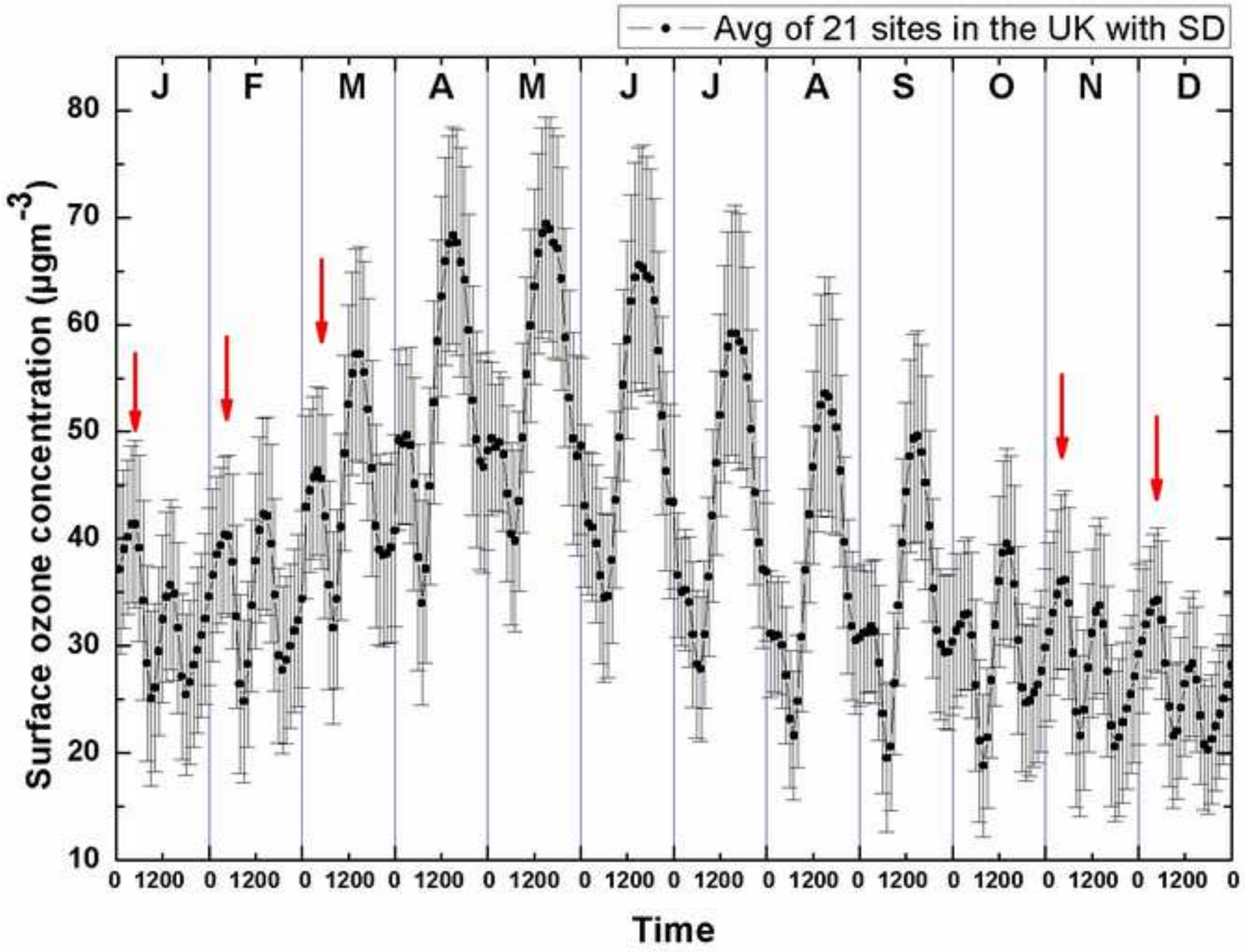

Figure 3
Click here to download Figure: Figure 3 -Annual MA O3 at different time.jpg

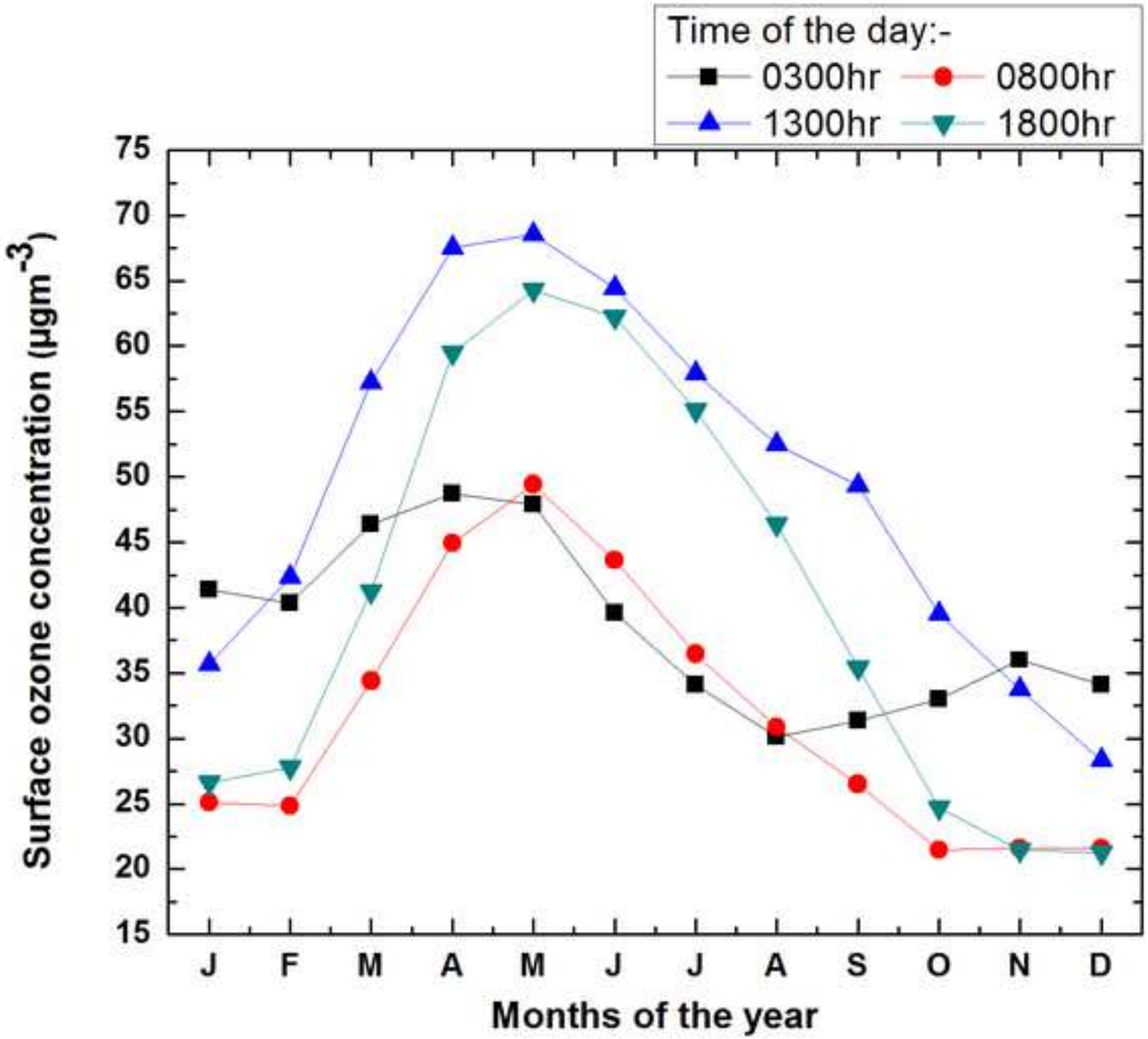

Figure 4

Click here to download Figure: Figure 4 -Winter months -MADV SoNo-UK.jpg

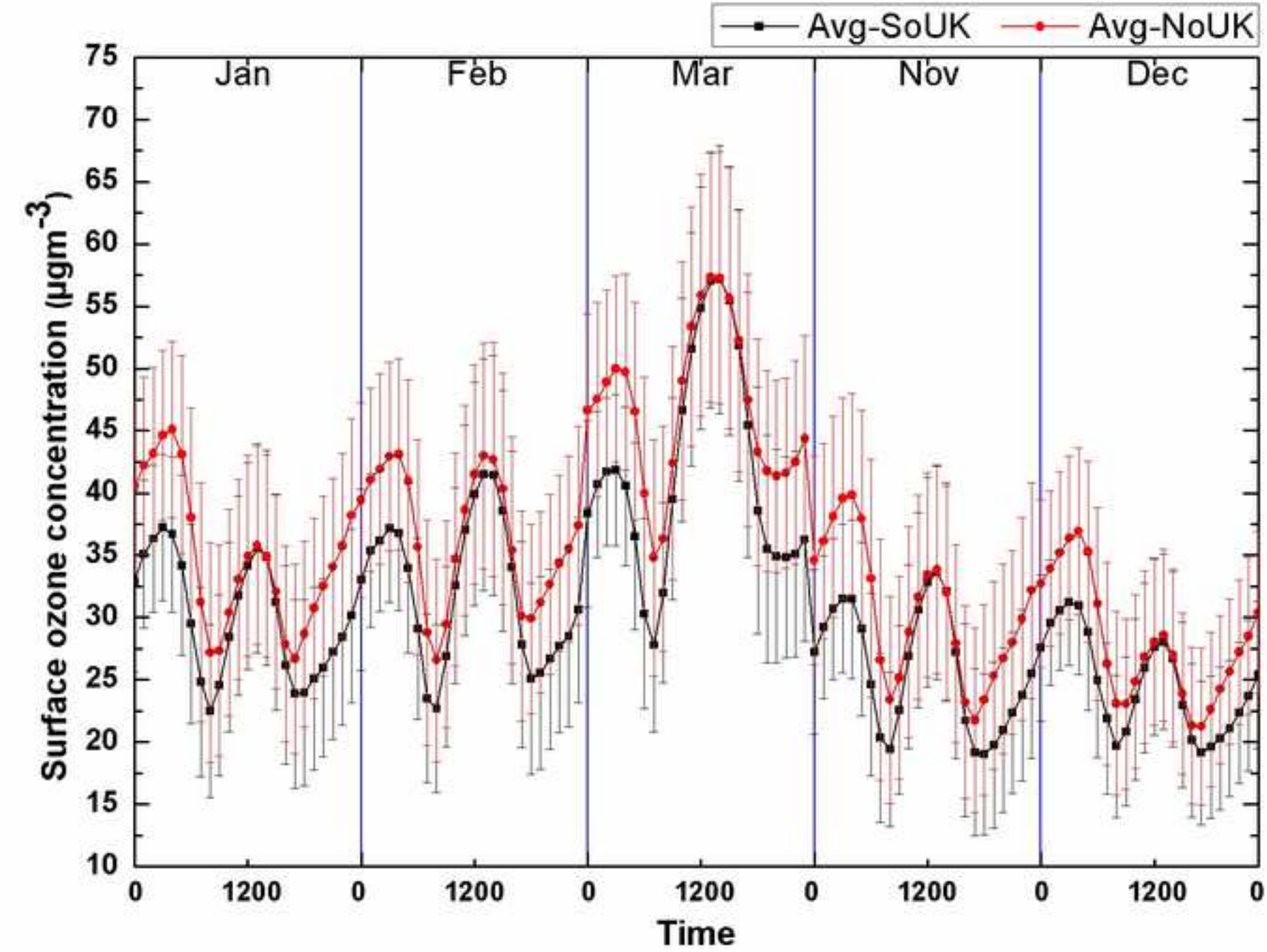

Figure 5

Click here to download Figure: Figure 5 -Winter months -MADV HSNS-LSNS of UK.jpg

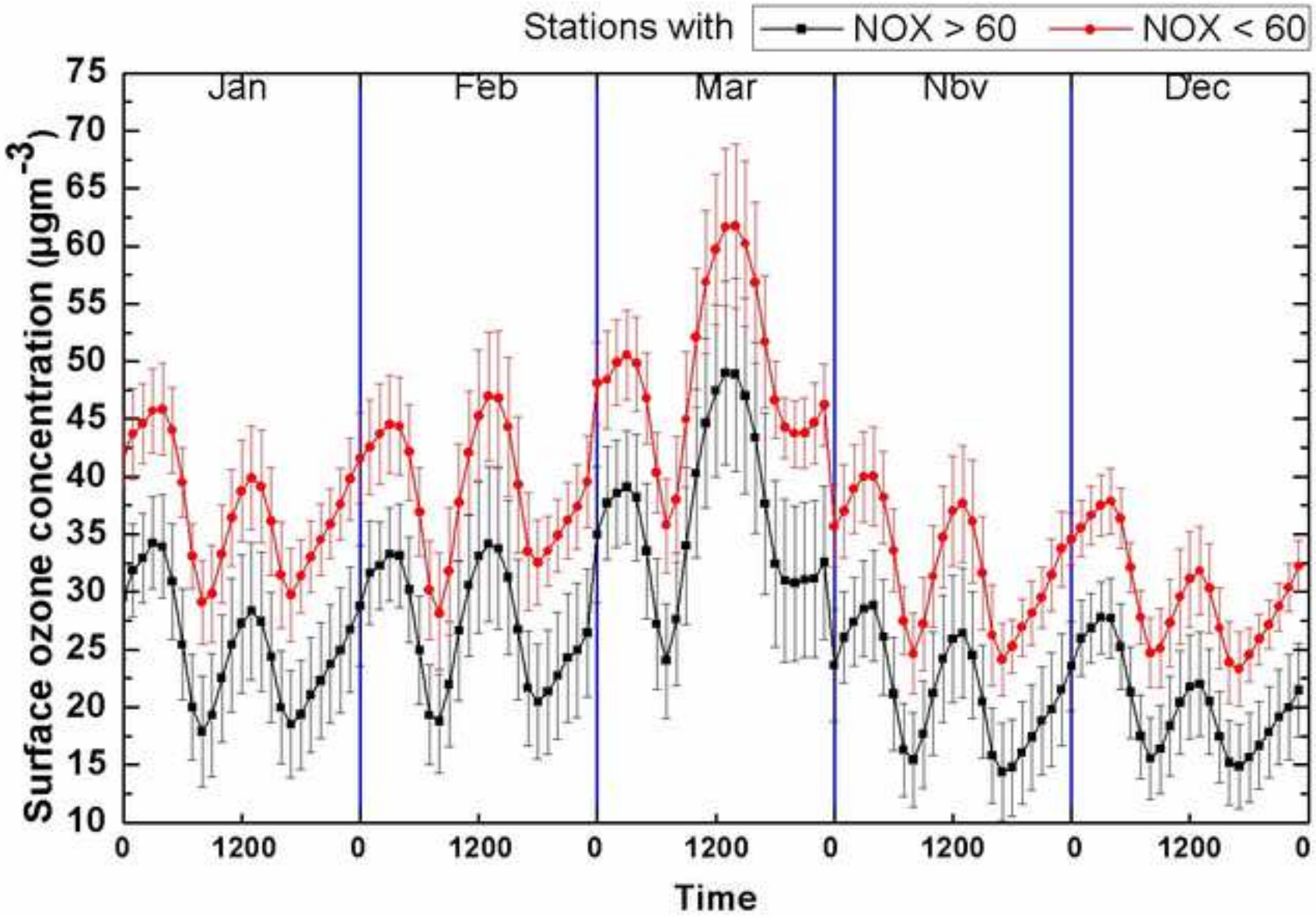

Figure 6
Click here to download Figure: Figure 6 -Freq Dis.jpg

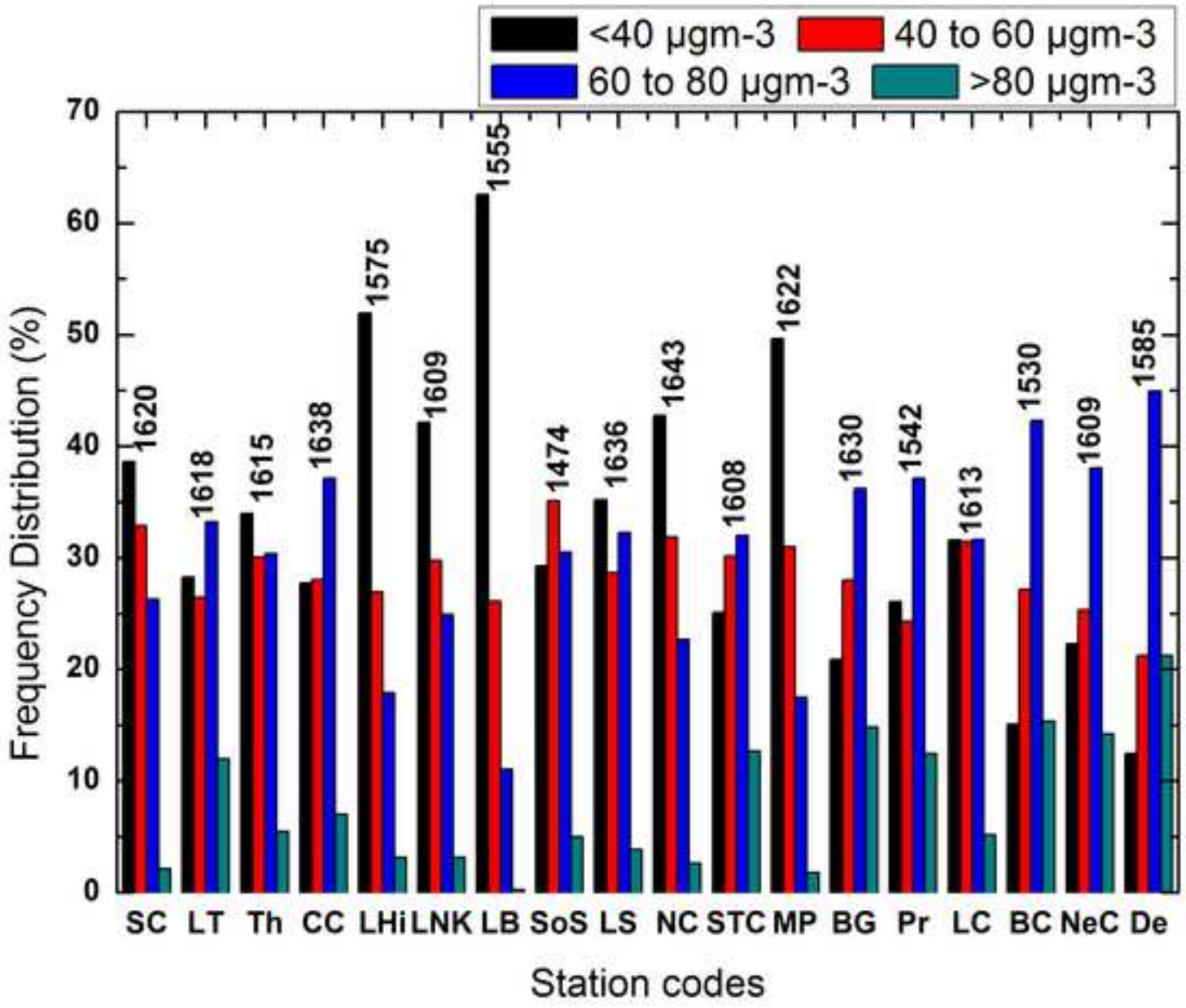

Table 1

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

Code	Site name[#] (NoUK/SoUK)[$]	UK-AIR ID	Lat	Long	Alt. (m)	A	A (%)	B (μgm^{-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*
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*

- urban background sites

$ - NoUK : North of UK ; SoUK : South of UK

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

B – 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 $\mu g/m^3$ and values in italics represents sites with Low Surface NO_X Stations (LSNS) with decadal mean NO_X concentration < 60 $\mu g/m^3$)

* - Annual mean surface NO_X concentration for the year 2010 instead of decadal mean

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
			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 $\mu g/m^3$.

Station code (A)	Max. NSO at (A)	Date	Maximum NSO concentration (at specific station)																	B
			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

B- No. of stations with NSO ≥80 $\mu g/m^3$

Reply to Reviewer's comments (Second revision):

We are thankful to the reviewer for reviewing the manuscript and for the helpful and positive comments. In response to the reviewer's comment (second revision), we have replied to the comment in this document and made required changes in the manuscript. As per the reviewer suggestion we have carefully revised the 'conclusion' section of the manuscript and incorporated all the suggestions/corrections. All the changes in the manuscript (second revision) are highlighted in 'Red' colour.

Reviewers' comments:

The manuscript improved against the originally submitted version. The study should be conclusive, which it is not really in the present stage. All repetitions from the results section should be removed from the conclusion section. The only conclusion really made (last paragraph) should be expanded in order to guide further investigation of the topic /phenomena: How can parameters influencing NSO events be addressed, which situations and sites are most promising to elucidate the mechanism (in the light of previous knowledge, referenced in the introduction)?

Reply: As per the reviewer suggestion we have carefully revised the 'conclusion' section of the manuscript, deleted repetition and incorporated all the suggestions/corrections. All the changes in the manuscript (second revision) are highlighted in 'Red' colour. We rewrote the last paragraph of the conclusion, which is as follows:

'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 warrants further investigation.'

Supplementary Material -Text

Click here to download Supplementary Material: NSO-UK_Supplementary material.doc

Supplementary Material -Table S1

Click here to download Supplementary Material: Table S1.doc

Supplementary Material -Figure S1

Click here to download Supplementary Material: Figure S1 -Surface urban background NOx concentration.jpg

Supplementary Material -Figure S2

Click here to download Supplementary Material: Figure S2 -SoUK NOX each station.jpg

Supplementary Material -Figure S3

Click here to download Supplementary Material: Figure S3 -NoUK NOX each station.jpg

Supplementary Material -Figure S4

Click here to download Supplementary Material: Figure S4 - Winter months -MADV of each station in SoUK.jpg

Supplementary Material -Figure S5

Click here to download Supplementary Material: Figure S5 - Winter months -MADV of each station in NoUK.jpg