

## Research Article

# Estimation of Daytime NO<sub>3</sub> Radical Levels in the UK Urban Atmosphere Using the Steady State Approximation Method

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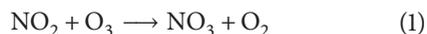
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The steady state approximation has been applied to the UK National Environment Technology Centre (NETCEN) data at three urban sites in the UK (Marylebone Road London, London Eltham, and Harwell) over the period of 1997 to 2012 to estimate the concentrations of daytime NO<sub>3</sub>. Despite the common assertion that NO<sub>3</sub> levels are negligible in the day as a consequence of photolysis, there are occasions where NO<sub>3</sub> reaches a few pptv. A seasonal pattern in NO<sub>3</sub> concentration was observed with higher levels in the spring with consistent peaks in April and May. A combination of temperature effects (the formation of NO<sub>3</sub> from the reaction of NO<sub>2</sub> with O<sub>3</sub> has a high activation energy barrier), a distinct pattern in O<sub>3</sub> concentration (peaking in spring), and loss via reaction with NO peaking in winter is responsible for this trend. Although reaction with OH is still the dominant loss process for VOCs during the day, there are VOCs (unsaturated) that will have an appreciable loss due to reaction with NO<sub>3</sub> in the daytime. Since the addition reaction of NO<sub>3</sub> with alkenes can lead directly to organic nitrate formation, there are implications for O<sub>3</sub> formation and secondary organic aerosol formation during daytime and these are discussed.

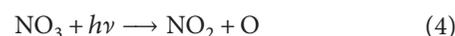
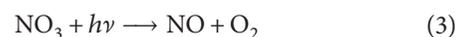
## 1. Introduction

The role of the nitrate radical (NO<sub>3</sub>) in the atmospheric cycle has long been recognized and it is believed to be one of the most important oxidizing species in the nighttime troposphere [1–4]. NO<sub>3</sub> is known to photolyse rapidly in the day [5] but in addition under high NO levels, NO<sub>3</sub> is titrated rapidly during the day and until recently it has been assumed that it is restricted to be at night-time hours where it can be an important sink of organic species [6]. NO<sub>3</sub> was observed in the day in previous studies [7, 8] and through its oxidation of VOCs it may be contributing a nonnegligible fraction to the total RO<sub>2</sub> budget [9].

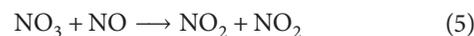
NO<sub>3</sub> radicals are produced by the relatively slow oxidation of NO<sub>2</sub> by O<sub>3</sub>, which then react with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub>. N<sub>2</sub>O<sub>5</sub> can thermally decompose giving back NO<sub>2</sub> and NO<sub>3</sub>:



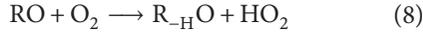
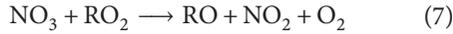
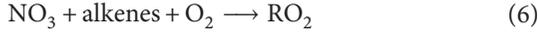
In the daytime, NO<sub>3</sub> is readily photolysed through the reactions (3)–(4), with a life time of ~5 s with the sun overhead [10] and hence its importance as an oxidant is greatly reduced [11]:



Urban daytime NO<sub>3</sub> can be removed efficiently via the reaction with NO [12]:



Another loss process of NO<sub>3</sub> involves reaction with alkenes leading to the production of peroxy radicals [10]:



$\text{NO}_3$  radicals can react with peroxy radicals via reaction (7) to produce alkoxy radicals and these can, depending on R, form  $\text{HO}_2$  radicals and be a source of  $\text{HO}_x$  [13–22]. Recent studies have indicated that the levels of  $\text{NO}_3$  through the day are higher than previously thought [7, 8, 23, 24]. Geyer et al. [8] found levels of daytime  $\text{NO}_3$  to range from 5 to 31 ppt with the maximum levels measured in the hours preceding sunset, when photolysis rates were lower. Brown et al. [7] and Horowitz et al. [23] have recognised that  $\text{NO}_3$  at even the tenths of pptv levels can begin to play a role in the oxidation of some VOCs (unsaturated). Horowitz et al. [23] have identified  $\text{NO}_3$  reactions with isoprene around dusk and into the early evening as being a small flux for isoprene loss (6%) but a disproportionately high flux for the formation of isoprene nitrates (49%), impacting on aerosol formation. Therefore, daytime  $\text{NO}_3$  may be a key component in controlling summertime  $\text{O}_3$  in the Eastern USA and in semipolluted areas in general.

Measurements of  $\text{NO}_3$  concentration in the atmosphere can be directly obtained, but typically sensitivities for various techniques (e.g., cavity ring down spectroscopy (CRDS), differential optical absorption spectroscopy (DOAS)) are in the pptv range [25]. It is known for  $[\text{NO}_3]$  that it exceeds these levels in polluted and semipolluted regions during night [26–30], but daytime measurements have rarely been made suggesting that levels are well below the instrumental detection limit [8]. The published daytime  $\text{NO}_3$  concentrations and the understanding of their role in the daytime oxidizing cycle are limited. However, there are other trace gases (e.g.,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$ , and unsaturated VOCs) that have been measured which can be used to estimate long-term daytime  $\text{NO}_3$  concentration by the steady state approximation.

Therefore, we estimate the urban daytime levels of  $\text{NO}_3$  over the time period of 1997 to 2012 at 3 urban sites in the UK (e.g., Marylebone Road London, London Eltham, and Harwell) using the steady state approximation as described by Brown et al. [7]. Data for  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$ , and some VOCs are taken from hourly measurements made as part of the NETCEN (National Environmental Technology Centre, Culham, Oxfordshire) data archive [31]. The conceivable impacts on the seasonal and daily variations of the level of  $\text{NO}_3$  for all of the selected sites are discussed in the study. Limitations of the method and interpretation of these results are also presented.

## 2. Methodology

*2.1. The Steady State Approximation.* Assuming the steady state approximation, the rate of total production of  $\text{NO}_3$  and the rate of loss of  $\text{NO}_3$  are equal; that is,

$$\frac{d[\text{NO}_3]}{dt} = 0 \quad (9)$$

Brown et al. [7] have shown that the production and loss processes of  $\text{NO}_3$  in the day are

$$\text{Production of } \text{NO}_3 = k_1 [\text{O}_3] [\text{NO}_2] \quad (\text{I})$$

$$\begin{aligned} \text{Loss of } \text{NO}_3 = & J_3 [\text{NO}_3] + J_4 [\text{NO}_3] \\ & + k_5 [\text{NO}] [\text{NO}_3] \\ & + \sum k_6 [\text{NO}_3] [\text{alkene}] \end{aligned} \quad (\text{II})$$

The loss due to photolysis only exists in daylight hours. In order to determine which hours of the day photolysis would occur, the solar zenith angle ( $\theta_z$ ) was calculated through (III)

$$\cos \theta = \sin \delta \sin \phi + \cos \phi \cos \phi \cos \omega, \quad (\text{III})$$

where  $\delta$  is equal to the declination of the sun,  $\omega$  is the hour angle, and  $\phi$  is the latitude. If  $\theta_z$  is greater than  $90^\circ$ , the region is in darkness and if less than  $90^\circ$ , it is daylight and photolysis is present as a loss process.

A photolysis constant ( $J$ ) was calculated as

$$J_x = \int \sigma_x(\lambda) \phi_x(\lambda) F(\lambda) \delta_x, \quad (\text{IV})$$

where  $F$  is a specific actinic flux,  $\sigma_x$  is the absorption cross-section,  $\phi_x$  is the quantum yield, and  $\lambda$  is the wavelength. More details about the calculation can be found in Landgraf and Crutzen [35]. It should be noted that in these calculations fixed layers of clouds are used to determine the photon flux and hence photolysis rate but in conventional parlance these are clear sky photolysis rates. The steady state concentration of  $\text{NO}_3$  during the day becomes

$$[\text{NO}_3] = \frac{k_1 [\text{O}_3] [\text{NO}_2]}{J_3 + J_4 + k_5 [\text{NO}] + \sum k_6 [\text{alkenes}]} \quad (\text{V})$$

The importance of alkenes to the budget of  $\text{NO}_3$  is negligible when compared with  $\text{NO}$  and photolysis. For example,  $1.5 \times 10^{12}$  molecules  $\text{cm}^{-3}$  isoprene (i.e., approximately 60 ppb) is required to achieve the loss rate of  $1 \text{ s}^{-1}$ . From London Eltham site in 2005, the median value for isoprene =  $7.0 \times 10^8$  molecules  $\text{cm}^{-3}$ , which is  $10^4$  lower than the required value, confirming the negligibility of the VOCs to the  $\text{NO}_3$  budget. Of course a sum of alkenes is required but a calculation using available alkene data and scaling up to include other possible alkenes all suggest that the direct loss via reaction with alkene is not significant for  $\text{NO}_3$ , although we show later that the loss via reaction with  $\text{NO}_3$  for some alkenes is very significant.

The resultant steady state equation used is therefore

$$[\text{NO}_3] = \frac{k_1 [\text{O}_3] [\text{NO}_2]}{J_3 + J_4 + k_5 [\text{NO}]} \quad (\text{VI})$$

Through knowledge of the concentrations of the relevant species, rate constants, and photolysis rates, the concentration of  $\text{NO}_3$  is calculated. The statistical language R and the associated ‘‘openair package’’ have been used for performing statistical analysis and making figures [36].

TABLE 1: Site description.

Site	Situation	Site type	Data series
London Eltham	Situated in the London Borough of Greenwich and surrounded by a number of sports field and a golf course.	Suburban	1997–2012
London, Marylebone Road	Situated 1 m from the busy Marylebone Road in the street canyon with traffic flows of 50000 vehicles per day.	Kerbside	1998–2012
Harwell	Situated in the outskirts of Oxford and surrounded by agricultural fields with a wooded area 25 meters southeast of it.	Rural	2001–2012

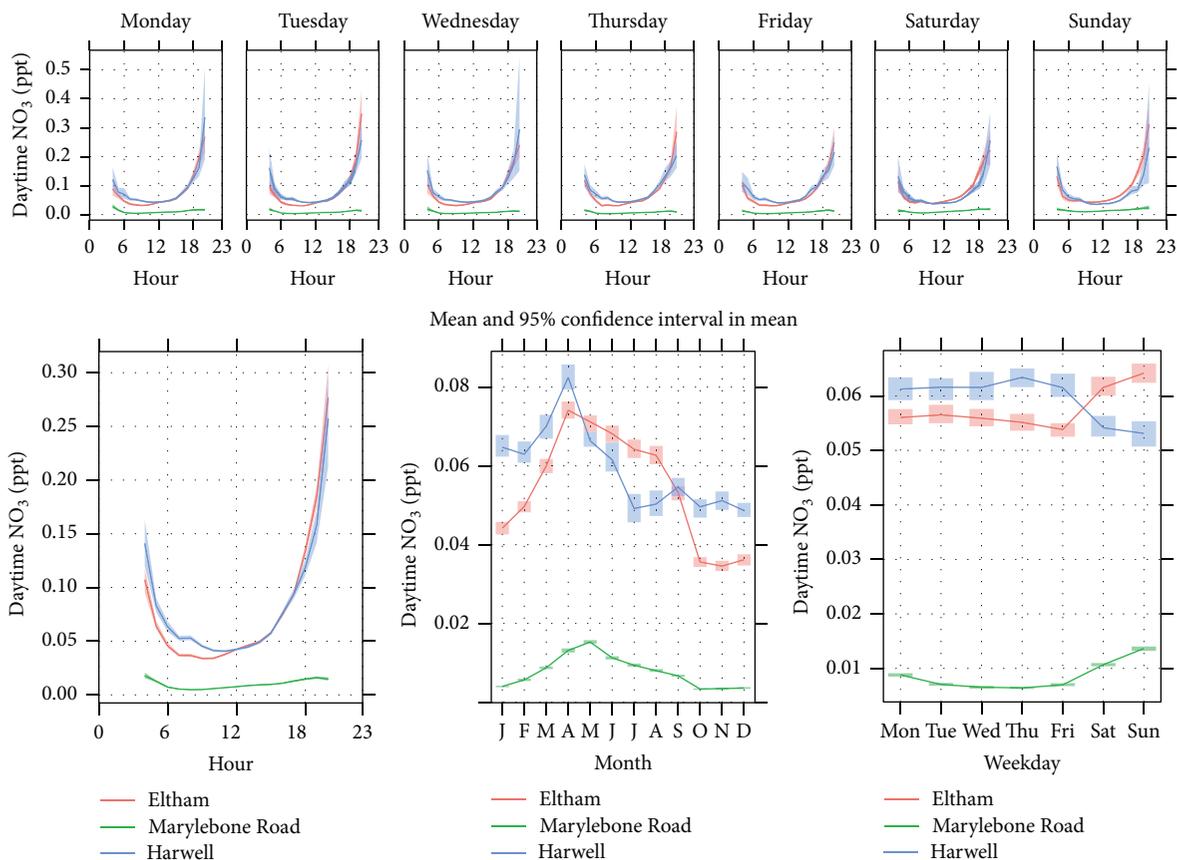


FIGURE 1: The hourly, monthly, and daily daytime NO<sub>3</sub> concentration in the three urban sites of UK over the time series of 1997 to 2012.

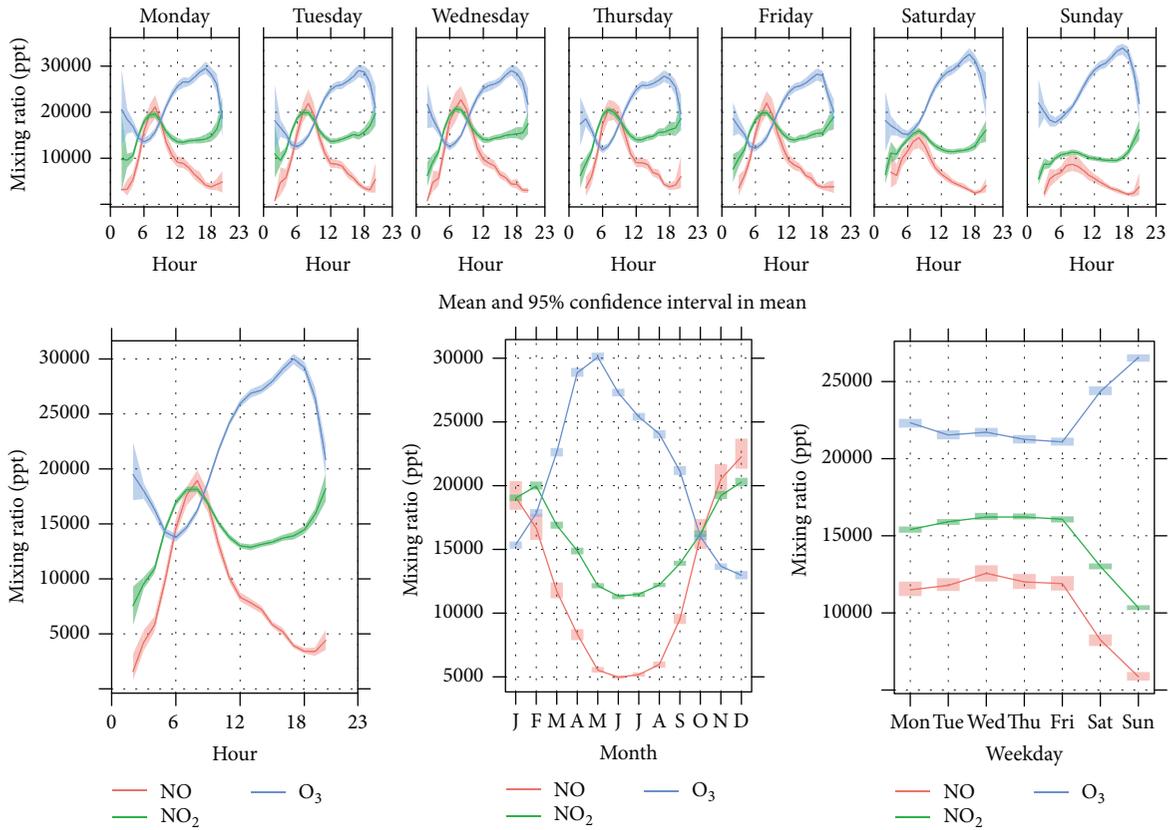
2.2. *Site Selection.* The monitoring sites in the NETCEN archive have been chosen in areas which give a range of urban environments (kerbside, suburban, and rural). Sites are different, ranging from being impacted heavily by vehicles (e.g., Marylebone Road) through to being heavily impacted by VOCs from vegetation (e.g., Harwell). All sites are at ground level and have continuous hourly data of all the species required for the calculation. The site description is summarised in Table 1.

### 3. Results and Discussion

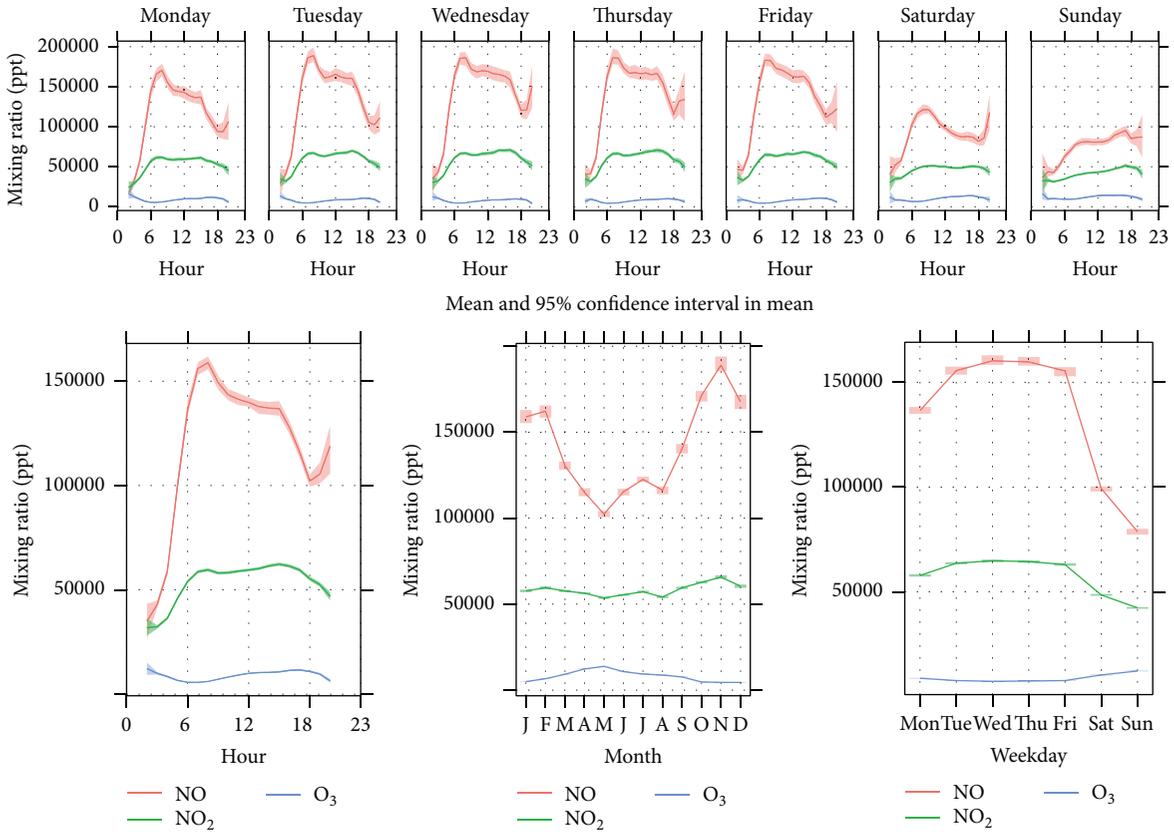
The average daytime NO<sub>3</sub> concentrations over the time period of 1997 to 2012 for all three urban sites of UK (e.g., London Eltham, London Marylebone Road, and Harwell) vary significantly throughout the daytime (see Figure 1). NO<sub>2</sub>

and O<sub>3</sub>, both involved in the major NO<sub>3</sub> production reaction, are of great importance for the variation of daytime NO<sub>3</sub> levels. As a result of the photolysis, a rapid reduction of NO<sub>3</sub> occurs throughout the daylight hours, and the reduction is more pronounced at the middle of the day. The levels of NO<sub>3</sub> in the early morning and early evening time are found to be comparatively higher than the midday NO<sub>3</sub> level because of the reduced effect of photolysis (see Figure 1). The loss of NO<sub>3</sub> by reaction with NO is high throughout the daylight hours (this peaks in the morning) (see Figure 2) and is also responsible for the regional variation in the magnitude of NO<sub>3</sub> across the three sites. Combined, these two major loss processes contribute together to the suppression of NO<sub>3</sub> concentrations in the day.

Table 2 provides the statistics of the daytime NO<sub>3</sub> level calculated by the steady state approximation for the three



(a)



(b)

FIGURE 2: Continued.

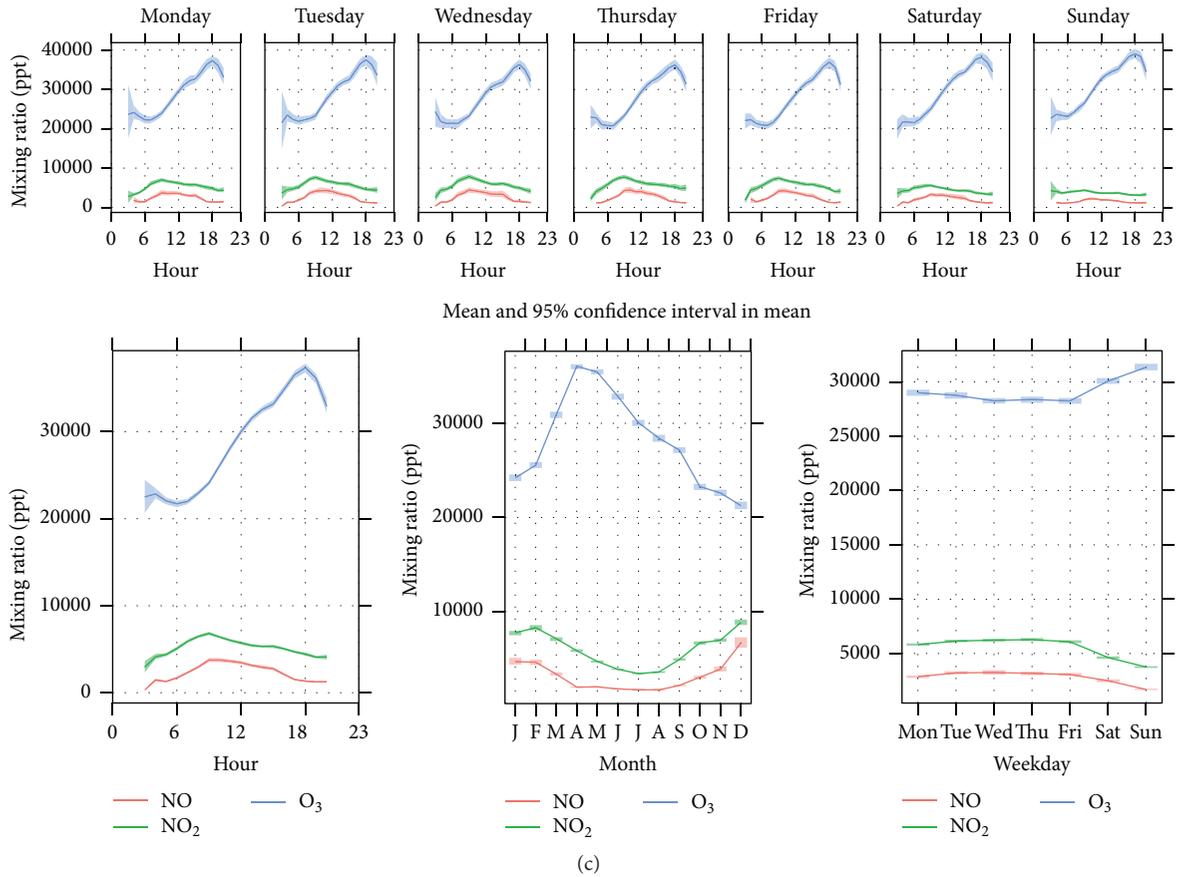


FIGURE 2: The hourly, monthly, and daily daytime NO, NO<sub>2</sub>, and O<sub>3</sub> concentration in the three sites of UK for the time series 1997–2012, (a) London Eltham, (b) Marylebone Road London, and (c) Harwell.

TABLE 2: Average and maximum daytime NO<sub>3</sub> at the different urban sites of UK for the time period of 1997 to 2012.

	Harwell	Marylebone Road	Eltham
Average NO <sub>3</sub> (ppt)	0.06 ± 0.09	0.01 ± 0.01	0.06 ± 0.08
Maximum NO <sub>3</sub> (ppt)	4.70	0.40	2.90

monitoring sites of UK over the time period of 1997 to 2012. The daytime NO<sub>3</sub> values calculated in this study are comparable with the previous observed results [7, 8]. Geyer et al. [8] measured NO<sub>3</sub> by LP-DOAS in August, 2000, at a site near Houston and found NO<sub>3</sub> levels of 5 pptv during 3 hours prior to sunset with a maximum of 31 pptv at sunset. Brown et al. [7] measured daytime NO<sub>3</sub> by CRDP from aircraft during the New England Air Quality Study in the summer of 2004 and found approximately 0.5 pptv near midday. In this latter campaign, the measurement of NO<sub>3</sub> was recorded only from 2 to 3 days of campaign results, which subsequently limits the scope of the comparison with our estimated NO<sub>3</sub> values. However, there are many occasions in our study where NO<sub>3</sub> reaches up to a few pptv in summer daytimes (e.g., 4.7 ppt on 5 June 2002 8:00 pm, 3.9 ppt on 13 July 2003 8:00 pm at Harwell site, 2.9 ppt on 10 August 2001 8:00 pm, and 2.8 ppt on 16 July 2010 8:00 pm).

The daytime NO<sub>3</sub> levels for Harwell and London Eltham locations are found to be very similar in magnitude (average of 0.06 ppt). However, the levels at Marylebone Road are found to be the lowest (average of 0.01 ppt) because of higher NO levels with a day time average value of 135 ppb for the period of 1998 to 2012 arising from heavy traffic congestion (50,000 vehicles per day). This results in the decreased ozone levels (average of 8.8 ppb) which leads to a decrease in the production of NO<sub>3</sub> and hence an overall decrease of NO<sub>3</sub> levels in Marylebone Road. Another reaction that produces NO is the conversion via photolysis of NO<sub>2</sub> whose concentration is also higher at Marylebone Road (average of 57.8 ppb) and this too contributes to a reduction of NO<sub>3</sub> concentrations. The relatively low levels of NO in Harwell (average of 2.9 ppb) and London Eltham (average of 10.6 ppb) lead to a reduction in the loss process of NO<sub>3</sub> that results in higher daytime NO<sub>3</sub> concentrations compared with Marylebone Road.

A clear seasonal variation of the levels of daytime NO<sub>3</sub> is observed at the three monitoring sites in the UK over the period 1997–2012 (Figure 1). Photolysis frequencies are mainly responsible for the diurnal variation as well as contributing to the seasonal variability of NO<sub>3</sub>. Through the daytime and the summer months, the solar zenith angle is at its lowest; hence levels of photolysis increase promoting NO<sub>3</sub> loss. The increase in photolysis is counteracted by increasing

O<sub>3</sub>, decreasing NO concentrations (see Figure 2), and increasing temperature which increases the production of NO<sub>3</sub> via reaction (1), resulting in the overall higher summer levels. However, in the summer months, the increase in OH levels leads to enhanced production of HNO<sub>3</sub> through the reaction of OH and NO<sub>2</sub>, which indirectly removes NO from the troposphere.

Overall, the daytime NO<sub>3</sub> levels peak in spring with lower concentrations throughout the winter months for all sites. Urban O<sub>3</sub> levels at the monitoring sites of UK tend to peak in late spring, whereas the changes in NO<sub>2</sub> throughout the year are less pronounced with slightly lower levels in the summer months (see Figure 2), and the seasonal variation of O<sub>3</sub> leads to the highest NO<sub>3</sub> concentration in spring. The lower concentrations of NO<sub>3</sub> in winter months were observed due to the suppression of NO<sub>3</sub> production from the temperature dependent reaction between NO<sub>2</sub> and O<sub>3</sub>. This reaction has an activation energy of 20.54 kJ mol<sup>-1</sup> and a resultant rate constant of  $3.52 \times 10^{-17}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 298 K; this rate constant experiences a large reduction of 50% (i.e.,  $1.76 \times 10^{-17}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 275 K), when the temperature is reduced by 23 K [37]. It has been found that NO<sub>3</sub> formation rates at Marylebone Road, Eltham, and Harwell sites vary by about 20% for the average summer winter temperature difference of 11 K.

Coupled with temperature, the NO and NO<sub>2</sub> concentrations can affect the seasonal variations of NO<sub>3</sub> concentration. The concentration of NO is the highest in winter months for all of the sites (see Figure 2). The reaction of NO with NO<sub>3</sub> is the major daytime loss process for NO<sub>3</sub> in the urban environment with a rate constant at 298 K =  $2.7 \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> [38]. At this rate constant, ~0.3 ppb of NO is required to produce a loss rate comparable with photolysis. On the Marylebone Road, the average winter NO concentration is found to be 165 ppb, which has a significant impact on the concentration of daytime NO<sub>3</sub> in winter time.

The concentrations of NO<sub>3</sub> for all sites vary throughout the week, as shown in Figure 1. The highest concentrations are observed at the weekends and are at their lowest during the weekdays in London Eltham and Marylebone Road. This trend follows the level of traffic congestion, which is reduced at the weekends. This causes the loss process by NO to be increased during weekdays (see Figure 2) due to high levels of congestion on the Marylebone Road as well as London Eltham and the subsequent anthropogenic contribution to the NO concentration, resulting in lower NO<sub>3</sub>. In Harwell, an opposite trend is observed with higher concentrations of NO<sub>3</sub> during weekdays in comparison with the weekend. Like other sites, the NO<sub>x</sub> concentrations at the Harwell site during weekdays ([NO] = 3.1 ppb and [NO<sub>2</sub>] = 6.1 ppb) are higher than that during weekend ([NO] = 2.1 ppb and [NO<sub>2</sub>] = 4.2 ppb). However, the relatively low NO at the Harwell site greatly reduces the impact of the major loss process for NO<sub>3</sub> and enhances the impact of the major production term,  $k_1[O_3][NO_2]$ , at higher concentration of O<sub>3</sub> during weekend (weekday's [O<sub>3</sub>] = 28.5 ppb and weekend's [O<sub>3</sub>] = 30.7 ppb).

In the study, extensive datasets of daytime NO<sub>3</sub> were obtained through the application of the steady state

approximation. Although the steady state provided an excellent way of calculating the concentrations given the availability of trace gases, there is a degree of error associated with the calculations. The rates of photolysis were calculated considering clear sky; in reality there are a number of different variables (e.g., cloud cover) that can affect photolysis rates, so the NO<sub>3</sub> estimated in this study would be a lower limit on balance. Given that at the sites analysed the NO<sub>3</sub> concentration calculation is dominated by the concentration of NO and not photolysis, typically photolysis is responsible for 22% of the loss for the typical NO concentration of 1 ppb, even though the photolysis rate could be reduced by cloud cover by 50% and the overall impact of the photolysis on the calculated NO<sub>3</sub> concentration is around 11%. The largest uncertainty in the calculation arises from the rate coefficients (typically  $\pm 10\%$ )  $k_1$  and  $k_5$  and in the concentrations of O<sub>3</sub>, NO<sub>2</sub>, and NO (typically  $\pm 10\%$ ), which combined gives an estimate of the overall uncertainty of  $\pm 40\%$ . Nevertheless, such an analysis provides insight into long-term measurements of daytime NO<sub>3</sub> concentrations that are currently absent.

**3.1. Impact of Daytime NO<sub>3</sub> on VOC Burdens.** The daytime oxidation of VOCs is dominated by their reactions with OH and O<sub>3</sub>. However, certain biogenic VOCs (e.g., terpenes) have rate coefficients for their reaction with NO<sub>3</sub>, which are similar or greater than with OH (see Table 3) and thus, provided sufficient levels of NO<sub>3</sub> exist, will provide competition with or dominate the daytime reactivity of these VOCs [39]. Using urban daytime concentrations of NO<sub>3</sub> and OH of 0.06 ppt and  $1 \times 10^6$  molecules cm<sup>-3</sup>, respectively, for calculating the comparison of VOC loss by NO<sub>3</sub> and OH, the ratio of loss rates of VOC ( $R_{voc}$ ) by NO<sub>3</sub> and OH (Table 3) shows that monoterpenes are removed more effectively by NO<sub>3</sub> during the daytime than by OH. The monoterpenes can be impacted to a greater extent by daytime levels of NO<sub>3</sub> in the urban sites of UK, particularly in the case of limonene; the relative rate of removal by NO<sub>3</sub> compared with OH is 33 for Harwell and London Eltham sites and 5.5 even for the Marylebone Road London. The pinene oxidation by OH experiences competition from NO<sub>3</sub> in these urban sites when the concentrations of NO<sub>3</sub> and OH are similar. However, if phenomena such as a higher NO<sub>3</sub> production occurs due to higher NO<sub>2</sub> and O<sub>3</sub> levels, oxidation of pinene via NO<sub>3</sub> can be of great significance. Geyer et al. [8] observed that 32% of all daytime  $\alpha$ -pinene oxidation was through its reaction with NO<sub>3</sub>. VOCs produced in areas around the Marylebone Road such as Regents Park, the wooded areas in London Eltham, and the vegetated area surrounding Harwell are likely to be affected by the recorded daytime levels of NO<sub>3</sub> via oxidation of these biogenic sources.

The products of biogenic VOC oxidation by NO<sub>3</sub> differ from those produced via reaction by OH and are of interest due to the relative abundance of isoprene and monoterpenes in the troposphere [40]. The direct impact of the daytime NO<sub>3</sub> levels on VOCs has not been analysed in our study, but considering the previous studies [7, 8, 23], the nonnegligible daytime NO<sub>3</sub> levels estimated using the steady state approximation from UK urban sites will have significant implications on the burdens of biogenic VOCs (e.g., monoterpenes).

TABLE 3: Relative rates of removal of hydrocarbon  $[R_{\text{voc}}]$  of some selected VOCs by  $\text{NO}_3$  and OH considering the mixing ratios of  $\text{NO}_3$  and OH are 0.06 ppt (this study for UK urban representative sites (e.g., London Eltham)) and  $1 \times 10^6$  molecules  $\text{cm}^{-3}$  (tropospheric average global concentration), respectively.

Compound	$k_{\text{OH}}$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	$k_{\text{NO}_3}$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	$[R_{\text{voc}}] = \frac{k_{\text{NO}_3}[\text{NO}_3]}{k_{\text{OH}}[\text{OH}]}$
Isoprene	$1.00 \times 10^{-10}$ [32]	$7.00 \times 10^{-13}$ [10]	0.01
$\alpha$ -Pinene	$5.33 \times 10^{-11}$ [32]	$5.83 \times 10^{-12}$ [33]	0.16
2-Methyl-2-butene	$8.69 \times 10^{-11}$ [10]	$9.37 \times 10^{-12}$ [10]	0.16
$\beta$ -Pinene	$7.81 \times 10^{-11}$ [32]	$2.81 \times 10^{-11}$ [32]	0.54
d-Limonene	$8.80 \times 10^{-14}$ [34]	$1.91 \times 10^{-12}$ [33]	32.6

The oxidation of alkenes by  $\text{NO}_3$  can produce peroxy radicals [41] which can contribute to the total peroxy radical concentrations in the urban sites. The reactions of conjugated double bond alkenes (e.g., isoprene, monoterpenes) with  $\text{NO}_3$  can produce organic nitrate compounds directly, which are significant  $\text{NO}_x$ -reservoir compounds affecting regional ozone formation [23, 42, 43]. Such nitrates have low enough vapour pressure to condense at the pressure and temperature experienced in UK urban sites and could have a large impact on SOA formation in the urban area [44–46].

#### 4. Conclusion

National data in the UK has been assessed to calculate the daytime  $\text{NO}_3$  levels at three sites in the UK (London Eltham, Marylebone Road, and Harwell) over the period 1997–2012. At each site, hourly measurements of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$ , with estimates of the photolysis frequency, were used to determine daytime  $\text{NO}_3$  radical levels. The maximum values of daytime  $\text{NO}_3$  for all sites are found to be in the hours proceeding sunset, when photolysis rates are at a minimum. The average daytime  $\text{NO}_3$  concentration ranges from 0.01 to 0.06 ppt, with the lowest value returned by the most polluted site (Marylebone Road). All sites experience the same overall trend in daytime  $\text{NO}_3$  throughout the calendar year. Peaks appear in spring, where  $\text{O}_3$  levels pass through a maximum. Decreased levels of  $\text{NO}$  vital to the loss process of  $\text{NO}_3$  see a slight decrease during the summer and provide further explanation for the seasonal trends observed. Higher levels of OH in summer are accountable for the decreased levels of  $\text{NO}$  as it reacts with  $\text{NO}_2$  to form  $\text{HNO}_3$ , which indirectly removes  $\text{NO}$  from the troposphere. Although the levels of  $\text{NO}_3$  are generally sub-pptv, they are high enough to see nonnegligible effects, particularly on the burdens of biogenic terpenes making a significant contribution to organic nitrate formation which could impact upon the formation of secondary organic aerosol during the day.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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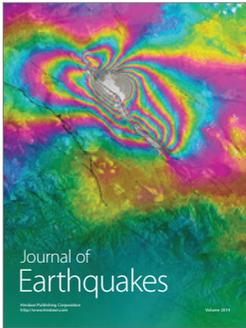
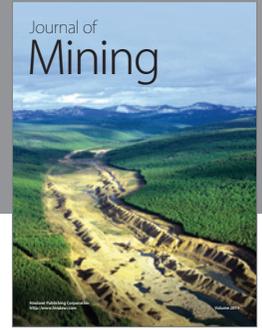
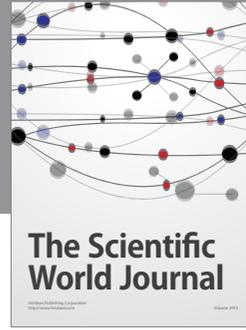
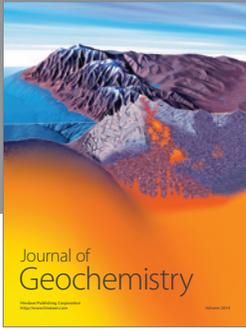
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