Estimation and comparison of night-time OH levels in the UK urban atmosphere using two different analysis methods

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Abstract

Night-time OH levels have been determined for UK urban surface environments using two methods, the decay and steady state approximation methods. Measurement data from the UK National Environmental Technology Centre archive for four urban sites (Bristol, Harwell, London Eltham and Edinburgh) over the time period of 1996 to 2000 have been used in this study. Three reactive alkenes, namely isoprene, 1,3-butadiene and trans-2-pentene were chosen for the calculation of OH levels by the decay method. Hourly measurements of NO, NO_2, O_3, CO and 20 VOCs were used to determine night-time OH level using the steady state approximation method. Our results showed that the night-time OH levels were in the range of 1×10^5–1×10^6 molecules/cm^3 at these four urban sites in the UK. The application of a t-test of these analyses indicated that except Bristol, there was no significant difference between the OH levels found from the decay and steady state approximation methods. Night-time levels of the OH radical appeared to peak in summer and spring time tracking the night-time O_3 levels which also passed through a maximum at this time.

Key words: night-time; urban; National Environmental Technology Center; steady state approximation; hydrocarbon decay method

Introduction

The OH radical is the dominant oxidant in the troposphere, whose levels peak in the day and were thought to decay rapidly to negligible levels at night. However, it has emerged that there are some oxidation processes that can contribute to night-time OH production. First, O_3 can react with alkenes to produce a significant amount of OH directly (Donahue et al., 1998; Kroll et al., 2001; Salisbury et al., 2001). Second, the nitrate radical (NO_3) is an important night-time oxidant and through the initiation of the degradation of several VOCs like monoterpenes (Rivett et al., 2003; Geyer et al., 2001), DMS (Winer et al., 1984; Allan et al., 1999) and phenols (Kurtenbach et al., 2002) significant amounts of peroxy- and even hydroxyl radicals can be generated during the night (Platt et al., 1990; Mihelcic et al., 1993; Carslaw et al., 1997; Geyer et al., 2003; Vrekoussis et al., 2007). Peroxy radicals are important chain carriers in the oxidation of hydrocarbons, as well as being intermediates in tropospheric ozone generation and precursors for night-time OH.

An understanding of compositional changes in the urban atmosphere and the effects of such changes on regional climate change and air quality require knowledge of OH levels in the urban atmosphere. There are a few field campaign studies of OH that have been able to characterize night-time OH chemistry only for the conditions during the campaign and the results cannot be generalized to other seasons or necessarily other locations (Emmerson and Carslaw, 2009; Kanaya et al., 2007; Shirley et al., 2006; Holland et al., 2003; Ren et al., 2003; Geyer et al., 2003; Platt et al., 2002; Eisele et al., 1996). In order to study seasonal changes long-term observations are necessary. To date there are no continental long-term night-time OH measurements. In this study, long-term OH concentration has been calculated using the decay and steady state approximation methods as they have typical life times of a few seconds (Khan et al., 2008; Rivett et al., 2003). Because of the short atmospheric lifetime of OH, the concentration level of OH is close to the steady state at which their production and loss are balanced. These production and loss processes are more complicated in urban environments because many hydrocarbons, carbonyl

species, and nitrogen species affect the chemistry of these processes.

Measurement data of O_3, NOx, CO and VOCs taken from the UK NETCEN (National Environmental Technology Centre, Culham, Oxfordshire) data archive have been used to infer year round OH night-time levels in four different urban sites of the UK using the decay and steady state approximation methods. The seasonal variations of the OH level for all of the selected sites were discussed.

1 Methodology

1.1 Decay method

At night-time, alkenes react chemically with OH, NO_3 and O_3 in addition to establishing a steady decay due to dispersion (Rivett et al., 2003). The rate of decay can be written as

$$\mathrm{d[Alkene]}_t/\mathrm{d}t = -[\mathrm{Alkene}]_0(k_{\mathrm{disp}} + k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{NO_3}}[\mathrm{NO_3}] + k_{\mathrm{O_3}}[\mathrm{O_3}]) \quad (1)$$

Defining the decay rate as $\frac{d[\mathrm{Alkene}]_t/[\mathrm{Alkene}]_0}{dt}$, the Eq. (1) can be written as

$$\text{Decay rate} = -k_{\mathrm{OH}}[\mathrm{OH}] - k_{\mathrm{NO_3}}[\mathrm{NO_3}] - k_{\mathrm{O_3}}[\mathrm{O_3}] - k_{\mathrm{disp}} \quad (2)$$

where, k_{OH}, $k_{\mathrm{O_3}}$, $k_{\mathrm{NO_3}}$ are the gas-phase rate coefficients for the reaction of the alkene with OH, O_3 and NO_3 and k_{disp} is a loss due to dispersion. By calculating the slopes of the graphs of $\ln([\mathrm{Alkene}]_t/[\mathrm{Alkene}]_0)$ vs. time for three alkenes (isoprene, 1,3-butadiene and trans-2-pentene) and by knowing the rate coefficients of the reaction of alkenes with O_3, NO_3, and OH, the OH concentration has been estimated using the following Eq. (3).

$$[\mathrm{OH}] = 1/\mathrm{det} \times (\mathrm{Slope}^{\mathrm{VOC1}}\left(k_{\mathrm{NO_3}}^{\mathrm{VOC2}} - k_{\mathrm{NO_3}}^{\mathrm{VOC3}}\right) +$$
$$\mathrm{Slope}^{\mathrm{VOC2}}\left(k_{\mathrm{NO_3}}^{\mathrm{VOC3}} - k_{\mathrm{NO_3}}^{\mathrm{VOC1}}\right) + \quad (3)$$
$$\mathrm{Slope}^{\mathrm{VOC3}}\left(k_{\mathrm{NO_3}}^{\mathrm{VOC1}} - k_{\mathrm{NO_3}}^{\mathrm{VOC2}}\right))$$

where,
$$\mathrm{det} = k_{\mathrm{OH}}^{\mathrm{VOC1}}\left(k_{\mathrm{NO_3}}^{\mathrm{VOC2}} - k_{\mathrm{NO_3}}^{\mathrm{VOC3}}\right) -$$
$$k_{\mathrm{NO_3}}^{\mathrm{VOC1}}\left(k_{\mathrm{OH}}^{\mathrm{VOC2}} - k_{\mathrm{OH}}^{\mathrm{VOC3}}\right) +$$
$$\left(k_{\mathrm{OH}}^{\mathrm{VOC2}} \times k_{\mathrm{NO_3}}^{\mathrm{VOC3}} - k_{\mathrm{NO_3}}^{\mathrm{VOC2}} \times k_{\mathrm{OH}}^{\mathrm{VOC3}}\right)$$

1.2 Steady state approximation method

Assuming the steady state approximation, the rate of total production of OH and the rate of loss of OH are equal, i.e.

$$\frac{d[\mathrm{OH}]}{dt} = \text{Production of OH} - \text{Loss of OH} = 0 \quad (4)$$

$$\text{Production of OH} = \sum k_1[\mathrm{O_3}][\mathrm{Alkenes}] + k_2[\mathrm{HO_2}][\mathrm{NO_3}] + k_3[\mathrm{HO_2}][\mathrm{O_3}] + k_4[\mathrm{HO_2}][\mathrm{NO}] \quad (5)$$

Table 1   List of volatile organic compounds (VOCs) used for the calculation of [OH]

Alkanes	Alkenes	Aromatics
Ethane	1,3-Butadiene	Benzene
Propane	1-Butene	Ethylbenzene
n-Butane	cis-2-Butene	Toluene
i-Butane	Ethene	
n-Pentane	Propene	
i-Pentane	Isoprene	
n-Hexane	trans-2-Butene	
n-Heptane	trans-2-Pentene	
Methylpentane		

where, $\sum k_1[\mathrm{O_3}][\mathrm{Alkenes}]$ is short-hand for summing up the contributions to OH production made from the ozonolysis of all alkenes and dienes etc., suitably weighted by their fractional OH yield.

$$\text{Loss of OH} = k_5[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}] + k_6[\mathrm{OH}][\mathrm{CO}] + k_7[\mathrm{OH}][\mathrm{NO}] + \sum k_8[\mathrm{OH}][\mathrm{VOCs}] \quad (6)$$

where, $\sum k_8[\mathrm{OH}][\mathrm{VOCs}]$ is short-hand for summing up the contributions to the loss of OH via reaction with all VOCs.

Therefore, the steady state concentration of OH over the night becomes:

$$[\mathrm{OH}] = \frac{\sum k_1[\mathrm{O_3}][\mathrm{Alkenes}] + k_2[\mathrm{HO_2}][\mathrm{NO_3}] + k_3[\mathrm{HO_2}][\mathrm{O_3}] + k_4[\mathrm{HO_2}][\mathrm{NO}]}{k_5[\mathrm{NO_2}][\mathrm{M}] + k_6[\mathrm{CO}] + k_7[\mathrm{NO}] + \sum k_8[\mathrm{VOCs}]} \quad (7)$$

VOCs (Table 1) including 9 alkanes, 8 alkenes and 3 aromatics were used for the calculation of the steady state OH concentrations. There is no information from the NETCEN dataset on [HO_2] and the implications of this omission for the calculation of [OH] are discussed.

The four sites chosen were a compromise between the availability of VOC data from the NETCEN archive for analysis and a range of urban environments. Three sites, London Eltham, Bristol and Edinburgh are designated as 'urban background' sites which are urban locations distanced from sources and broadly representative of city-wide background concentrations e.g. elevated locations, parks and urban residential areas. But the other site, Harwell is a 'rural' site which is open country location distanced from population centers, roads and industrial areas. In practice, the sites were established at a range of locations that reflect emissions from a variety of sources including motor vehicles and industry. Except the Harwell site, they were all in locations representative of exposure to the general public.

2 Results and discussion

Table 2 provides the statistics of the calculation and comparison of night-time [OH] from the decay and steady state approximation methods for the four monitoring sites over the time series of 1996 to 2000. The average night-time OH calculated by both methods is very similar in magnitude, i.e. between 10^5–10^6 molecule/cm^3. Using the t-test, both the methods gave quite similar results for all of the sites except Bristol. Platt et al. (2002) measured OH levels of 1.4×10^5 molecules/cm^3 in and around the Berlin

Table 2 Average and maximum [OH] values from decay and steady state method and the comparison of the methods for the four different locations of UK over the time period of 1996 to 2000.

	Monitoring sites	Bristol	Harwell	London Eltham	Edinburgh
Decay method	n	396	23	53	31
	Average $\pm$ error [OH] (molecules/cm^3)	$(5.9 \pm 6.3) \times 10^5$	$(2.3 \pm 2.1) \times 10^5$	$(2.2 \pm 2.1) \times 10^5$	$(3.0 \pm 2.3) \times 10^5$
	Maximum [OH] (molecules/cm^3)	5.0×10^6	7.4×10^5	9.0×10^5	8.1×10^5
Steady state method	n	1146	440	578	719
	Average $\pm$ error [OH] (molecules/cm^3)	$(3.1 \pm 3.5) \times 10^5$	$(1.8 \pm 1.6) \times 10^5$	$(1.9 \pm 1.6) \times 10^5$	$(2.8 \pm 3.4) \times 10^5$
	Maximum [OH] (molecules/cm^3)	4.0×10^6	8.9×10^5	1.1×10^6	3.1×10^6
Comparison of the methods	T	10.89	1.07	1.54	0.27
	Actual confidence level (%)	100	71.6	87.5	21.0
	Significantly different	Yes	No	No	No

area. Shirley et al. (2006) also measured night-time OH in the Mexico City Metropolitan Area that ranged from approximately 1×10^6 to 2×10^5 molecules/cm^3. The OH levels calculated in this study are in good agreement with these results. The application of these two methods by Rivett et al. (2003) for a small dataset from some summer measurements in Bristol also yielded night-time OH levels that were around 10^5 molecules/cm^3.

Among the monitoring sites, Bristol and Edinburgh both have the highest concentration of night-time OH radical because both are urban background sites (Rivett et al., 2003). Bristol is an industrial area with the largest concentration of chemical and oil industries in the south west of England. Edinburgh is also an industrial area including brewing, electronics, printing and publishing industries and surrounded by hills. High concentrations of reactive organic compounds including alkenes persist into the night and coupled with higher levels of O_3 at night, can produce elevated OH at these two sites. The calculated [OH] values are lower in Harwell and London Eltham. The level of night-time VOC is lower at Harwell, being a rural site, hence lower [OH] values are generated. At London Eltham, the site is very close to a high flow of traffic and experiences much higher NO levels than the other three sites. The higher NO levels react with NO_3 and O_3 and thus suppress the formation of OH.

Comparing it with the decay method, a slightly lower [OH] level has been estimated using the steady state approximation for all of the sites since only a relatively small number of alkenes are measured and can be used in the steady state approximation calculation and production from HO_2 is ignored. If more alkenes were used in the calculation, particularly if heavier and more reactive alkene species were considered and the production of OH from HO_2 was included, the estimation from the steady state method would be more accurate. In a similar way, because a limited number of VOCs were used in the OH loss calculation, there is also underestimation of the loss term that may result in an overestimate of the OH concentration. Clearly the level of VOC in each environment used in these calculations will be a lower limit, the impact on OH will depend on the type of VOC, the more alkenes the greater the production, the greater the saturated species the greater the loss. On balance OH is probably underestimated by this method.

The time series of the monthly average night-time [OH] calculated by the decay method for the four sites from
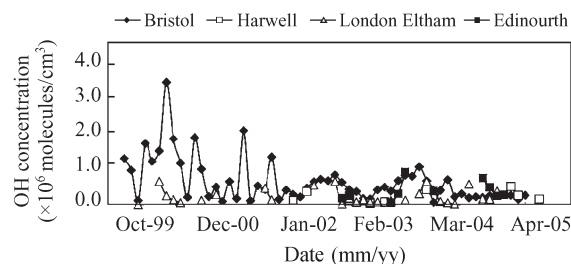
Fig. 1 Monthly average night-time OH concentration (calculated using the decay method) at four sites in UK from 1996 to 2000.
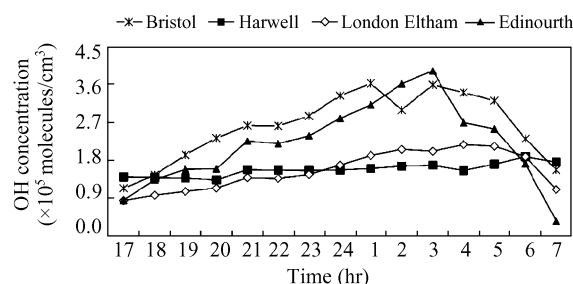
Fig. 2 Hourly average night-time OH concentration (calculated using the steady state approximation method) at four sites in UK for the time series of 1996–2000.

1996–2000 is shown in Fig. 1. Monthly average [OH] values for all four sites show a similar variation pattern. However, the values at Bristol site show the highest variability. It should be noted that there are less data for the Edinburgh and Harwell sites. It would seem sensible to assume that the main reason for the difference of OH levels retrieved from the four different sites is because of different chemical and physical conditions in each urban environment. In particular, a key factor is the very different NOx levels experienced at the different four sites.

Figure 2 shows the average night-time [OH] calculated using the steady state approximation method at the four sites over the whole time period of 1996 to 2000. The figure clearly shows the difference in the OH concentration for the different four sites because of their different production and loss rates involved over the time period. The variation is mainly due to the degree of local variability in the night-time concentrations of species such as O_3, NO_2, NO, CO, VOCs. The hourly average night-time OH show a steady increase from the early night with a slight decrease at 21:00 to reach a maximum late into the night before disappearing just before dawn (Fig. 2). Loss of OH via reaction with VOCs, NO, NO_2 and CO all decline
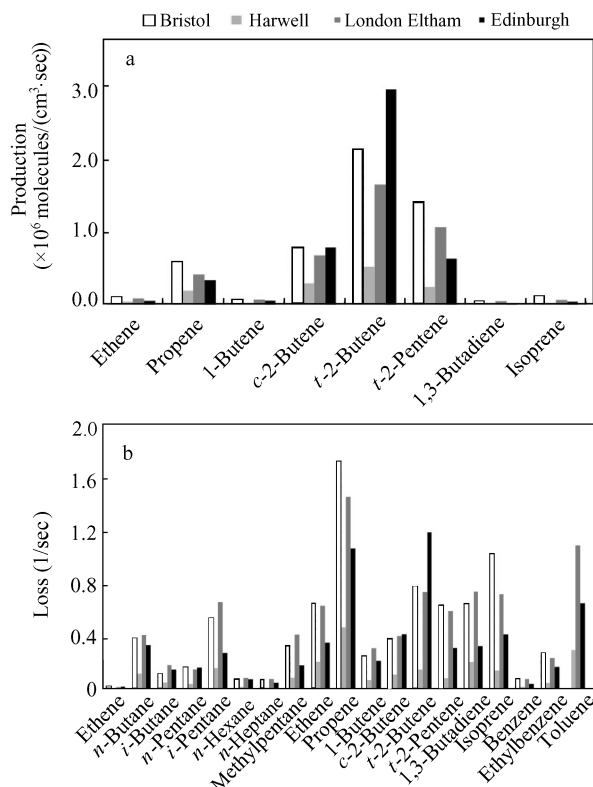
Fig. 3 Contribution of VOCs to OH production rates (a) and OH loss rates (b).
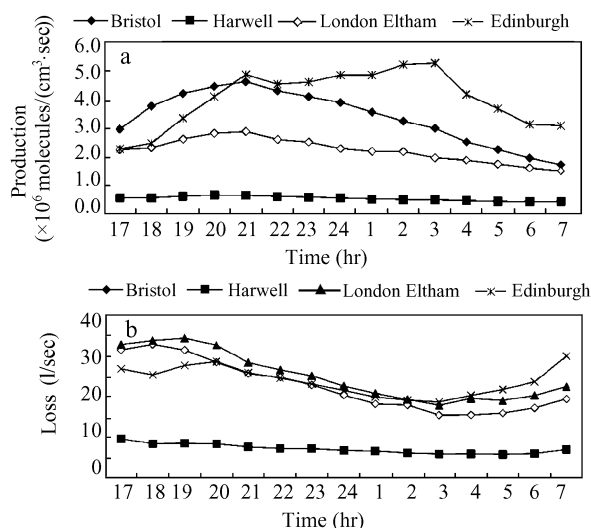

Fig. 4 Average production rates (a) and loss rates (b) for OH at four sites in UK for the time series of 1996–2000.
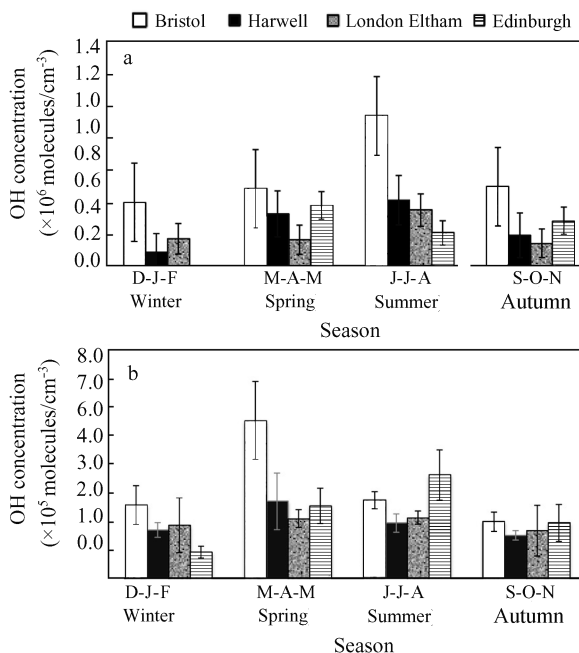

Fig. 5 Seasonal variation of night-time OH concentrations at the four sites for the time period of 1996 to 2000. (a) decay method; (b) steady state approximation method. Error bars represent 1 s.d. for the whole set of calculation.

into the night as the species decrease in concentration and although VOCs (alkenes) are an important component of OH production at night too, the net result is an increase in OH as night proceeds. The analysis of the steady state method reveals that the dominant alkenes responsible for production are trans-2-butene, trans-2-pentene and cis-2-butene (Fig. 3a), whereas the dominant VOCs responsible for destruction are propene, isoprene, 1,3-butadiene, trans-2-pentene, trans-2-butene (Fig. 3b).

The calculated OH level is higher for Bristol and Edinburgh and lower for Harwell and London Eltham. Edinburgh and Bristol both have the highest OH concentration because the sites experience higher VOC levels than the other sites while having comparable NO_x and CO. The production processes are elevated at Edinburgh and Bristol (Fig. 4) because high concentrations of reactive volatile organic compounds including alkenes are present. Loss processes (Fig. 4) are more pronounced at London Eltham because of the higher concentration of NO and CO arising from its proximity to traffic sources. The variation in loss drives the overall concentrations of OH in the steady state approximation method. The production of OH from the reaction of HO_2 with NO_3, NO and O_3 was not included in the calculation because of the lack of HO_2 data. If the surface NO_3 is in the region of 1–5 pptv and HO_2 is typically 1–10 pptv in the urban environment, the additional processes will raise OH by 10%–20%.

Averaging all [OH] data into different seasons namely spring, summer, autumn and winter, an interesting set of trends emerge is illustrated in Fig. 5. There is a clear seasonal variation for the levels of OH at the four differ-

ent sites. The decay method shows that all sites except Edinburgh give a peak in summer dropping to a minimum in winter. The seasonal trend for Edinburgh has deviated from the other sites because of the limited number of OH values derived from the decay method calculation. In the winter time, there is less alkene decays observed in all of the sites. The OH peak in summer is due to the higher O_3 levels (leading to more direct formation via ozonolysis) and lower hydrocarbon levels (less removal of OH formed). Kanaya et al. (2007) also observed higher OH at summer time (3.7×10^5 molecules/cm^3) than winter time (1.8×10^5 molecules/cm^3). There was no correlation between OH levels and O_3 mixing ratios in winter but a relatively strong correlation in summer was also observed

in the previous measurement results (Kanaya et al., 2007; Martinez et al., 1999). In addition, there are more biogenic reactive alkenes (e.g. isoprene) produced in the urban area at summer time that react rapidly with O_3 at night-time producing higher OH values (Faloona et al., 2001). The steady state approximation method reveals a higher OH level in spring for Bristol, London Eltham and Harwell, whereas a peak appears in summer for Edinburgh. O_3 is vital for night-time production of the OH radical and generally its night-time level peaks in spring for most of the sites.

3 Conclusions

The decay and steady state approximation methods have been applied to the NETCEN data archive at four sites in the UK over the period 1996–2000. Both methods give similar results; the average night-time OH concentration ranges from 10^5–10^6 molecules/cm^3. The higher OH values observed at both Bristol and Edinburgh seems to arise because they contain higher levels of reactive hydrocarbons. Lower values are observed at the rural Harwell site because there are lower levels of reactive hydrocarbons and at London Eltham, NOx levels are high, suppressing OH formation. Given the large errors associated with measurements and rate coefficients used the overall error associated with the methods is of the order of a factor of at least 2, nevertheless, such an analysis provides insight into long term measurements of night-time radicals that are currently absent. For the decay method, the OH radical appears to peak in summer whereas in steady state method, it appears to peak in spring time.

References

Allan B J, Carslaw N, Coe H, Burgess R A, Plane J M C, 1999. Observations of the nitrate radical in the marine boundary layer. *Journal of Atmospheric Chemistry*, 33: 129–154.

Carslaw N, Carpenter L J, Plane J M C, Allan B J, Burgess R A, Clemitshaw K C et al., 1997. Simultaneous observations of nitrate and peroxy radicals in the marine boundary layer. *Journal of Geophysical Research*, 102: 18917–18933.

Donahue N M, Kroll J H, Anderson J G, 1998. Direct observation of OH production from the ozonolysis of olefins. *Geophysical Research Letters*, 25: 59–62.

Eisele F L, Tanner D J, Cantrell C A, Calvert G J, 1996. Measurements and steady-state calculations of OH concentrations at Mauna Loa Observatory. *Journal of Geophysical Research*, 101: 14665–14679.

Emmerson K M, Carslaw N, 2009. Night-time radical chemistry during the TORCH campaign. *Atmospheric Environment*, 43(20): 3220–3226.

Faloona I, Tan D, Brune W, Hurst J, Jr Barket D, Couch T L et al., 2001. Night-time observations of anomalously high levels of hydroxyl

radicals above a deciduous forest canopy. *Journal of Geophysical Research*, 106: 24315–24333.

Geyer A, Alicke B, Konrad S, Schmitz T, Stutz J, Platt U, 2001. Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin. *Journal of Geophysical Research*, 106(D8): 8013–8025.

Geyer A, Bachmann K, Hofzumahaus A, Holland F, Konrad S, Klupfel T et al., 2003. Night time formation of peroxy and hydroxyl radicals during the BERLIOZ campaign: observations and modelling studies. *Journal of Geophysical Research*, 108(D4): 8249.

Holland F, Hofzumahaus A, Schafer H J, Kraus A, Patz H W, 2003. Measurement of OH and OH_2 radical concentration and photolysis frequencies during BERLIOZ. *Journal of Geophysical Research*, 108: 8246.

Kanaya Y, Cao R, Akimoto H, Fukuda M, Komazaki Y, Yokouchi Y et al., 2007. Urban photochemistry in central Tokyo: 1. Observed and modeled OH and OH_2 radical concentrations during the winter and summer 2004. *Journal of Geophysical Research*, 112: D21312.

Khan M A H, Ashfold M J, Martin D, Watson L A, Hamer P D, Wayne R P et al., 2008. Nighttime NO_3 and OH radical concentrations in the United Kingdom inferred from hydrocarbon measurements. *Atmospheric Science Letters*, 9(3):140–146.

Kroll J H, Clarke J S, Donahue N M, Anderson J G, Demerjian K L, 2001. Mechanism of HOx formation in the gas-phase ozone-alkene reaction. 1. Direct pressure-dependent measurements of prompt OH yields. *Journal of Physical Chemistry*, 105A: 1554–1560.

Kurtenbach R, Ackermann R, Becker K H, Geyer A, Gomes J A G, Lorzer J C et al., 2002. Verification of the contribution of vehicular traffic to the total NMVOC emissions in Germany and the importance of the NO_3 chemistry in the city air. *Journal of Atmospheric Chemistry*, 42: 395–411.

Martinez M, Harder H, Kovacs T A, Simpas J B, Bassis J, Lesher R et al., 2003. OH and HO_2 concentrations, sources and loss rates during the southern oxidants study in Nashville, Tennessee, summer 1999. *Journal of Geophysical Research*, 108(D19): 4617.

Mihelcic D, Klemp D, Müsgen P, Pätz H W, Volz-Thomas A, 1993. Simultaneous measurements of peroxy and nitrate radicals at Schauinsland. *Journal of Atmospheric Chemistry*, 16: 313–335.

Platt U, Le Bras G, Poulet G, Burrows J P, Moortgat G K, 1990. Peroxy radicals from night-time reaction of NO_3 with organic compounds. *Nature*, 348: 147–149.

Platt U, Alicke B, Dubois R, Geyer A, Hofzumahaus A, Holland F et al., 2002. Free radicals and fast photochemistry during BERLIOZ. *Journal of Atmospheric Chemistry*, 42: 359–394.

Ren X, Harder H, Martinez M, Lesher R L, Oliger A, Simpas J B et al., 2003. OH and OH_2 chemistry in the urban atmosphere of New York City. *Atmospheric Environment*, 37(26): 3639–3651.

Rivett A C, Martin D, Gray D J, Price C S, Nickless G, Simmonds P G et al., 2003. The role of volatile organic compounds in the polluted urban atmosphere of Bristol, England. *Atmospheric Chemistry and Physics*, 3: 1165–1176.

Salisbury G, Rickard A R, Monks P S, Allan B J, Bauguitte S, Penkett S A et al., 2001. Production of peroxy radicals at night via reactions of ozone and the nitrate radical in the marine boundary layer. *Journal of Geophysical Research*, 106: 12669–12687.

Shirley T R, Brune W H, Ren X, Mao J, Lesher R, Cardenas B et al., 2006. Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003. *Atmospheric Chemistry and Physics*, 6: 2753–2765.

Vrekoussis M, Mihalopoulos N, Gerasopoulos E, Kanakidou M, Crutzen P J, Lelieveld J, 2007. Two-years of NO_3 radical observations in the boundary layer over the Eastern Mediterranean. *Atmospheric Chemistry and Physics*, 7: 315–327.

Winer A M, Atkinson R, Pitts J N, 1984. Gaseous nitrate radical: Possible night time atmospheric sink for biogenic organic compounds. *Science*, 224: 156–159.