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Atmospheric Chemistry and Physics

The role of volatile organic compounds in the polluted urban atmosphere of Bristol, England

A. C. Rivett, D. Martin, D. J. Gray, C. S. Price, G. Nickless, P. G. Simmonds, S. J. O'Doherty, B. R. Greally, A. Knights, and D. E. Shallcross

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Abstract. The results of a field campaign carried out from early spring through to the late summer of 2000, in Bristol, England, are presented. Continuous measurements of over 40 hydrocarbons have been made at an urban background site, located at Bristol University, for approximately nine months using a Gas Chromatography – Flame Ionisation Detection (GC-FID) system and for a selection of halocarbons for approximately one month using a Gas Chromatography – Electron Capture Detection (GC-ECD) system. In this paper we present the time-series of the nine halocarbons and selected hydrocarbons. Daytime and night-time hydroxyl radical concentrations have been estimated based on the diurnal variations of a selection of the measured hydrocarbons. The average summer daytime concentration of OH was found to be 2.5×10^6 molecules cm^{-3} and the night-time concentration to be in the range 10^4 to 10^5 molecules cm^{-3}. In addition, the role played by certain VOCs in the formation of ozone is assessed using the POCP (Photochemical Ozone Creation Potential) concept.

1 Introduction

The urban environment contains a complex mixture of chemicals, however, due to the high levels of NO_x that generally persist, ozone formation is VOC (volatile organic compound) limited (e.g. Sillman, 1999). Therefore, it is of great importance to determine the type of VOC that is present in the urban environment, its concentration and how this varies both spatially and temporally. This study has investigated both local and remote effects on levels of pollutants in the Bristol conurbation. A detailed understanding of the different influences on local air quality is important to inform relevant policy decisions such as transport planning and healthcare provision and this type of research provides such information.

The behaviour of halocarbons in the stratosphere and the remote troposphere is well understood due to their major role in ozone depletion, yet there have been few studies in urban areas. A handful of investigations have been carried out in Taiwan, Brazil and Japan (Wang et al., 1998; Grosjean et al., 1999; Yamamoto et al., 2000). There are several reasons for the study halocarbons in urban atmospheres. Their degradation products are sources of the Cl radical which acts like the OH radical and so may change the oxidising capacity of the troposphere. In addition, the health effects are significant, these compounds are potentially toxic, irritant and carcinogenic. Emissions in Britain are regulated by the UK Environment Agency, but are not systematically monitored.

In urban conurbations, the sources and behaviour of hydrocarbons are generally well identified and understood (Wayne, 2000; UK PORG, 1997; Derwent et al., 2000). Their overwhelming source is rush-hour traffic, inducing a diurnal cycle upon which is added transported air masses bringing polluted or clean air from other regions. In addition to being a measure of air quality, the hydrocarbon measurements can also provide useful information about the chemistry of the polluted atmosphere. For example, the formation of ozone and other photochemical pollutants in the NO_x-rich urban atmosphere is VOC-limited, so it is useful to determine which species are making the greatest contribution to ozone formation. Concentrations of OH and other radicals can be calculated during the day and night, as can the magnitude of dispersion processes taking place. Simple source identification is also possible using these types of data but this analysis is not discussed here.

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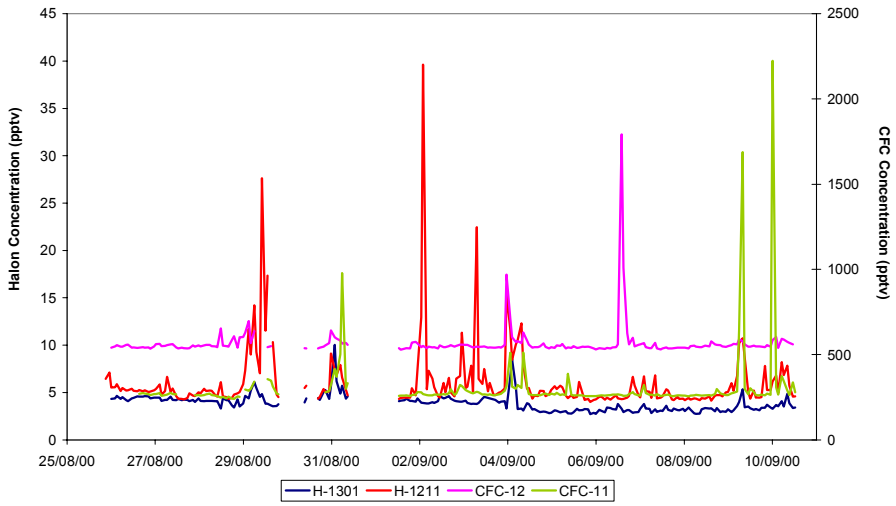

Fig. 1. Time-series of halons and CFCs.

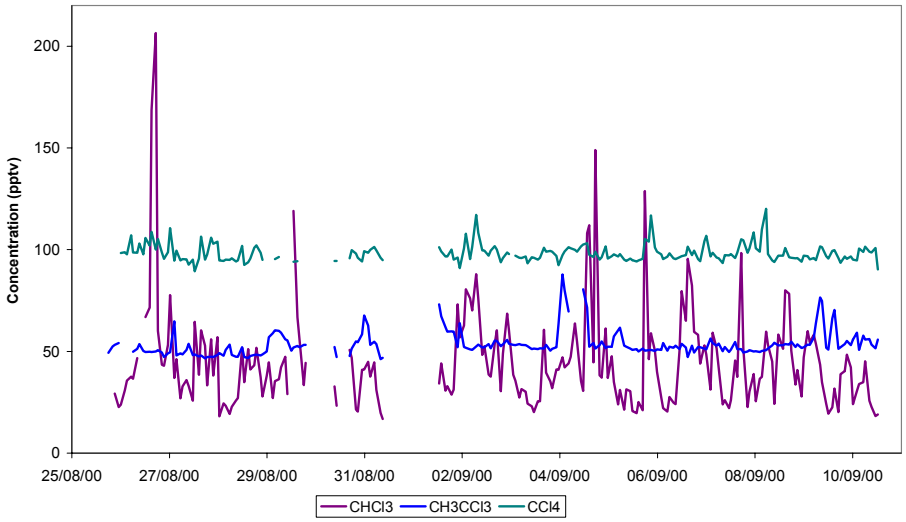

Fig. 2. Time-series of the three chlorinated compounds.

2 Experimental

Bristol (51.5° N, 2.75° W), with a population of almost half a million people, is situated in the south-west of Britain, 120 miles west of London. Like any other town or city, Bristol has its own distinctive atmospheric characteristics. It is located a short way from the coast, and is surrounded by hills. The city centre basin covers an area of approximately 25 square kilometres, although the suburbs extend much further. To the west of the city is a large industrial area (Avonmouth) and other key industries include manufacturing and business. Two major motorways run nearby and the volume of traffic around the area is generally high. The basin geography combined with heavy traffic flow can lead to the build-up of pollutants during anti-cyclonic weather conditions, although prevailing winds are often from the clean, western Atlantic sector.

From early spring to late summer 2000, continuous measurements of VOCs were made at an urban background site, located at the University of Bristol. The Automatic Adsorption-Desorption System (ADS) and GC technology developed at Bristol (Simmonds et al., 1995; Sheppard, 1999; Bassford et al., 1998) was used to perform routine analysis of air and standard samples in a continuous cycle. Over 40 hydrocarbon species were measured using a GC-FID system with a Peltier-cooled ADS to achieve low temperature trapping at minus 40°C. The measurement period was approximately nine months. A GC-ECD was deployed concurrently at the same sampling point to monitor a selection of nine halocarbons for one month using an ADS which

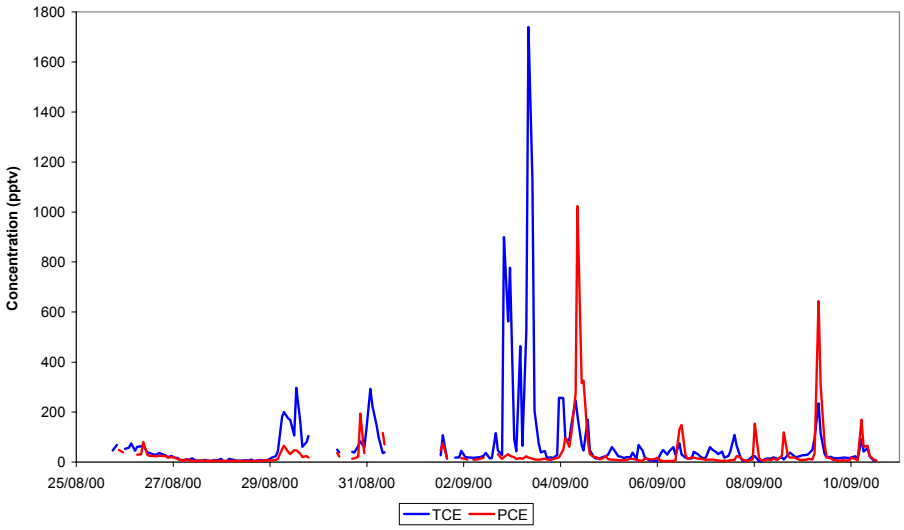

Fig. 3. Time-series of trichloroethene and perchloroethene.

traps at ambient temperature (Bassford et al., 1998). Measurements of a smaller set of hydrocarbons were taken simultaneously at a roadside site in the centre of Bristol, as part of the UK national monitoring network, NETCEN (Derwent et al., 2000). The species monitored by the three systems were; C_2–C_8 Hydrocarbons, CFCs 11 and 12, Halons 1211 and 1301, $CHCl_3$ (Chloroform), CH_3CCl_3 (Methyl Chloroform), CCl_4 (Carbon Tetrachloride), TCE (Trichloroethene) and PCE (Perchloroethene).

3 Halocarbons in the City

Figures 1 to 3 show the concentrations of the nine halocarbons measured in Bristol between August and September 2000. A complex time-series is observed for the halocarbons, with large variations in the concentrations measured. There are some episodes where several compounds are simultaneously elevated, however there are also periods where just one compound is elevated, in complete contrast to the coherent variations observed for most hydrocarbons, which are driven primarily by vehicular sources. Figure 4 shows the halocarbon time-series overlaid with toluene as a representative hydrocarbon. No weekly or diurnal trends were found for any of the halocarbons, as might be expected for compounds with no significant biogenic or automobile sources. In general, halocarbon levels measured at the urban site are similar to those measured at Mace Head, Ireland, a rural background site which is part of the AGAGE (Advanced Global Atmospheric Gases Experiment) monitoring network (Prinn et al., 2000). The only exceptions are chloroform and methyl chloroform which are significantly elevated above background levels. Results of the halocarbon monitoring campaign and correlations between the halocarbons and hydrocarbons are discussed further in Rivett et al. (2003).

4 Hydrocarbons in the City

The summer time-series of a representative selection of the hydrocarbons measured are shown in Fig. 5. The concentration time-series' are very similar for each of the compounds measured. This is consistent with what would be expected as these compounds all have a primarily vehicular source. There are periods of high pollution when many compounds are elevated and "clean" periods where most species are at relatively low levels. In the sections which follow, the hydrocarbon dataset is interrogated to estimate both daytime and night-time OH levels.

In the analysis of this type of dataset, investigation of the variation in hydrocarbon ratios can be a powerful tool (Calvert, 1976). Calculating the ratios of each of the hydrocarbons to one reference compound enables differences in their sources and reactivity to be elucidated. Using ratios removes day-to-day variations, meteorological factors and differences in emission strengths between the compounds (Roberts et al., 1984; Parrish et al., 1998). In this study, benzene has been used as the reference compound because its lifetime is longest of all the compounds measured (it has the slowest reaction rate with OH) and no significant non-traffic sources have been characterised in the UK VOC emission inventory (Derwent et al., 2000). Therefore, as an air mass is chemically processed, the ratios of all the other species to benzene will decrease.

4.1 Daytime OH

It is well established that the OH radical is the main initiator of atmospheric chemistry during the day (Wayne, 2000). The concentration of the hydroxyl radical during the day was estimated from the variation in concentration ratios of four aromatic species (ethyl benzene, toluene, *o*-xylene and

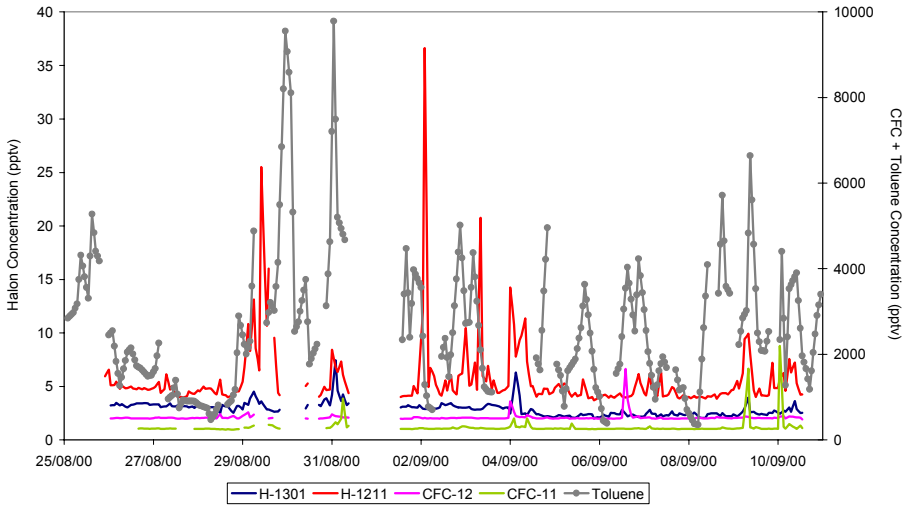

Fig. 4a. Time-series of halons and CFCs overlaid with a representative hydrocarbon, toluene.

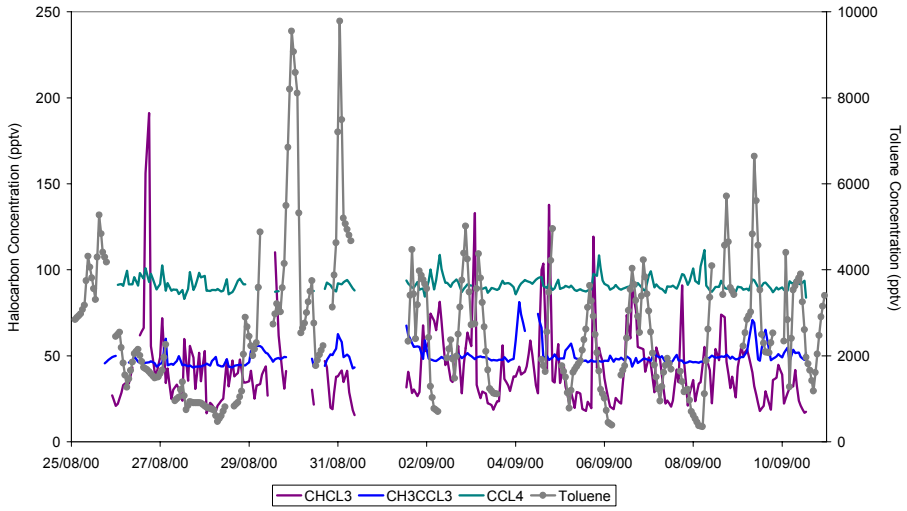

Fig. 4b. Time-series of the 3 chlorinated compounds overlaid with a representative hydrocarbon, toluene.

Table 1. Daytime hydroxyl radical concentrations in Bristol, UK (Summer 2000), estimated from the mean ratios of four aromatic species to benzene

OH Concentration (molecules cm^{-3})	
Average	2.5×10^6
Maximum	8.8×10^6
Minimum	1.5×10^5

$m+p$-xylene) to benzene (Blake et al., 1993; Moschonas et al., 2001). Aromatics are most suitable for this type of calculation because they have similar lifetimes and sources to benzene and decay almost exclusively by reaction with the hydroxyl radical. From the change in a compounds' ratio to benzene between the morning rush hour period (7:00–10:00) and the midday period (10:00–16:00) the concentration of daytime OH can be calculated using the following equation, the derivation of which is given in Appendix A:

$$[\mathrm{OH}] = \frac{\ln\left(\frac{X_t}{B_t}\frac{X_i}{B_i}\right)}{t(K_B - K_X)} \tag{1}$$

X_i/B_i is the ratio of hydrocarbon X to benzene (B) during the morning rush hour, X_t/B_t is the ratio of hydrocarbon X to benzene (B) over midday, t is the time elapsed between morning rush hour and midday, K_B is the rate constant for the reaction of benzene and OH and K_X is the rate constant for the reaction of hydrocarbon X with OH. This gives an

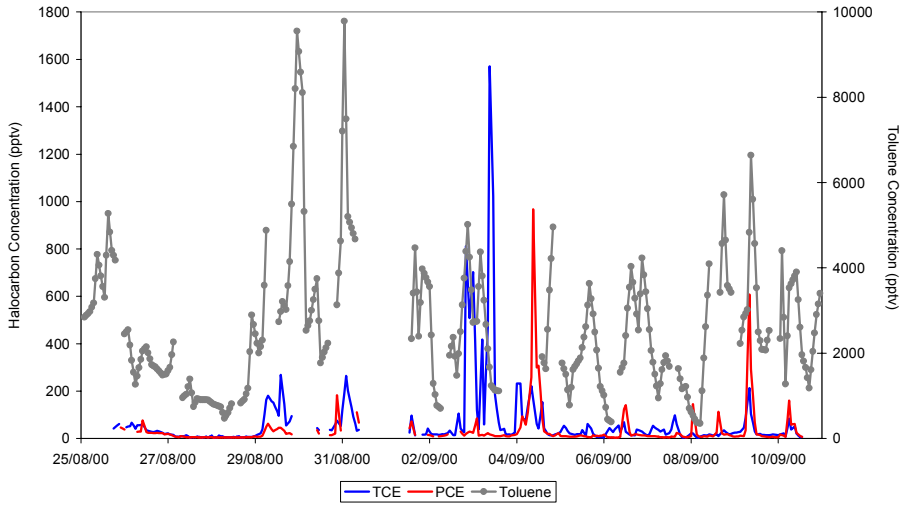

Fig. 4c. Time-series of TCE and PCE overlaid with a representative hydrocarbon, toluene.

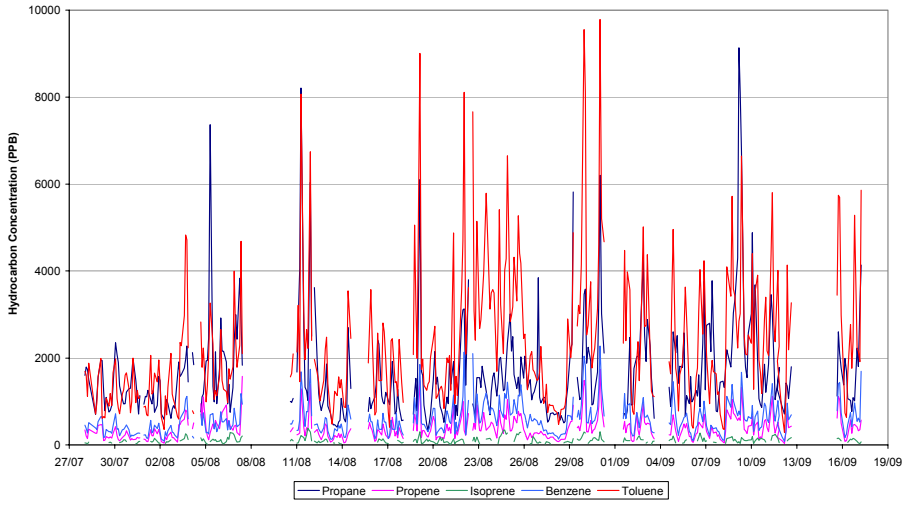

Fig. 5. Hydrocarbon time-series.

average OH concentration over the time elapsed. The rates of reaction of the VOCs with OH are given in Table 2.

Ratios to benzene were calculated over the entire campaign to give a typical ratio for each of the four aromatic species during the morning rush hour and midday time-periods. These ratios were then used to determine an average daytime OH concentration during the summer. The mean of the four different OH concentrations calculated from the different aromatic species is given in Table 1 along with the maximum and minimum concentrations calculated.

The average daytime OH concentration calculated over the course of the campaign was 2×10^6 molecules cm^{-3}. This compares well with what would be expected, as the lifetime of OH is less than 1 s and consequently noon-time concentrations generally only reach 0.04–0.4 ppt (10^6–10^7 molecules cm^{-3}) (Wayne, 2000). Field campaigns such as the EASE 1996 and 1997 European background air experiments (Creasey et al., 1997; Creasey et al., 2002) and BERLIOZ (Platt et al., 2002), sampling in the Berlin area, have measured daytime [OH] of between 1–10×10^6 molecules cm^{-3} during summer-time.

4.2 Night-time OH

Although NO_3 is generally thought to be the main oxidising species at night, hydroxyl radicals can be generated even after dark from several reactions (Platt et al., 1990; Mihelcic et al., 1993; Canosa-Mas et al., 1996; Carslaw et al., 1997; Paulson et al., 1997).

OH can be formed from the reaction of HO_2 with the nitrate radical (Eq. 2a), with ozone (Eq. 2b) or with nitric oxide (Eq. 2c):

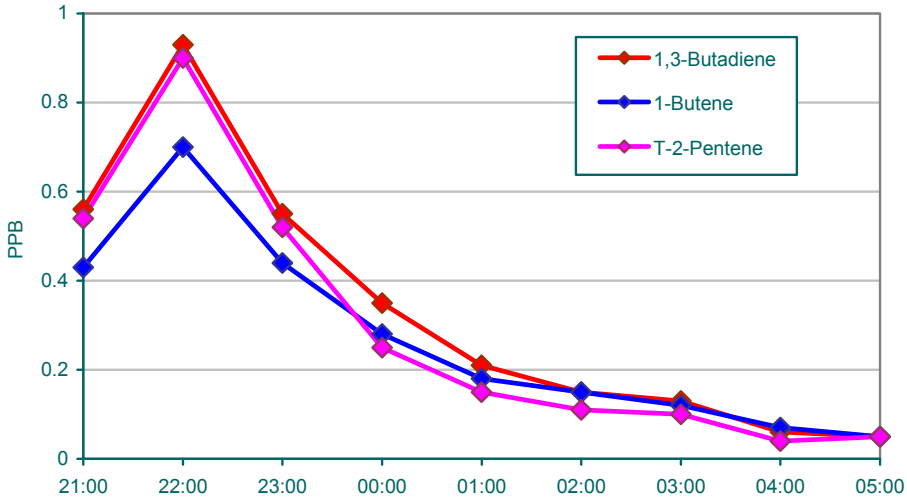

Fig. 6. Representative decay of hydrocarbons on the night of 30–31 August 2000.

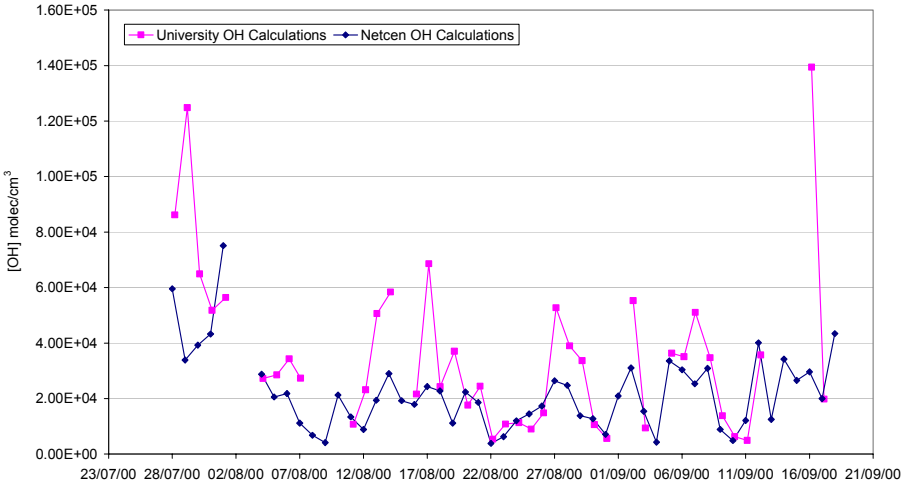

Fig. 7. Steady-state night-time [OH] calculated for University (urban background) and NETCEN (urban centre) sites.

$$HO_2 + NO_3 \longrightarrow OH + NO_2 + O_2 \quad (2a)$$

$$HO_2 + O_3 \longrightarrow OH + 2O_2 \quad (2b)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \quad (2c)$$

The reaction of alkenes with the nitrate radical can lead to the formation of HO_2, which can be converted to OH via reactions (2a), (2b) and (2c):

$$NO_3 + CH_2 = CH_2 \longrightarrow\longrightarrow CH_2(ONO_2)CHO + HO_2 \quad (3)$$

The ozonolysis of alkenes is a complex reaction, believed to involve the formation of a Criegee intermediate (Eqs. 4 and 5). However, strong evidence exists to suggest that OH can be formed from these reactions which can proceed all day:

$$O_3 + CH_2 = CH_2 \longrightarrow\longrightarrow OH + HCO \quad (4)$$

$$HCO + O_2 \longrightarrow CO + HO_2 \quad (5)$$

[OH] can be calculated from an analysis of the decay of VOCs during the night in 2 ways:

Alkene Decays

Data from nights (such as that shown in Fig. 6) where several alkene species undergo a steady decay due to dispersion and reaction with OH, NO_3 and O_3 has been compiled. The rates of reaction of the VOCs and the VOC concentration over the night are known, therefore re-arranging the equation below, radical concentrations can be calculated.

$$d[\mathrm{VOC}]/dt = (-k[\mathrm{OH}] - k[\mathrm{NO_3}] - k[\mathrm{O_3}] - k_{dispersion}) \cdot [\mathrm{VOC}] \quad (6)$$

Table 2. Rate constants used in the calculation of daytime and night-time radical concentrations (Atkinson, 1994; Master Chemical Mechanism, 2001)

	Rate of reaction with OH (cm^3 molecules^{-1} s^{-1})	Rate of reaction with O_3 (cm^3 molecules^{-1} s^{-1})	Rate of reaction with NO_3 (cm^3 molecules^{-1} s^{-1})
1,3-Butadiene	6.66×10^{-11}	6.31×10^{-18}	1.03×10^{-13}
1-Butene	3.14×10^{-11}	9.65×10^{-18}	1.21×10^{-14}
2-Methyl Pentane	5.60×10^{-12}		
3-Methyl Pentane	5.40×10^{-12}		
Benzene	1.32×10^{-12}		5.50×10^{-17}
Ethane	2.57×10^{-13}		
Ethene	8.64×10^{-12}	1.59×10^{-18}	2.10×10^{-16}
Ethyl benzene	7.10×10^{-12}		5.70×10^{-16}
Ethyne	8.15×10^{-13}		
i-Butane	2.33×10^{-12}		
i-Pentane	3.90×10^{-12}		
Isoprene	1.01×10^{-10}	1.28×10^{-17}	6.78×10^{-13}
m+p-Xylene	1.90×10^{-11}		3.45×10^{-16}
n-Butane	2.54×10^{-12}		6.60×10^{-17}
n-Hexane	5.60×10^{-12}		1.05×10^{-16}
n-Pentane	3.96×10^{-12}		8.10×10^{-17}
o-Xylene	1.37×10^{-11}		3.77×10^{-16}
Propane	1.15×10^{-12}		
Propene	2.70×10^{-11}	1.01×10^{-17}	9.40×10^{-15}
t-2-Butene	6.40×10^{-11}	1.90×10^{-16}	
t-2-Pentene	6.69×10^{-11}	1.60×10^{-16}	3.70×10^{-13}
Toluene	5.96×10^{-12}		6.17×10^{-17}

A matrix method was used to derive the equations given in Appendix C. Rates of reaction of the alkenes with OH, O_3 and NO_3 are given in Table 2. The degradation of alkenes by ozone is ignored, as it is very slow in comparison with the reaction of alkenes with OH and NO_3. Thus, decay data for three different alkenes is required on each night to perform these calculations. During the summer period of the campaign there were seven such nights where sufficient data was collected.

The average night-time OH concentration was calculated to be 3.8×10^5 molecules cm^{-3}. The estimated OH concentrations varied over a range of 6.3×10^4 molecules cm^{-3} to 1×10^6 molecules cm^{-3}. Levels of NO_3 calculated by this method range from 2 to 7 ppt, with an average from the seven nights being 4.2 ppt. This is consistent with (although somewhat lower than) NO_3 concentrations previously measured in urban areas (Platt et al., 2002; Smith et al., 1995). The concentration of NO_3 at night is strongly dependent on the levels of alkenes, with which it readily reacts. So in the polluted urban environment, NO_3 production could be substantially suppressed. The average rate of dispersion of the alkenes on these seven nights was calculated to be $8\times10^{-5}\,s^{-1}$. This gives a transport lifetime ($1/k_{dispersion}$) of about three and a half hours, which seems reasonable.

Steady-State Concentration

The steady-state concentration over one whole night can also be estimated using the following equation:

$$d[\mathrm{OH}]/dt = k[\mathrm{O_3}][\mathrm{alkenes}](all\ summed) + k[\mathrm{HO_2}][\mathrm{NO_3}] + k[\mathrm{HO_2}][\mathrm{O_3}] + k[\mathrm{HO_2}][\mathrm{NO}] - k[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}] - k[\mathrm{OH}][\mathrm{CO}] - k[\mathrm{OH}][\mathrm{VOC}] \quad (7)$$

Reaction rates of VOCs, NO_2 and CO with OH and alkenes with ozone are given in Table 2 and Appendix B. The change in OH is assumed to be equal to the production from the reaction of alkenes with ozone (production from HO_2 is ignored, because the concentrations of this radical cannot be known), minus the loss from reactions with NO_2, CO and other VOCs present.

Figure 7 shows OH levels calculated for each night of the campaign for the University site and for the city centre site. It can be seen that agreement is generally very good between the two sites. Average [OH] over the summer campaign period at the University was calculated to be 3.6×10^4 molecules cm^{-3}, ranging from 4.9×10^3 to 1.4×10^5 molecules cm^{-3}. This is a much lower level than that calculated by the decay rate method because only five simple alkene species are used in the calculation and production from HO_2 is ignored. If more alkenes were used

Table 3. γ_R and $\varepsilon^{\mathrm{POCP}}$ indices, taken from Jenkin, 1998

	γ_R	$\varepsilon^{\mathrm{POCP}}$
1,3-Butadiene	4.205	109.6
1-Butene	1.82	106.3
2-Methyl Pentane	0.205	48.8
Benzene	0.061	18.7
c-2-Butene	3.264	115.3
c-2-Pentene	3.028	111.4
Ethane	0.0255	12
Ethene	1	97.8
Ethyl benzene	0.235	40.5
Ethyne	0.113	30.8
i-Butane	0.125	34.5
i-Pentane	0.169	37.9
Isoprene	4.99	107
m+p-Xylene	0.66	49.9
n-Butane	0.136	36
n-Heptane	0.227	47.2
n-Hexane	0.205	48.8
n-Pentane	0.171	38.1
o-Xylene	0.476	46
Propane	0.08	29.3
Propene	2.08	113.7
t-2-Butene	3.704	115.3
t-2-Pentene	3.097	111.4
Toluene	0.23	42.1

in the calculation, particularly if heavier and more reactive alkene species were considered, such as isoprene and other monoterpenes, the estimation would be more accurate. Unfortunately, the isoprene data collected was insufficient and monoterpene concentrations were not measured during the campaign. Thus these species cannot be included in the calculations.

Few measurements have been made of OH at night in similar environments but some comparisons can be made. During the MLOPEX campaign at a remote background site in Hawaii, night-time [OH] was found to be 1×10^5 molecules cm^{-3} (Eisele et al., 1996; Cantrell et al., 1997). The PROHET campaign, which took place in a heavily forested area of Michigan measured [OH] as high as 1×10^6 molecules cm^{-3} after dark (Faloona et al., 2001). A similar campaign in a forest in northern Greece (AEROBIC) also found that OH in the order of 10^5 molecules cm^{-3} persisted into the night (Creasey et al., 2001). The BERLIOZ experiment (Platt et al., 2002), measuring in and around the Berlin area, (the area which is probably most similar to the environment studied here) found levels of 1.4×10^5 molecules cm^{-3}. The hydroxyl radical concentrations of 10^4 to 10^5 molecules cm^{-3} calculated here, even by a relatively simple method, are nevertheless in good agreement with those found in other environments. It is reassuring to note that by using the data derived for [OH], [NO_3] and dispersion from the decay method, the calculated decay of measured alkanes is totally consistent.

4.3 Ozone Creation Potential

Classifying a wide variety of VOCs in terms of their ability to form ozone is a complex problem, since those compounds which are oxidised quickly lead to significant ozone formation close to the point of emission, whereas those which are oxidised more slowly will lead to ozone being formed further away from the source of the compound, for example in rural areas. Using the concept of Photochemical Ozone Creation Potential (POCP), the role played by each of the hydrocarbons in the creation of ozone has been revealed. In this work $\varepsilon^{\mathrm{POCP}}$ (estimated POCP) values have been used (Jenkin, 1998), which use a mathematical formula (as shown in Eq. 8) to calculate POCP, rather than using a modelling approach:

$$\varepsilon^{\mathrm{POCP}} = \alpha_1 \cdot \gamma_S \cdot \gamma_R^{\beta}(1 - \alpha_2 \cdot \eta_C) \tag{8}$$

α_1, α_2 and β are constants, η_C is the carbon number of the VOC and γ_S and γ_R are the structure-based and reactivity-based ozone formation indices respectively. This method replicates well POCPs calculated from the modelling work and also rationalises the POCP values in terms of the intrinsic structural and reactive properties of the VOCs themselves.

γ_R is a simple approach which defines the relative ozone formation potential of a series of VOCs based on how quickly they form ozone in the boundary layer. γ_R is based on the rate coefficient (k_{OH}) per reactive bond (η_B) (Jenkin, 1998). This is normalised to a value of 1.0 for ethene as shown in Eq. (9):

$$\gamma_R = (k_{\mathrm{OH}}/\eta_B) \cdot (6/k_{\mathrm{OH}^{ethene}}) \tag{9}$$

γ_R gives a better indication of the impact of VOCs on ozone formation on a local scale, compared to $\varepsilon^{\mathrm{POCP}}$, which gives an indication of the overall regional scale formation. In calculating the contribution to ozone formation all compounds were ratioed to propane. The $\varepsilon^{\mathrm{POCP}}$ and γ_R indices are given in Table 3.

Plots of the proportion of ozone formed by each class of hydrocarbon as a percentage of the total are shown in Fig. 8. Alkenes produce the greatest amount of ozone (45% of total) closest to the source of emissions (as calculated using γ_R) with aromatic species generating a further 30%. From a large suite of national measurements the UK PORG Report (1997) calculated that alkenes were responsible for 53% and aromatic species for 28% of ozone production close to source during summer in the UK. The $\varepsilon^{\mathrm{POCP}}$ values calculated for this campaign show that alkane and aromatic hydrocarbon species have the greatest effect on regional scale ozone production, accounting for approximately 50% and 30% respectively. This ties in very well with what would be expected. Close to the point of emission, more reactive compounds such as alkenes will contribute most to ozone formation. As

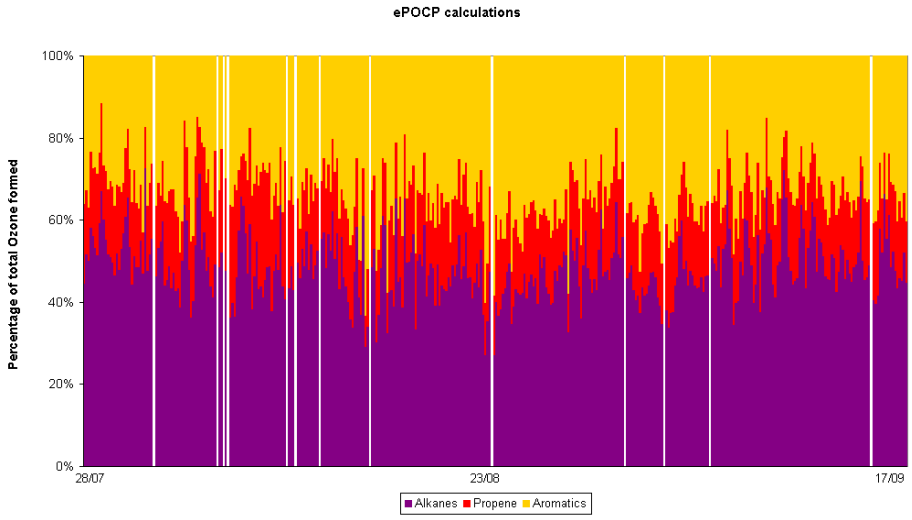

Fig. 8a. Percentage of total ozone formed, calculated by $\varepsilon^{\mathrm{POCP}}$ method.

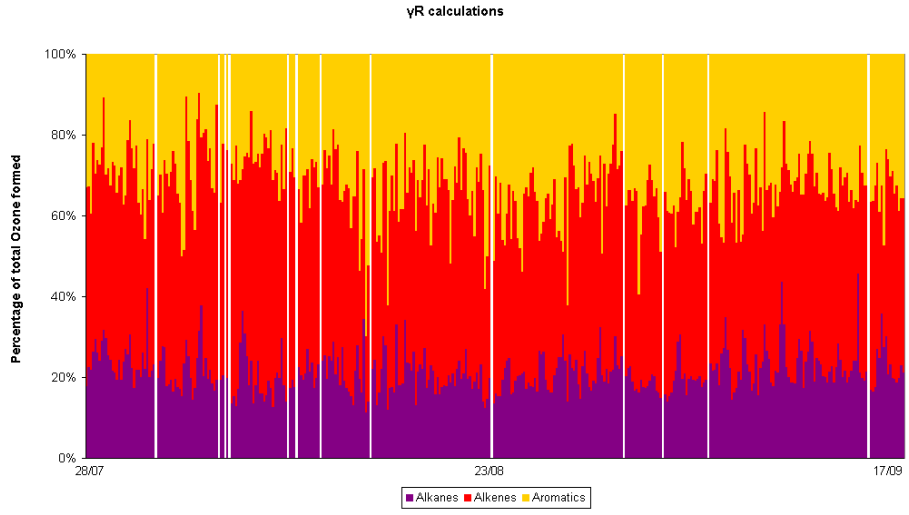

Fig. 8b. Percentage of total ozone formed, calculated by γ_R method.

time goes on, slower reacting compounds such as the alkanes will become more important in producing ozone.

5 Conclusions

Simultaneous measurements of nine different halocarbon species and over forty hydrocarbon species have been made during summer 2000 at an urban background site in a large British city. This unusual dataset has provided a unique opportunity to compare two classes of compounds which display very different behaviour in the urban atmosphere.

The lifetimes of the hydrocarbons measured are all in the order of days, whereas those of the halocarbons measured vary much more considerably from a few days to over a hundred years. Similarly the halocarbons originate from a much more diverse range of sources than do the hydrocarbons studied. Whereas the C_2–C_8 hydrocarbons measured at this typical urban site are overwhelmingly emitted by traffic, the halocarbons are emitted from a wide variety of industrial activity, both big factories and smaller businesses, from landfill and other waste processing activity and from the natural environment. Such diversity in lifetime and sources will naturally mean that the behaviour of hydrocarbons compared to halocarbons is very different but it also means that the various halocarbon compounds will not behave in a similar way to each other either. Consequently the time-series of the nine halocarbons are not simple to interpret, they do not display any significant diurnal cycle and each compound has shown large excursions from baseline levels at different points during the campaign.

A detailed analysis of the hydrocarbon dataset has been made possible by the large number of species measured during this campaign. Radical concentrations have been calculated for both day and night and the estimated OH concentrations compare well with field measurements made in similar environments. The contribution of different types of hydrocarbons to the formation of ozone in the city centre and further afield has also been quantified.

This type of investigation is an example of how such datasets can be a powerful tool to explore the chemistry and behaviour of urban environments. At this time, when there are numerous schemes to reduce different types of emissions in cities and towns across the world, analyses such as this can have a valuable part to play in informing the decision-making process.

Appendix A

Derivation of equation used to calculate daytime OH concentrations. X_i and B_i are the concentrations of of hydrocarbon X and benzene (B) at the morning rush hour and X_t and B_t are the concentrations at midday. t is the time elapsed between morning rush hour and midday, k_B is the rate constant for the reaction of benzene and OH and k_X is the rate constant for the reaction of hydrocarbon X with OH.
Concentration of compound X at midday: $X_t = X_i \cdot e^{-k_x[\mathrm{OH}]t}$
Concentration of benzene at midday: $B_t = B_i \cdot e^{-k_B[\mathrm{OH}]t}$

$$\frac{X_t}{B_t} = \frac{X_i \cdot e^{-k_X[\mathrm{OH}]t}}{B_i \cdot e^{-k_B[\mathrm{OH}]t}} \tag{10}$$

$$\frac{X_t}{B_t} = \frac{X_i}{B_i} e^{(-k_X[\mathrm{OH}]t-(-k_B[\mathrm{OH}]t))} \tag{11}$$

$$\frac{\frac{X_t}{B_t}}{\frac{X_i}{B_i}} = e^{(t\cdot[\mathrm{OH}]\cdot(-k_X+k_B))} \tag{12}$$

$$\ln \frac{\frac{X_t}{B_t}}{\frac{X_i}{B_i}} = t \cdot [\mathrm{OH}] \cdot (k_B - k_X) \tag{13}$$

$$[\mathrm{OH}] = \frac{\ln\left(\frac{\frac{X_t}{B_t}}{\frac{X_i}{B_i}}\right)}{t(k_B - k_X)} \tag{14}$$

Appendix B

Additional rate constants used in the calculation of nighttime [OH] using a steady-state approximation. Rates of reaction with OH:
CO: $2.08\times10^{-13}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$ (Master Chemical Mechanism, 2001)
NO_2: $1.43\times10^{-11}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$ (See below for calculation)

The rate of reaction of NO_2 and OH is effectively second order under normal atmospheric conditions and is calculated using the Troe expression:

$$k_t = \left(\frac{k_0[M]}{1 + k_0[M]/k_\infty}\right) F^{(1+[\log_{10}(k_0[M]/k_\infty)]^2)^{-1}} \tag{15}$$

where k_0 and k_∞ are the limiting low and high-pressure rate constants respectively, both incorporating a $(T/300)^{-n}$ temperature dependence and $[M]$ is the atmospheric density. The values used in this calculation were (Master Chemical Mechanism, 2001):
$k_0 = 2.6 \times 10^{-30}\,\mathrm{cm^6\,molecules^{-2}\,s^{-1}}$
$k_\infty = 7.7 \times 10^{-11}\,\mathrm{cm^6\,molecules^{-2}\,s^{-1}}$
$[M] = 2.5 \times 10^{19}\,\mathrm{molecules\,cm^{-3}}$
F=0.41
k_t was calculated to be $1.43\times10^{-11}\,\mathrm{cm^3\,molecules^{-1}\,s^{-1}}$.

Appendix C

These equations were derived using a matrix method and used to calculate OH, NO3 and dispersion at night from the decay of alkenes.

$$[\mathrm{OH}] = \frac{1}{det} \cdot (Slope^{\mathrm{VOCl}}(k_{\mathrm{NO_3}}^{\mathrm{VOC2}} - k_{\mathrm{NO_3}}^{\mathrm{VOC3}}) + Slope^{\mathrm{VOC2}}(k_{\mathrm{NO_3}}^{\mathrm{VOC3}} - k_{\mathrm{NO_3}}^{\mathrm{VOCl}}) + Slope^{\mathrm{VOC3}}(k_{\mathrm{NO_3}}^{\mathrm{VOCl}} - k_{\mathrm{NO_3}}^{\mathrm{VOC2}})) \tag{16}$$

$$[\mathrm{NO_3}] = \frac{1}{det} \cdot (Slope^{\mathrm{VOCl}}(k_{\mathrm{OH}}^{\mathrm{VOC3}} - k_{\mathrm{OH}}^{\mathrm{VOC2}}) + Slope^{\mathrm{VOC2}}(k_{\mathrm{OH}}^{\mathrm{VOCl}} - k_{\mathrm{OH}}^{\mathrm{VOC3}}) + Slope^{\mathrm{VOC3}}(k_{\mathrm{OH}}^{\mathrm{VOC2}} - k_{\mathrm{OH}}^{\mathrm{VOCl}})) \tag{17}$$

$$K_{dispersion} = \frac{1}{det} \cdot (Slope^{\mathrm{VOCl}}(k_{\mathrm{OH}}^{\mathrm{VOC2}} \cdot k_{\mathrm{NO_3}}^{\mathrm{VOC3}} - k_{\mathrm{NO_3}}^{\mathrm{VOC2}} \cdot k_{\mathrm{OH}}^{\mathrm{VOC3}}) + Slope^{\mathrm{VOC2}}(k_{\mathrm{NO_3}}^{\mathrm{VOCl}} \cdot k_{\mathrm{OH}}^{\mathrm{VOC3}} - k_{\mathrm{OH}}^{\mathrm{VOCl}} \cdot k_{\mathrm{NO_3}}^{\mathrm{VOC3}}) + Slope^{\mathrm{VOC3}}(k_{\mathrm{OH}}^{\mathrm{VOCl}} \cdot k_{\mathrm{NO_3}}^{\mathrm{VOC2}} - k_{\mathrm{NO_3}}^{\mathrm{VOCl}} \cdot k_{\mathrm{OH}}^{\mathrm{VOC2}})) \tag{18}$$

$$det = k_{\mathrm{OH}}^{\mathrm{VOCl}}(k_{\mathrm{NO_3}}^{\mathrm{VOC2}} - k_{\mathrm{NO_3}}^{\mathrm{VOC3}}) - k_{\mathrm{NO_3}}^{\mathrm{VOCl}}(k_{\mathrm{OH}}^{\mathrm{VOC2}} - k_{\mathrm{OH}}^{\mathrm{VOC3}}) + (k_{\mathrm{OH}}^{\mathrm{VOC2}} \cdot k_{\mathrm{NO_3}}^{\mathrm{VOC3}} - k_{\mathrm{NO_3}}^{\mathrm{VOC2}} \cdot k_{\mathrm{OH}}^{\mathrm{VOC3}}) \tag{19}$$

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