

## Ozone photochemistry and elevated isoprene during the UK heatwave of august 2003

James D. Lee<sup>a,\*</sup>, Alastair C. Lewis<sup>a</sup>, Paul S. Monks<sup>c</sup>, Mark Jacob<sup>c</sup>,  
Jacqueline F. Hamilton<sup>a</sup>, James R. Hopkins<sup>a</sup>, Nicola M. Watson<sup>a</sup>, Julie E. Saxton<sup>a</sup>,  
Christopher Ennis<sup>a</sup>, Lucy J. Carpenter<sup>a</sup>, Nicola Carslaw<sup>b</sup>, Zoe Fleming<sup>c</sup>,  
Brian J. Bandy<sup>d</sup>, David E. Oram<sup>d</sup>, Stuart A. Penkett<sup>d</sup>, Jana Slemr<sup>d</sup>, Emily Norton<sup>e,1</sup>,  
Andrew R. Rickard<sup>f</sup>, Lisa K. Whalley<sup>f</sup>, Dwayne E. Heard<sup>f</sup>, William J. Bloss<sup>f</sup>,  
Thomas Gravestock<sup>f</sup>, Shona C. Smith<sup>f</sup>, Jenny Stanton<sup>f</sup>, Michael J. Pilling<sup>f</sup>,  
Michael E. Jenkin<sup>g</sup>

<sup>a</sup>Department of Chemistry, University of York, York YO10 5DD, UK

<sup>b</sup>Environment Department, University of York, York YO10 5DD, UK

<sup>c</sup>Department of Chemistry, University of Leicester, Leicester, UK

<sup>d</sup>School of Environmental Sciences, University of East Anglia, Norwich, UK

<sup>e</sup>The University of Wales, Aberystwyth, UK

<sup>f</sup>Department of Chemistry, University of Leeds, Leeds LS2 9JT, UK

<sup>g</sup>Centre for Environmental Policy, Imperial College London, London, UK

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### Abstract

A wide range of chemical and physical parameters has been observed over the course of a severe Europe-wide air pollution episode in August 2003. Detailed surface observations made at the rural perimeter edge of London, UK, indicated significantly elevated levels of primary volatile organic compounds (VOCs), ozone ( $>110$  ppbV), other photochemical by-products such as PAN, HCHO, and oxygenates but not  $\text{NO}_x$ . Reactive tracers in combination with Doppler wind radar and back trajectories have been used to establish that initial morning rises in  $\text{O}_3$  during the episode were caused by entrainment of air from aloft, polluted on regional scales from mainland Europe. Total VOC reactivity to OH approximately doubled during this episode, with similar distribution between functional groups, but showing a temperature dependent contribution from biogenic isoprene (maximum 1.2 ppbv). Under episodic conditions total peroxy radicals in excess of 60 pptv were observed in late afternoon with strong correlation to a later and higher peak in ozone. Episodic alkyl peroxy radicals were calculated to be substantially influenced by peroxy acetyl, via the thermal dissociation of PAN at high temperatures.

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\*Corresponding author. Tel.: +44 1904 432575; fax: +44 1904 4322516.

E-mail address: [jd13@york.ac.uk](mailto:jd13@york.ac.uk) (J.D. Lee).

<sup>1</sup>Now at: School of Earth, Atmospheric and Environmental Science, University of Manchester, Manchester M60 1QD, UK.

## 1. Introduction

Public association of poor air quality with extremely warm weather is firmly established in the UK and is a very visible area where atmospheric chemistry impacts on quality of life and public health. Significantly enhanced levels of pollutants such as ozone ( $O_3$ ), particles and the oxides of nitrogen (collectively termed  $NO_x$ ) experienced during photochemical pollution ‘episodes’, are the result of combinations of meteorological effects, atmospheric chemical reactions and changes to both the rates and types of terrestrial emissions, which occur at elevated temperatures. Simplistically, for the UK, the degree of severity of summertime photochemical episodes tends to scale with daytime air temperature, and very high summertime air pollution events (for example with ozone concentration  $>90$  ppbV) are almost always associated with anticyclonic conditions and temperatures in excess of 28–30 °C.

The removal of organic compounds from the atmosphere is driven by the hydroxyl radical (OH), which in combination during the daytime with the hydroperoxy radical ( $HO_2$ ) and larger peroxy radicals ( $RO_2$ ) is responsible for ozone production (Logan et al., 1981). The main urban  $HO_x$  sources are the photolysis of ozone, formaldehyde (HCHO) and nitrous acid (HONO), with the latter two often being the most significant, especially in early morning and late evening. OH and  $HO_2$  undergo propagation reactions that lead to rapid interconversion between these two radicals. OH reacts with CO or  $O_3$  to produce  $HO_2$ , and the oxidation of hydrocarbons by OH leads to the formation of  $RO_2$  and  $HO_2$ . In the presence of NO,  $RO_2$  is converted to  $HO_2$ , which reacts with NO or  $O_3$  to reform OH. Hydrocarbon oxidation may also lead to the formation of HCHO, increasing this source of  $HO_x$ . The reaction of  $HO_2$  or  $RO_2$  with NO during daytime leads to the in situ production of ozone through photolysis of the resulting  $NO_2$ . Steady-state theory suggests that ozone production from  $HO_2$  should decrease as  $NO_x$  increases to more than a few ppbV, due to the reaction of OH with  $NO_2$  terminating the cycle. Thus ozone production should be most efficient at moderate levels of  $NO_x$  of around 1 ppbV, depending on the production rate of  $HO_x$  and the partitioning of radicals between  $HO_2$  and  $RO_2$  (Ehhalt, 1999; Monks, 2005). These chemical conditions are often associated with rural and semi rural locations.

UK terrestrial emissions of both nitrogen oxides and volatile organic compounds (VOCs), the key chemical precursors to ozone production, have been reduced with modest success over the past 10 years (Goodwin and Salway, 2002), albeit matched by a gradual increase in background ozone values (Derwent et al., 2003). The ability to predict the magnitude of UK ozone events and understand the key chemical reactions occurring under very high temperature conditions has been little studied or tested since periods with air temperature in excess of 30–35 °C are currently rare.

The potential importance of improving understanding during high temperature air pollution episodes was highlighted in August 2003. During a 10-day period, a blocking anticyclone persisted over Western Europe, with air temperatures of up to 40 °C. This led to severe health problems, particularly in France, where around 15000 extra deaths were reported. In the UK, temperatures regularly exceeded 30 °C with the Office of National Statistics reporting over 2000 excess deaths during the heatwave period. Between 400–800 of these deaths were directly attributed to poor air quality (Stedman, 2004) through a combination of elevated concentrations of ozone and  $PM_{10}$ . Put in a national perspective, between 20–40% of all excess UK deaths over this heatwave period were attributable to air pollution. A similar number of excess deaths were reported in the Netherlands during the same period (Fischer et al., 2004). The meteorological conditions were causal to an unusually long photochemical episode, with peak ozone values in excess of 110 ppbV being measured by the UK air monitoring network (data available from [www.airquality.co.uk](http://www.airquality.co.uk)) at a number of locations in the S.E. of England. It is important to understand the chemical and physical processes occurring under such conditions, as climate models suggest that the occurrence of extreme high temperature periods are likely to significantly increase over the period to 2080 (Schar et al., 2004; Stott et al., 2004). The current probability in the UK of exceeding 35 °C is 0.6%, however by 2080 it is estimated to become 6%, (e.g. temperatures in excess of 35 °C currently occur roughly one day every two years whereas in 2080 we may expect 5 days  $yr^{-1}$ , or once every 2.5 weeks during summer.

Limited mixing and dilution under typically clear sky anticyclonic conditions are key factors in allowing high pollutant concentrations to establish, as are the synoptic transport pathways that often

bring already highly polluted air from mainland Europe to the UK Derwent and Jenkin (1991) reported the importance of atmospheric transport in contributing to high UK ozone events (see also Jenkin et al., 2002). In this study we aim to demonstrate that active ozone chemistry is occurring within the boundary layer during high temperature conditions, and that the enhanced pollutant levels experienced are a combination of relatively local processes in combination with more regional transport. Calculating the relative contributions from background, regional and local scale ozone sources is extremely complex however due to not only scale issues in models, but also because chemical processing leading to ozone under episodic high temperatures may be substantially different to that which occurs at lower more typical temperatures. This difference may be a consequence of gas kinetic properties, (e.g.  $T$  dependent  $k_{OH}$ ), thermal decomposition processes (e.g. peroxyacetylnitrate), photolysis conditions, and importantly non-linear temperature dependencies of terrestrial primary pollutant emission rates.

In this paper we report a series of detailed chemical observations relating to ozone, non methane hydrocarbons, nitrogen oxides, a range of carbonyl species and reactive intermediates such as  $RO_2$  made during summer 2003 at a rural site 25 miles North East of London. The observational period covered the period of extreme temperatures and high ozone concentrations as well as more typical Westerly cyclonic conditions both before and after this event. This paper will use observations to determine possible sources of ozone, with particular reference to increased concentrations of biogenic hydrocarbons and peroxy radicals, and use tracers to demonstrate the extent of mixing-in of polluted air from the wider regional background.

## 2. Experimental

### 2.1. Site description

In August 2003 seven University institutes in the United Kingdom took part in a field measurement programme as part of the Tropospheric ORganic CHEMistry experiment (TORCH). Measurements were made at Writtle College, Writtle, Essex ( $51^{\circ}44'12''N$ ;  $0^{\circ}25'28''E$ ), a location approximately 25 miles North East of central London. The site comprised several shipping container laboratories and temporary buildings located in a

grass field situated to the South East of the main college buildings, which was little influenced by local road sources of pollutants. The site was over 2 miles from the nearest busy road (to the South), with the prevailing wind direction (South Westerly) coming from an area of flat arable farmland with scattered agricultural buildings for a distance of  $\sim 2$  miles. Electricity for the measurement instruments was provided by a diesel powered generator situated  $\sim 200$  metres to the East of the sampling location. Data from this sector was automatically removed from the dataset. The location of the site had been chosen as a typical rural location in the South East of England, relatively close to London, which would allow for the study of freshly polluted air masses that had passed over densely populated areas of London and the South East of England.

### 2.2. Measurement details

The observations reported here encompass a wide range of gas phase measurements including  $O_3$ ,  $NO$ ,  $NO_2$ ,  $CO$ ,  $C_2$ – $C_{10}$  non methane hydrocarbons (NMHCs),  $C_2$ – $C_7$  carbonyl compounds, PAN, and peroxy radicals. Measurements were also made of a range of photolysis rates including  $j(O^1D)$ ,  $j(NO_2)$  and  $j(HCHO)$  along with a large suite of aerosol number and composition measurements. A brief description of the instrumentation relevant to this paper is given below.

Ozone was measured on site using a UV absorption detector (Thermo Environmental Instruments, Model 49C). The estimated uncertainty in the  $O_3$  concentrations was  $\pm 2$  ppbV. In addition, measurements were made using a mobile laboratory in the regions around the measurement location to examine homogeneity of distribution.  $NO$  was measured using a  $NO/O_3$  chemiluminescence analyser (Thermo Environmental Instruments, Model 42C—trace level), with the instrument sequentially measuring  $NO$  and  $NO_x$  ( $NO + NO_2$ ) by use of a heated Molybdenum converter. Detection limit for the instrument was approximately 0.1 ppbV for  $NO$  and total  $NO_x$ . Calibrations for  $NO$  and  $NO_2$  were carried out using a gas standard (Air Products) and a resulting uncertainty for  $NO$  and  $NO_2$  measurements was estimated to be  $\pm 0.2$  ppbV. A direct measurement of  $NO_2$  was also made using a tunable diode laser system, and, although there was limited data coverage, it showed good agreement with the converted  $NO_2$  measurement for periods when both instruments were measuring simultaneously.  $C_2$ – $C_7$

NMHCs and C<sub>2</sub>–C<sub>5</sub> oxygenated volatile organic compounds (o-VOCs) including alcohols, aldehydes and ketones were measured using a two-column, gas chromatograph (GC) with two flame-ionisation detectors. Detection limits were between 1 and 10 pptV for NMHCs and 10–40 pptV for o-VOCs (Hopkins et al., 2002). Higher molecular weight hydrocarbons (C<sub>6</sub>–C<sub>10</sub>) were measured using comprehensive GC (GCXGC), with modulation between the columns enabled by a high-speed switching valve (Hamilton and Lewis, 2003). The GCXGC approach adds additional uncertainty since there is a degree of peak reconstruction from the individual secondary chromatograms, where the primary peak is sub-sampled at a level that is not optimal. Errors on heavy weight hydrocarbon concentrations are around 10%, and species that overlap with the dual channel approach, generally agree to within 10%. Formaldehyde was measured by an instrument using the liquid-phase reaction of formaldehyde with acetylacetone (2,4 pentadione) and an amine (Aerolaser GmbH, Germany). The uncertainty of the measurements was found to be less than 5%, with a time resolution of 90 s. Measurements of peroxy radicals (HO<sub>2</sub> + ΣRO<sub>2</sub>) were carried out using the jointly operated University of Leicester—University of East Anglia (UEA) PEROxy Radical Chemical Amplifier (PERCA IV) instrument, reported for the first time in Fleming et al. (2006). Peroxy radical mixing ratios were derived on a 1 min basis. The errors on a 1 min measurement are 35%. Measurements of OH and HO<sub>2</sub> radicals were made by the University of Leeds using on-resonance, low pressure laser-induced fluorescence (LIF) at 308 nm, through the fluorescence assay with gas expansion [FAGE] (Smith et al., 2005). Unfortunately, no measurements are available during the photochemical episode discussed in this paper, but a full description and analysis of the HO<sub>x</sub> measurements is given in Emmerson et al. (2006). Measurements of alkyl nitrates were made using a GC quadrupole mass spectrometer operating in negative ion chemical ionisation mode (Agilent Technologies, 6890/5973N). The rates of photolysis of a variety of species were measured using a 2π spectral radiometer (Edwards and Monks, 2003). 2πsr filter radiometers were also employed to measure *j*(O<sup>1</sup>D) and *j*(NO<sub>2</sub>). Wind speed and direction, temperature and relative humidity were also measured through the campaign. Data analysis was aided by 5-day back trajectory calculated every 2 h

using the European Centre for Medium Range Weather Forecast (ECMWF) package supplied by British Atmospheric Data Centre (BADC).

### 3. Results

Time series of trace gas measurements from the TORCH campaign are shown in Fig. 1 for 1–30 August 2003. The 5-day back trajectory calculations revealed a range of air mass types. From 1–3 August, the air was Atlantic in origin, passing subsequently over the Southern UK and London before arriving at the site from a southerly/south-westerly direction. On 4th and 5th August the air was also Atlantic in origin, but passed over Northern France and the North Sea before arriving at the site from an easterly direction. For these 5 days, wind speeds at the site ranged between 5 and 8 ms<sup>-1</sup> and peak daytime temperatures ranged from 19 to 25 °C. From 6–10 August, a high-pressure weather system presided over the UK and much of Western Europe. Very low wind speeds, ranging from 0.5 to 5 ms<sup>-1</sup> were experienced, with a typically westerly local wind direction and maximum daily temperatures of 26–37 °C. Temperatures exceeded 35 °C on 6–10 August, and the highest-ever recorded UK air temperature was observed during this period at Faversham, Kent (around 30 miles from the site) at 38.5 °C. During the period from 13–24 August, the air was again Atlantic in origin, passing over the UK and arriving at the site in a westerly/north-westerly direction. Wind speed was generally higher during this period, ranging from 7 to 15 ms<sup>-1</sup>, with temperatures between 20 and 25 °C. From 25–30 August, the air originated in the Arctic, travelling over the North Sea before arriving at Writtle from a northerly/north-easterly direction. Wind speeds ranged from 5 to 8 ms<sup>-1</sup> during this period, with maximum temperatures between 17 and 20 °C.

The most interesting period from the point of view of air pollution is from 5–11 August and will be described as the ‘heatwave period’. Although back trajectories under these conditions are less reliable than under cyclonic flow, they demonstrate that air arriving at the Writtle site at midday on all days from 6–10 August had been slow moving over the UK or Europe for at least the previous 5 days, providing an unusually long period for the accumulation of photochemical pollutants. This stagnation of air over areas of elevated emissions allowed both primary and secondary pollutants to reach significant concentrations.

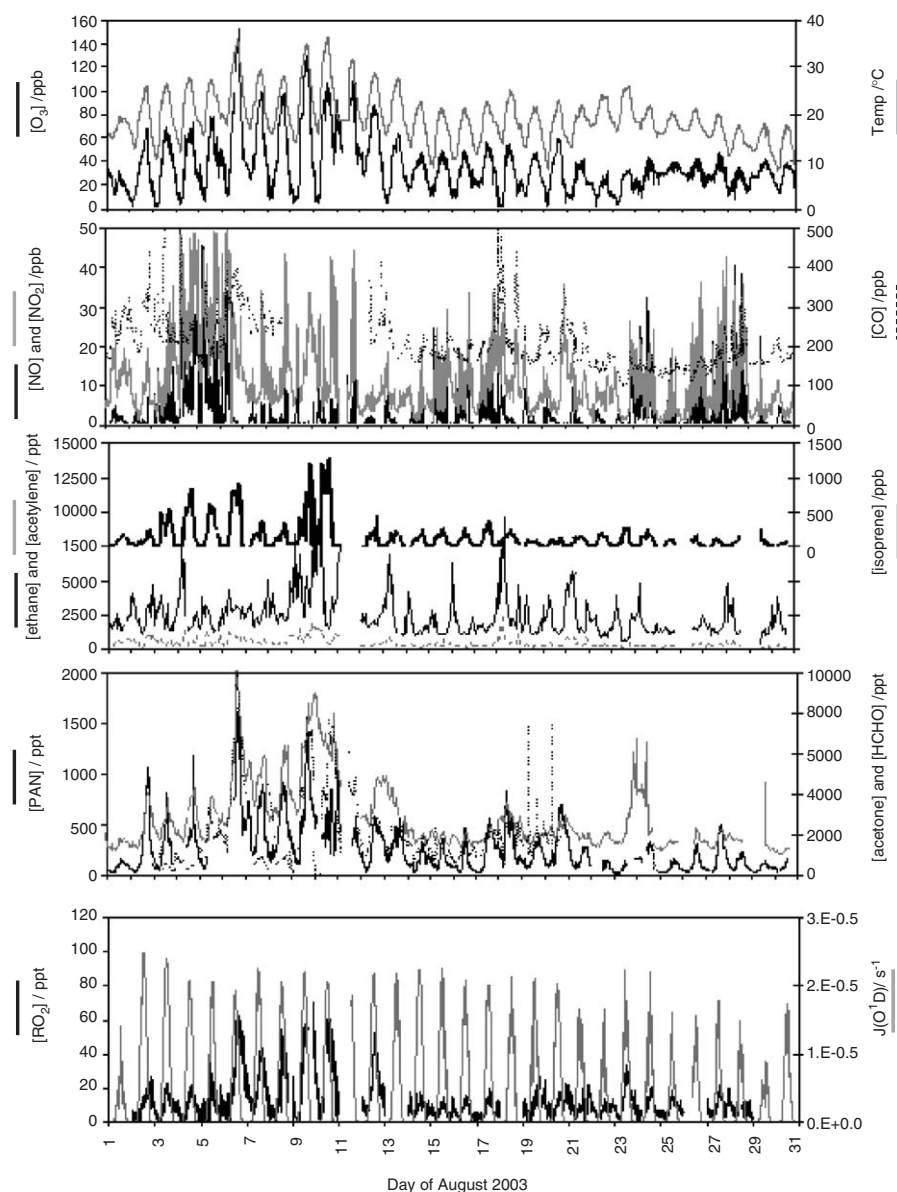


Fig. 1. Time series of selected gas phase measurements taken at Writtle during the TORCH field campaign.

### 3.1. Ozone/ $\text{NO}_x$

Surface ozone concentrations showed a marked difference during the heatwave period compared to the rest of August 2003. Ozone is plotted alongside ambient temperature in Fig. 1 and during the non-heatwave period, exhibits a diurnal cycle, typically peaking at 40–60 ppbV around 1–2 h after solar noon. At night, ozone falls to between 0 and 10 ppbV. This behaviour is very typical of moderately polluted suburban locations. However, on 6–11 August, the period when maximum daytime

temperatures were 27–37 °C, peak ozone was observed >100 ppbV, with 1-min concentrations measured from the mobile laboratory as high as 150 ppbV on 6th August. The nights of 6 and 7 and 10 and 11 August also saw elevated nighttime concentrations of ozone. The very high (>80 ppbV) concentrations on the night of 10th and 11th correspond to a change in wind direction and were due to air being transported to the site from the North Sea, where ozone surface deposition was much less than for an equivalent airmass over land. The difference in the behaviour of measured species



between the heatwave period and the rest of the campaign is further demonstrated by examining the average diurnal profiles for the two periods, summarised in Fig. 2. Similar average ozone concentrations were observed during the early morning, and in both cases, start to rise just after 08:00. However in

the heatwave period, the concentrations rise more sharply and reach a peak of approximately 110 ppbv at 18:00. In contrast, during the rest of the campaign, the concentrations rise more gradually and reach a peak of approximately 50 ppbv at 18:00.

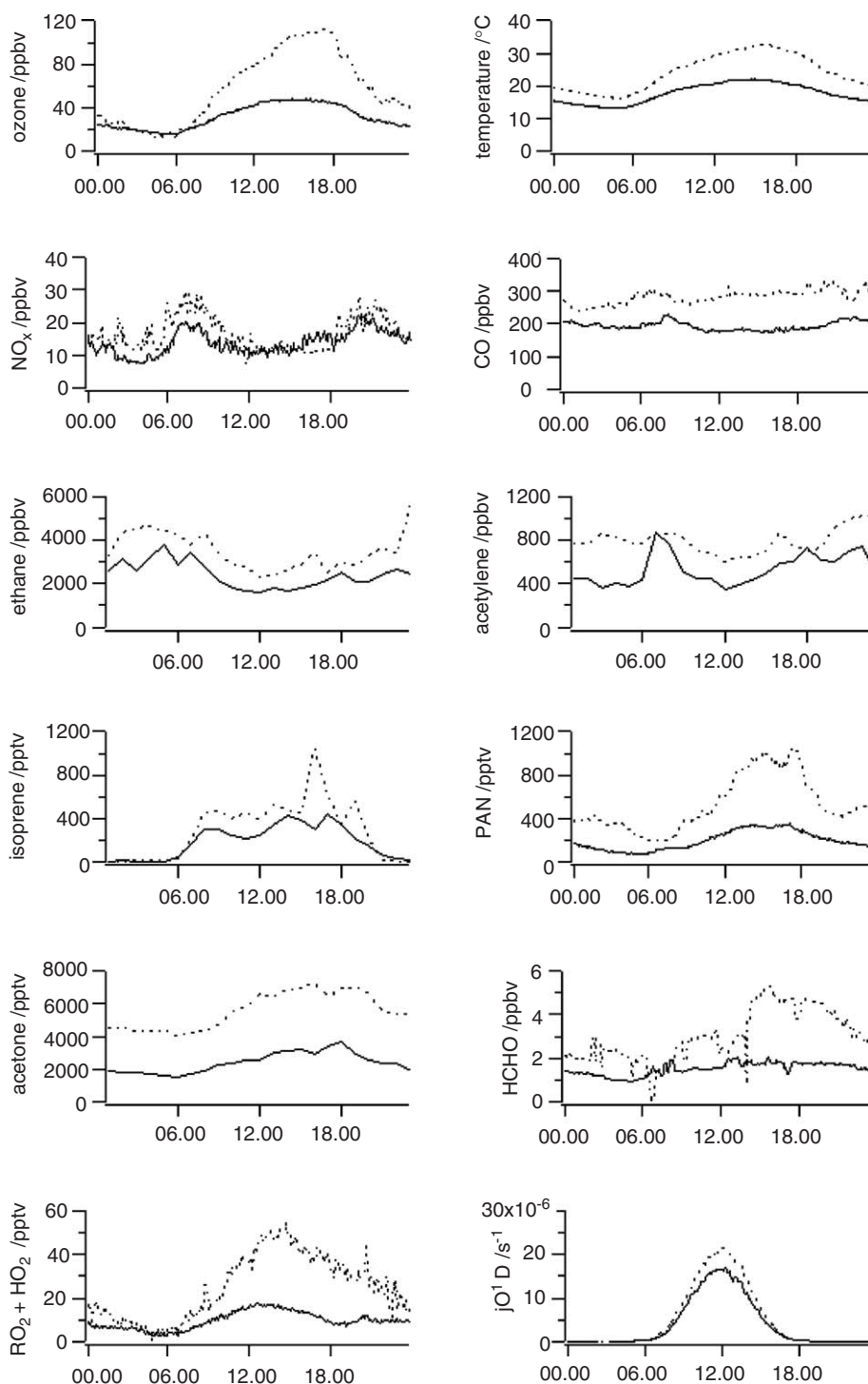


Fig. 2. Average diurnal profiles of selected species during the heatwave period (6–10 August - dashed lines) and for the rest of the field campaign (solid lines). Data are binned into hourly time periods the averaged for the two periods.

the heatwave period, the steep increase in ozone begins early in the day and is sustained later through the afternoon, reaching a peak of 112 ppbV, just before 18:00, compared to a peak of 48 ppbV at 15:00 in the non-heatwave period. The time series for NO and NO<sub>2</sub> from TORCH is also plotted in Fig. 1, with NO exhibiting a diurnal cycle with high values in early to late morning. Typical peak NO concentrations are of the order of 5–10 ppbV, with some excursions up to 30–40 ppbV, when the site experienced pollution from local sources. Daytime NO<sub>2</sub>/NO ratios ranged from 5 to 20 during the non-heatwave period, with ratios of 10–60 measured during the heatwave. The average diurnal profile of total NO<sub>x</sub> shows very similar behaviour during the two different periods, with peaks at around 09:00, corresponding to highest traffic levels during morning rush hour. During the heatwave, peak average morning concentrations reached ~25 ppbV, with ~20 ppbV reached during the non-heatwave period. There is then a drop in NO<sub>x</sub> levels to a steady value of 10–15 ppbV by 12:00 for the rest of the day, followed by a second peak up to ~20 ppbV (for both heatwave and non-heatwave) at around 19:00.

### 3.2. Emissions tracers

The data series for surface emissions tracers ethane, acetylene and isoprene are also shown in

Fig. 1. Typical ethane and acetylene concentrations of 2500 and 400 pptV, respectively are observed throughout the whole of the campaign, with peaks up to 10,000 pptV of ethane seen on some days. There is no distinct diurnal cycle in either ethane or acetylene, but both species exhibit generally higher concentrations at night, behaviour that is illustrated more clearly in Fig. 2. Ethane is on average ~1000 pptV higher during the heatwave period compared to the rest of the campaign. Acetylene is on average 200–400 pptV higher during the heatwave period. Isoprene exhibits a very clear diurnal cycle, with zero concentration measured at night, followed by a rapid increase to typically 200–400 pptV from 06:00, levels which are maintained throughout daylight hours. During the heatwave period, particularly on 6–10 August, peak isoprene concentrations reached > 1000 pptV. This behaviour is shown in the averaged diurnal profile for the heatwave period, with a maximum observed at around 16:30.

Table 1 shows measurements of 65 different VOC species, averaged over daytime (05:00–20:00 GMT) and nighttime (20:01–04:59 GMT) periods and then averaged for the heatwave period and the rest of the campaign. The table demonstrates that for the vast majority of species concentrations are elevated during the heatwave period, both for primary organic compounds emitted directly, and those

Table 1  
Concentrations and calculated OH reactivity of measured hydrocarbons

	Concentration (pptV)				Reactivity s <sup>-1</sup>	
	Day	Night	Day heatwave	Night heatwave	Day	Day heatwave
Ethane	2039	2344	3038	4344	0.018	0.027
Ethene	469	600	865	999	0.138	0.255
Propane	956	1194	1736	3000	0.002	0.004
Propene	148	206	237	285	0.135	0.216
Iso-butane	289	324	602	774	0.023	0.049
<i>n</i> -butane	546	591	1095	1413	0.048	0.096
Propadiene	7	11	11	17	0.002	0.004
Acetylene	395	433	699	893	0.011	0.020
Trans-2-butene	11	14	13	17	0.025	0.030
1-butene	36	42	62	64	0.039	0.068
Iso-butene	34	46	63	80	0.061	0.112
Cis-2-butene	6	9	9	12	0.013	0.018
Cyclo-pentane	29	32	45	57	0.005	0.008
Iso-pentane	446	508	962	1273	0.060	0.130
<i>n</i> -pentane	232	367	388	561	0.032	0.053
1,2 butadiene	26	28	45	50	0.023	0.041
1,3-butadiene	14	27	17	32	0.033	0.039

Table 1 (continued)

	Concentration (pptV)				Reactivity s <sup>-1</sup>	
	Day	Night	Day heatwave	Night heatwave	Day	Day heatwave
Propyne	9	12	16	228	0.002	0.003
Cyclopentene	3	6	5	213	0.000	0.000
Trans-2-pentene	7	9	8	12	0.016	0.020
1-pentene	9	7	16	16	0.022	0.037
2methyl1butene	14	18	24	32	0.015	0.027
2methyl2butene	7	9	10	14	0.015	0.020
Cis-2-pentene	4	11	7	9	0.013	0.020
Dimethylbutane	78	93	172	250	0.005	0.012
Cyclohexane	24	29	50	65	0.006	0.013
2 + 3 methylpentane	189	221	370	526	0.015	0.030
<i>n</i> -hexane	42	47	113	157	0.008	0.022
Isoprene	134	24	380	34	0.469	1.330
<i>n</i> -heptane	29	31	57	65	0.007	0.014
dms (nmhc)	10	13	18	20	0.002	0.003
Benzene	136	162	336	524	0.006	0.015
Octane	37	45	70	95	0.008	0.014
Toluene	281	359	510	723	0.084	0.153
Ethyl-benzene	45	56	68	95	0.011	0.017
<i>m</i> -xylene + <i>p</i> -xylene	135	184	160	252	0.089	0.105
Styrene	11	13	10	14	0.021	0.021
<i>o</i> -xylene	49	65	63	99	0.023	0.030
<i>i</i> and <i>n</i> -propyl-benzene	17	20	20	34	0.004	0.005
3 and 4-ethyltoluene	28	41	27	58	0.018	0.016
1,3,5-trimethyl-benzene	8	12	10	18	0.016	0.019
<i>t</i> -butyl-benzene + 1,2,4TMB + 2-ethyl-toluene	41	67	38	93	0.031	0.029
1,2,3-trimethyl-benzene	31	38	24	36	0.036	0.027
Acetaldehyde	1528	1855	3059	3934	0.836	1.673
Methanol	3785	4086	5135	5168	0.124	0.168
Acetone	2292	2132	5174	4973	0.017	0.039
Methacrolein	26	16	76	59	0.029	0.085
Ethanol + mvk + mek	1214	1379	2873	2560	0.094 <sup>a</sup>	0.107 <sup>a</sup>
Propanol	100	115	215	205	0.020	0.043
Butanal	109	81	55	44	0.108	0.054
Butanone	135	111	135	108	0.006	0.006
2-methyl-propanal	11	13	12	15	0.010	0.011
pentanal	20	19	66	52	0.017	0.056
2-pentanone	9	7	3	1	0.001	0.000
hexanal	29	41	51	81	0.030	0.053
PAN	236	141	649	428	0.001	0.002
HCHO	1610	1390	3320	2760	0.557	1.150
				Total reactivity	3.396	6.612

<sup>a</sup>The ethanol + mvk + mek reactivity is calculated assuming the total amount is made up entirely of ethanol.

produced from the photo-oxidation of primary species. Also shown in Table 1 for the daytime concentrations is the product of the average concentration of each species with its rate coefficient for reaction with OH. This gives a measure of the importance of each hydrocarbon in producing free

radicals, and is again calculated for the heatwave period, and compared to the rest of the campaign. In non-heatwave periods the largest contribution to VOC reactivity is from acetaldehyde, contributing 25% of the total VOC reactivity, with the total contribution from all oxygenated secondary species



being 36%. Formaldehyde and isoprene are also significant, contributing 16% and 14% of the total reactivity, respectively. During the heatwave period, acetaldehyde again contributes the most to total reactivity ( $\sim 25\%$ ). The total from oxygenated species and formaldehyde is very similar at 35% and 16%, respectively. However, the contribution from isoprene to the total reactivity during the heatwave period increases to 20%. The balance of reactivity between functional group types is broadly similar in the two periods, but absolute concentrations of organic compounds are generally higher.

### 3.3. Measurements of isoprene

Whilst biogenic emissions inventories exist for the UK (Stewart et al., 2003), in general, it is not considered a geographic region which is strongly influenced by biogenic VOCs. Isoprene is emitted globally from plants and trees (Guenther et al., 1993) and also, to a lesser extent from combustion sources (McLaren et al., 1996). European isoprene emissions are estimated to be approximately  $4000 \text{ kt C yr}^{-1}$  (Simpson et al., 1995), which, combined with its short atmospheric lifetime (approximately 5 h, assuming an average OH concentration of  $5.5 \times 10^5 \text{ molecules cm}^{-3}$ ), make isoprene highly important in the atmosphere in terms of an OH sink and ozone and radical source. Biogenic emissions of isoprene are dependent upon both light and temperature (Guenther et al., 1993) and consequently, atmospheric concentrations of isoprene exhibit a strong diurnal cycle with a maximum in the daytime falling to zero at night. Over the heatwave period in 2003 isoprene concentrations were seen to increase dramatically with a non-linear relationship to temperature in line with the algorithms developed by Guenther et al. (1993) (Fig. 3).

The nature of the site was such that only limited trees were present in the vicinity, and the dominant vegetation type was grazing grassland. Although on-line measurements were not made, a small number of monoterpene measurements were made using carbon adsorbent tubes, which were analysed off-site using GC–time-of-flight mass spectrometry. Data for these species are limited; however, there is a strong indication of elevated monoterpene concentrations, concurrent with those of isoprene. The high concentrations of isoprene and other VOCs observed in the late afternoon on episodic days, coupled with high reactivity and ozone-forming potential suggest that ozone could be generated in

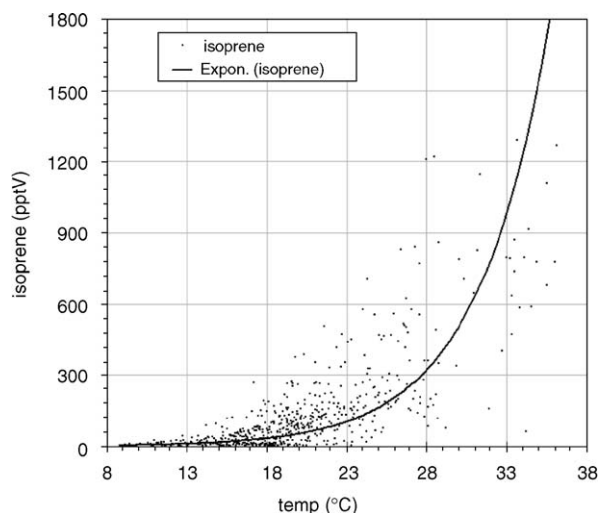


Fig. 3. Plots showing the relationship between measured isoprene concentration and ambient temperature. Data shown were taken with the GC-FID instrument and are from 1 to 31 August 2003.

situ on the day of observation. It is also notable that the average profile of ozone on the episodic days continued to increase into the very late afternoon. A determinant of ozone generation is the abundance of peroxy radicals, and these were also seen to reach their maximum in the late afternoon on episodic days (see Section 3.4). There is evidence that the emission of additional isoprene over the heatwave was not limited solely to rural locations such as Writtle. Measurements taken at Marylebone Road in central London showed concentrations as high as 1.6 ppbV in August 2003, and where the relationship becomes clearly temperature dependent as the dominant source switches from anthropogenic to biogenic (Dollard, 2005).

### 3.4. Other photochemical by-products

Figs. 1 and 2 also show photochemical products such as PAN, acetone and HCHO. These species clearly show significant enhancement during the heatwave period, much greater than was seen in many of the precursor NMHCs, with peak daytime concentrations more than doubled. This behaviour was also seen in other secondary products such as the higher aldehydes and ketones. Alkyl nitrates were also measured during the campaign; however, data is unavailable for much of the heatwave period. From 9 to 11 August, 2-butyl nitrate and 3-methyl-2-butyl nitrate were measured with concentrations

ranging from 32 and 71 pptV, respectively at mid-day to 35 and 58 pptV, respectively around mid-night. These species are photochemically derived from their hydrocarbon precursors *n*-butane and *iso*-pentane. High concentrations were observed to coincide with the high ozone levels detected on the night of 10 and 11, evidence for photochemical products being transported to the site. The average diurnal variations of the alkyl nitrates for the non-heatwave period show maxima in the afternoon similar to other photochemical products, i.e., ozone, PAN, peroxy radicals.

The bottom panel of Fig. 1 shows the data series obtained for the reactive peroxy radical intermediates  $\text{HO}_2 + \Sigma\text{RO}_2$ . Overlaid on this plot is a measure of photolysis frequency for generation of  $\text{O}^1\text{D}$  from ozone— $j(\text{O}^1\text{D})$ . During the heatwave period mixing ratios of peroxy radicals reached 60 pptV during mid-afternoon. The peroxy radicals had an hourly average mixing ratio of 50 pptV at 14:30 GMT over the 5 days of the heatwave over three times that of the average for the rest of the campaign, which peaked at 12:30 GMT. These levels are lower than values recorded during the ESCOMPTE campaign of summer 2001 in Southern France where mixing ratios of up to 200 pptV were observed (Coll et al., 2005). During the heatwave period, peroxy radicals were strongly correlated to ozone, PAN and peroxides, i.e. secondary products of photochemical oxidation. The average peroxy radical diurnal profile over the whole TORCH campaign is similar in shape and magnitude to that from the suburban Berlioz campaign that took place outside Berlin in 1998 (Mihelcic et al., 2003). As with BERLIOZ, the

peroxy radical mixing ratios increase with  $j(\text{O}^1\text{D})$  to a maximum shortly after solar noon. They also show a nighttime phase with radical mixing ratios rising from a minimum at approximately 18:00 GMT when the main source of peroxy radicals switches from photochemical to so called ‘dark reactions’ i.e., oxidation of VOCs via oxidation by  $\text{NO}_3$  and ozone (see for example Salisbury et al., 2001).

As discussed in Section 1, the main photochemical sources of  $\text{HO}_x$  in a polluted environment are photolysis of ozone, HCHO and HONO (Monks, 2005). Additional sources of  $\text{RO}_x$  are photolysis of higher aldehydes and ketones, along with thermolysis of PAN and PAN analogues and ozonolysis of alkenes. Table 2 shows the relative significance of four of these sources for which data are available. Whilst HONO was not measured, its contribution to  $\text{RO}_x$  production in a semi-rural location such as Writtle is considered more significant in the early morning hours as it builds up overnight and is, therefore, present in lower concentrations in the afternoon (Alicke et al., 2003). Average radical production rates for the heatwave period from ozone photolysis, formaldehyde photolysis, ozonolysis of alkenes and thermolysis of PAN for the afternoon period (12:00–18:00) are shown in Table 2. Thermolysis of PAN is the largest source of  $\text{RO}_x$  production at this time ( $1.85 \times 10^7 \text{ radicals cm}^{-3} \text{ s}^{-1}$ ) with 67% of radical production attributed to it, with ozone photolysis ( $5.22 \times 10^6 \text{ radicals cm}^{-3} \text{ s}^{-1}$ ) accounting for 24%. Formaldehyde photolysis and ozonolysis of alkenes make up 3.4% and 5.3% of  $\text{RO}_x$  production,

Table 2  
Contributions to  $\text{RO}_x$  production over the heatwave period (12:00–18:00)

Date in August	$\text{RO}_x$ production molecule <sup>-1</sup> cm <sup>-3</sup> s <sup>-1</sup> ( $\times 10^{-7}$ ) from				
	$\text{O}_3$ photolysis	HCHO photolysis	Alkene ozonolysis	PAN thermolysis	Total
6	0.673	0.152	0.253	3.57	4.45
	14.5%	3.3%	5.4%	76.8%	
7	0.464	0.0224	0.0592	0.918	1.46
	31.7%	1.5%	4.1%	62.7%	
8	0.514	0.0220	0.0513	0.759	1.35
	38.2%	1.6%	3.8%	56.4%	
9	0.525	0.148	0.165	2.79	3.63
	14.5%	4.1%	4.54%	76.9%	
10	0.435	0.129	0.168	1.21	1.94
	22.4%	6.7%	8.7%	62.3%	
Average	0.522	0.0860	0.139	1.85	2.61
	24.3%	3.4%	5.3%	67.0%	

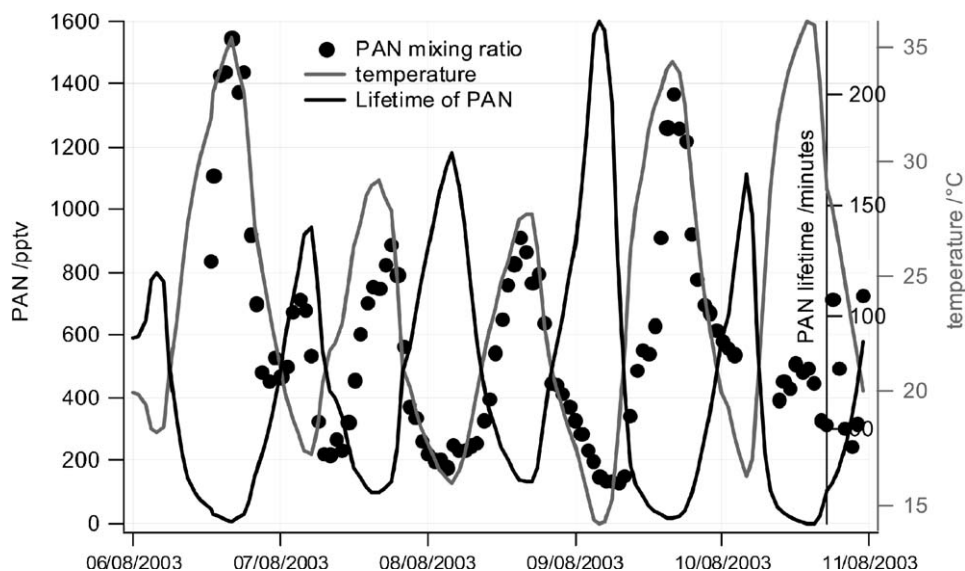
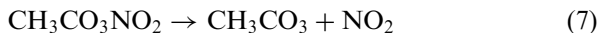
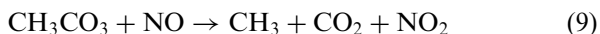


Fig. 4. PAN mixing ratios and lifetimes over the heatwave period (6–10 August).

respectively. The magnitude of  $\text{RO}_x$  production from PAN is much greater than that of maximum ozone photolysis for 6–10 August, coinciding with the days when ozone mixing ratios were at their highest. PAN as an afternoon reservoir of  $\text{RO}_x$  is not surprising considering its extremely short lifetime at temperatures experienced during this heatwave period; the PAN lifetime (with respect to thermal dissociation) being as short as 7.5 min for temperatures of 36 °C (Fig. 4) with average PAN lifetime with respect to decomposition of 18.3 min (12:00–18:00, 6–10 August). The thermolysis of PAN produces a peroxy acetyl radical (PA) and  $\text{NO}_2$ :



The PA radical can then undergo reformation with  $\text{NO}_2$  to reform PAN, or react with NO:



with resulting NO– $\text{NO}_2$  oxidation. Therefore, the fractional reformation of PAN can be expressed as

$$\frac{k_8[\text{CH}_3\text{CO}_3][\text{NO}_2]}{k_8[\text{CH}_3\text{CO}_3][\text{NO}_2] + k_9[\text{CH}_3\text{CO}_3][\text{NO}]} \quad (10)$$

$k_8$  and  $k_9$  are  $1.2 \times 10^{-11}$  and  $2.1 \times 10^{-12}$  molecule  $\text{cm}^3 \text{s}^{-1}$ , respectively, hence the reformation of PAN is largely controlled by the ratio of  $\text{NO}_2/\text{NO}$ . During the heatwave period, daytime  $\text{NO}_2/\text{NO}$  ranged from 10–60, hence the fractional

PAN reformation can be calculated to range from 0.85–0.95. This analysis shows that although PA radicals are formed from thermolysis of PAN (and will be measured as radicals by the PERCA instrument), a large fraction of them will reform to PAN via reaction with  $\text{NO}_2$ . Depending on prevailing  $\text{NO}_x$  distribution, however, the steady-state concentration of PA radicals may be higher in episodic conditions over cyclonic, due to the higher temperatures and shifting of the equilibrium from PAN to PA, in conjunction with higher quantities of the initial feedstock in the form of reactive carbon. PA itself is important as an intermediate and precursor to the formation of other peroxy radicals and as a result, more detailed modelling studies would be required to ascertain whether PAN is a net source or sink of radicals. A further radical source could also come from other PAN species, such as PPN and mPAN, which were not measured in this study. A full analysis of the radical chemistry in polluted environments would need measurements of these species, so future work in similar environments should include their measurement.

#### 4. Discussion

The exceptionally hot, dry and sunny weather that occurred during the summers of 1976, 1990 and 1995 also led to very high levels of ozone in the UK. Although the amount of ozone monitoring data available in 1976 is limited, two major ozone

episodes were encountered. From 22nd to 29th June, ozone peaked at 211 ppbV at Teddington, Middlesex and from 3rd to 5th July when 254 ppbV was measured at Harwell Oxfordshire (4th PORG report, 1997). Air mass back trajectories to the South of England for these episodes show that although the air masses arrived by different routes, on both occasions they had travelled over high-emission areas of Europe, where photochemical pollution would have accumulated. For the period 1986–95, there was a reduction in the magnitude of the maximum ozone values occurring during summer photochemical episodes. Ozone concentrations during the 1990 heatwave reached >100 ppbV on 2–4 August over much of the UK, with a peak of 161 ppbV at Lullington Heath. During 1995, ozone levels never reached the levels of 1976 or 1990, but were significantly higher than those reported in previous and subsequent years. Levels reached 90 ppbV at rural monitoring sites on several occasions during July and August, with 4 episodes where concentrations reached >110 ppbV. Back trajectory analysis during these episodes showed a different pattern to those seen in 1976, with the majority of the trajectories passing through relatively unpolluted regions, before entering the UK (4th PORG report, 1997). Finding elevated concentrations during a heatwave is not therefore surprising. Given the reductions in emissions of VOCs and NO<sub>x</sub> over the past decade it is perhaps unexpected however that peak ozone in 2003 exceeded levels above 100 ppbV, since the reduction in the magnitude of such peaks has been considered a generally successful outcome of UK emissions reduction policy. It is therefore useful to determine why ozone was so high over this period, and whether this is likely to occur again should temperatures of 2003 be seen in future years.

A key part of understanding the 2003 highs is to determine the relative sources of ozone observed at the Writtle site and any potential nonlinearities in this generation process. For the longer-lived secondary products such as ozone (and also species such as acetone etc.), what is observed at this location during a heatwave will be a combination of the general Northern Hemisphere background + regionally produced products (at this location likely to be predominantly from mainland Europe but will also include some production from the local area). During the heatwave of 2003, ozone data from other air quality monitoring sites in SE England (Harwell [Oxon], Wicken Fen [Cambs], Rochester

[Kent] and Lullington Heath [E Sussex] (Air quality archive, 2005) exhibited the same characteristics as the Writtle site, indicative of a regional scale phenomenon. Model studies such as that by Jenkin et al. (2002), point to Europe as a major source of ozone during such anticyclones and that will also hold true for this case. However, the direct (and perhaps unexpected) observation of extremely active local chemistry in this study, through non-linear emissions of isoprene, elevated peroxy radical intermediates and labile products such as PAN suggests at least a *prime facie* case for significant additional local (that is, within the boundary layer of the UK and on the day of observation) generation of ozone, to be added to an already-enhanced regional background. This scenario assumes that physical loss processes to the surface remain constant in both episodic and non-episodic conditions.

The meteorological conditions during the heatwave were such that a daytime convective boundary layer (mixed layer) developed throughout the day reaching a maximum height of approximately 1800 m by 15:00 (Norton et al., 2005). At nighttime, a shallow surface inversion formed that was decoupled from the residual boundary layer. During the morning, surface heating caused this shallow inversion layer to be entrained with the residual layer aloft to form a single well-mixed layer. The mixing down of polluted air is likely to be the primary driver behind the rapid increases in ozone seen during the heatwave morning periods. From a surface measurement of ozone it is impossible, however, to differentiate ‘older’ ozone (i.e. that which has been produced over mainland Europe over the previous 2–5 days) from that which has been produced close to the measurement site (i.e. over the last 24 h).

Benzene:toluene (b:t) ratios can be used as indicators of air mass processing and the degrees to which OH and dilution affect an air mass when integrated over the day timescale. The dominant emissions of benzene and toluene are from petrochemical sources at a ratio of approximately 1:4. The atmospheric removal of toluene by OH is faster than benzene. The b:t ratio has been calculated for the TORCH campaign using the longer time-integrated concentrations obtained using GCXGC (3 h frequency) and is shown in Fig. 5 with a ratio that varies between 0.3 and 1.8. Generally, the ratio has a maximum during the day (indicating active OH removal) but there is no significant difference in

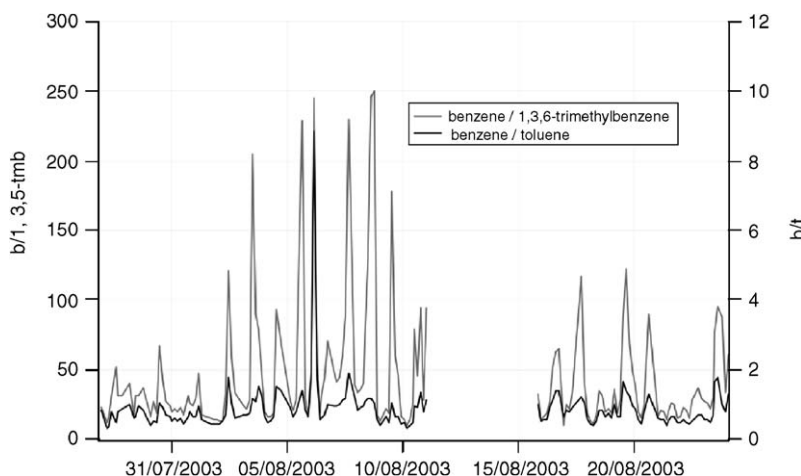


Fig. 5. Ratios of benzene/toluene (b/t) and benzene/1,3,5 tri-methyl benzene (b/135 tmb) for the TORCH campaign. Data used were taken with the GC  $\times$  GC instrument.

the behaviour of this ratio during the heatwave period compared to other times. Also shown on Fig. 5 is the ratio of b:1,3,5-TMB observed at Writtle over the course of the campaign. During established westerly conditions with airflow from London, b:1,3,5-TMB is close to the ratio predicted by the National Atmospheric Emissions Inventory (NAEI), indicating that under emissions and dilution are the dominant factors controlling abundance under these conditions. During the 3–11 August, the ratio became diurnally varying with b:1,3,5-TMB peaking during the afternoon: [1,3,5-TMB] reaches very low concentrations. During the nights over this period b:1,3,5-TMB returned rapidly to the predicted emission ratio. A possible explanation is that this behaviour is driven by mixing and entrainment of air from aloft during the morning collapse of the shallow inversion layer to form the daytime boundary layer. Trajectories would indicate that the air entrained from aloft is likely to be significantly polluted but also highly processed, with no contact with fresh surface emissions for many hours. Hence the air within this region would be depleted in 1,3,5-TMB and have a high b:1,3,5-TMB ratio, but not necessarily be depleted in longer-lived tracers such as toluene. It follows that air from aloft dominates the aromatic composition over local surface emissions—the opposite to the case seen in strong westerly flow. The absence of 1,3,5-TMB is a proxy for the likely incursion of regionally produced secondary species such as ozone. The ratio change can be used to estimate the possible fraction of ozone entrained from above,

to provide an approximation of the amount of ozone that is derived from regional sources versus that produced on the day of observation. Using a b:1,3,5-TMB aloft ratio of 1:1000 (equivalent to around 24 h OH processing with no fresh emissions) then a crude estimate of  $1:10 \pm 5$  can be made of the relative proportions of ‘surface’ and ‘aloft’ air which make up the mixture observed at the site. There is significant uncertainty introduced into this estimate, owing to the estimate of the aloft and surface emission ratios. If ozone is assumed to scale linearly with surface VOC emissions, a similar ratio would be expected for the relative proportions of ‘old’ aloft ozone versus more recently produced surface ozone. This is not likely to be the case, however, as biogenic VOCs are major contributors to  $O_3$  formation and do not follow the same emission pattern as anthropogenic species. In summary, however, the very short-lived tracers such as multi-substituted aromatics (the behaviour is seen in other aromatics in addition to 1,3,5-TMB) provide strong evidence of the very significant mixing down of polluted air during the early and middle part of day, and air from aloft dominates the composition with respect to anthropogenic organic compounds.

Utembe et al. (2005) discussed how tracers such as NMHCs and their by-products such as carbonyls and ozone could be simulated at the Writtle site in 2003 using a trajectory model including detailed chemical reaction schemes. In general, NMHCs could be recreated well in terms of levels and variability although naturally some small-scale features differed between measurement and model.



The model could also predict the observed change in b:1,3,5-TMB supporting the notion that this is a widespread regional phenomena and not a peculiarity of local meteorology, and also that the treatment of boundary layer behaviour in the model was representative. One of the key conclusions from the Utembe et al. (2005) work is that the emissions inventory for anthropogenic VOCs and their chemistry within the trajectory model is well represented, but that estimation of ozone during the heatwave is not straightforward. The ability to correctly simulate ozone over this heatwave period using a trajectory model was closely tied to the biogenic emissions that were introduced by that model from the surface.

## 5. Summary and conclusions

A comprehensive set of gas-phase measurements and meteorological parameters were made at Writtle, Essex, during the TORCH field campaign

in August 2003. The measurements included a period (6–10 August) of high pressure over the UK and most of Western Europe that was characterised by low wind speeds ( $0.5\text{--}5\text{ ms}^{-1}$ ) and exceptionally high UK maximum temperatures ( $26\text{--}37^\circ\text{C}$ ). This period was also characterised by high ozone concentrations, with peak levels  $>110\text{ ppbV}$  observed on each of the 5 days of the heatwave period. This paper reports measurements made at a single site, North-East of London; however, the high ozone concentrations observed were also seen over the whole of South East England. This behaviour is shown in Fig. 6, which uses data from 76 of the air-quality monitoring sites in the UK taken on 6 August and shows the maximum levels of ozone centring on South East England. Concentrations of  $\text{NO}_x$  did not exhibit significant elevation concentrations during this heatwave period when compared to the rest of the month of August. Anthropogenic VOCs showed a significant enhancement in concentrations during

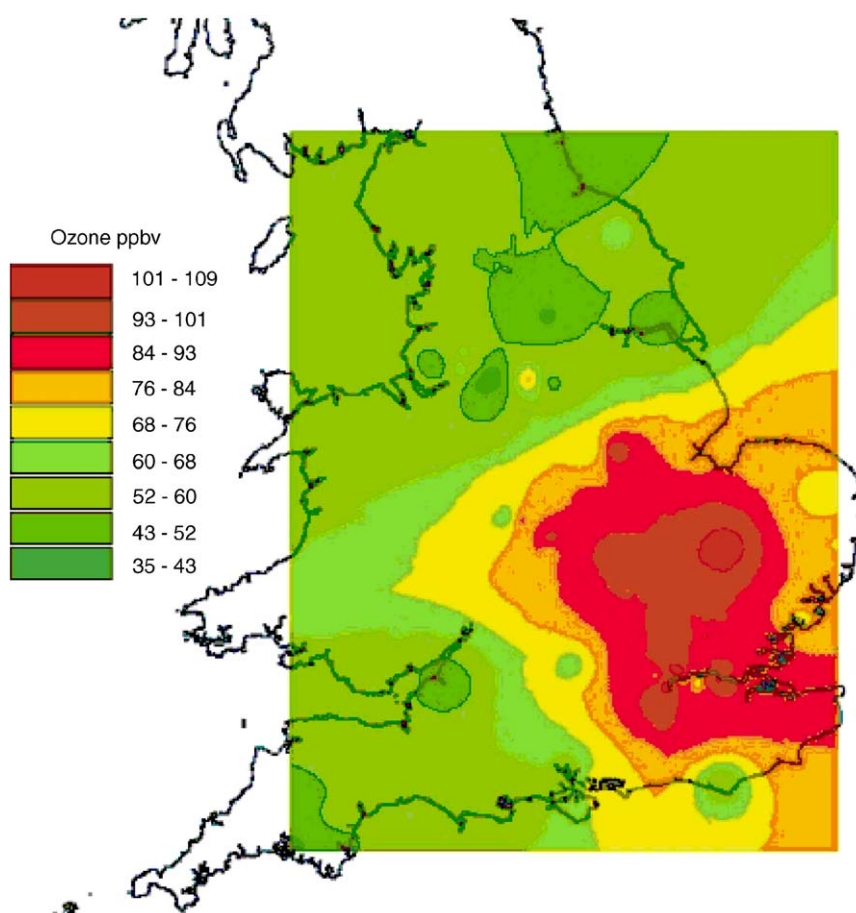


Fig. 6. The distribution of ozone over the UK on 6 August 2003, compiled from data from 76 UK air quality monitoring sites.

the heatwave (e.g. ethane and acetylene 1000 and 400 pptV) when compared to non-heatwave periods. Reactive aromatic hydrocarbon ratios indicated that the morning collapse of a shallow inversion layer resulted in significant entrainment of air from the polluted residual boundary layer aloft, and that this air, which had been polluted on a regional scale, controls the abundance of anthropogenic VOCs and longer-lived photochemical byproducts on episodic days.

The profile of ozone on episodic days, showed both a more rapid rise in the morning, which we attribute to entrainment of high ozone air from European sources, and sustained and continued increases into the late afternoon. We identify that the late afternoon maximum in ozone coincides with a high maximum in peroxy radicals and photochemical by-products such as PAN, peak values of which were an order of magnitude higher in the heatwave. The decomposition of PAN to form peroxy acetyl radicals (PA), and its possible subsequent reactions or reformation with NO<sub>2</sub> is clearly highly sensitive to temperature, NO/NO<sub>2</sub> distribution and amount of hydrocarbon precursor. Although PAN has many precursors, the types of VOCs observed in heatwave and non-heatwave periods were somewhat similar, albeit that total VOC reactivity was around double during the episode with proportionally higher concentrations. The most noticeable difference between periods was the strong temperature dependence of ambient isoprene, increasing exponentially with *T* to a maximum in excess of 1200 pptV, with the maximum concentration being coincident in the late afternoon with maximum PAN and O<sub>3</sub>. Our conclusions, therefore, are that the potential for net ozone production exists on the day of observation building on a high background in ozone, which may be entrained at the beginning of an episodic day. The abundance of ozone on the final day of an airmass trajectory arriving in the in the UK during an anticyclone may therefore be influenced not only by longer range transport, but also by UK emissions including importantly biogenic species which have nonlinear emissions and temperature-dependant chemistry, and which have a clear sensitivity to future changes in meteorology and climate.

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### References

- 4th PORO report, 1997. Ozone in the United Kingdom.
- Air quality archive, 2005. Available at [airquality.co.uk](http://airquality.co.uk).
- Alicke, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Patz, H.W., Schafer, J., Stutz, J., Volz-Thomas, A., Platt, U., 2003. OH formation by HONO photolysis during the BERLIOZ experiment. *Journal of Geophysical Research* 108, 8247.
- Coll, I., Pinceloup, S., Perros, P.E., Laverdet, G., Le Bras, G., 2005. 3D analysis of high ozone production rates observed during the ESCOMPTE campaign, *Atmospheric Research* 74, 477–505.
- Derwent, R.G., Jenkin, M.E., 1991. Hydrocarbons and the long-range transport of ozone and pan across Europe. *Atmospheric Environment Part A—General Topics* 25, 1661–1678.
- Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., Simmonds, P.G., Passant, N.R., Dollard, G.J., Dumitrean, P., Kent, A., 2003. Photochemical ozone formation in north west Europe and its control. *Atmospheric Environment* 37, 1983–1991.
- Dollard, G.J., 2005. Personal Communication.
- Edwards, G.D., Monks, P.S., 2003. Performance of a single mono-chromator diode array spectro-radiometer for the determination of actinic flux and atmospheric frequencies. *Journal of Geophysical Research* 108, 8546–8588.
- Ehhalt, D.H., 1999. Photooxidation of trace gases in the troposphere. *Physical Chemistry Chemical Physics* 1, 5401–5408.
- Emmerson, K.M., Carslaw, N., Carslaw, D.C., Lee, J.D., McFiggans, G., Bloss, W.J., Gravestock, T., Heard, D.E., Hopkins, J.R., Ingham, T., Pilling, M.J., Smith, S.C., Jacob, M., Monks, P.S., 2006. Free radical modelling studies during the UK TORCH campaign in summer 2003, *Atmospheric Chemistry and Physics*, submitted.
- Fischer, P.H., Brunekreff, B., Lebet, E., 2004. Air pollution related deaths during the 2003 heatwave in the Netherlands. *Atmospheric Environment* 38, 1083–1085.
- Fleming, Z., Monks, P.S., Rickard, A.R., Heard, D.E., Bloss, W.J., Still, T., Sommariva, R., Pilling, M.J., Morgan, R.B., Green, T.J., Brough, N., Penkett, S.A., Lewis, A.C., Lee, J.D., Saiz-Lopez, A., Plane, J.M.C., 2006. Peroxy radical chemistry at Mace Head, Ireland during the summer of 2002. *Atmospheric Chemistry and Physics* 5, 2193–2214.
- Goodwin, J.W.L., Salway, A.G., 2002. UK emissions of air pollutants 1970–2000, AEA Technology Report—AEAT/ENV/R/1283, ISBN:1-85580-33-0.
- Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate

- variability—model evaluations and sensitivity analyses. *Journal of Geophysical Research—Atmospheres* 98, 12609–12617.
- Hamilton, J.F., Lewis, A.C., 2003. Monoaromatic complexity in urban air and gasoline assessed using comprehensive GC and fast GC-TOF/MS. *Atmospheric Environment* 37, 589–602.
- Hopkins, J.R., Lewis, A.C., Read, K.A., 2002. A Two-column method for long-term monitoring of Non-methane hydrocarbons (NMHC) and oxygenated volatile organic compounds (o-VOCs). *Journal of Environmental Monitoring* 5, 8–13.
- Jenkin, M.E., Davies, T.J., Stedman, J.R., 2002. The origin and day-of-week dependence of photochemical ozone episodes in the UK. *Atmospheric Environment* 36, 999–1012.
- Logan, J.A., Prather, M.J., Wofsy, S.C., McElroy, M.B., 1981. Tropospheric chemistry: A global perspective. *Journal of Geophysical Research* 86, 7210–7254.
- McLaren, R., Singleton, D.L., Lai, J.Y.K., Khouw, B., Singer, E., Wu, Z., Niki, H., 1996. Analysis of motor vehicle sources and their contribution to ambient hydrocarbon distributions at urban sites in Toronto during the Southern Ontario oxidants study. *Atmospheric Environment* 30, 2219–2232.
- Mihelcic, D., Holland, F., Hofzumahaus, A., Hoppe, L., Konrad, S., Musgen, P., Patz, H.W., Schafer, H.J., Schmitz, T., Volz-Thomas, A., Bachmann, K., Schlomski, S., Platt, U., Geyer, A., Alicke, B., Moortgat, G.K., 2003. Peroxy radicals during BERLIOZ at Pabstthum: Measurements, radical budgets and ozone production. *Journal of Geophysical Research—Atmospheres*, 108, art-8254.
- Monks, P.S., 2005. Gas-phase radical chemistry in the troposphere. *Chemical Society Reviews* 34, 376–395.
- Norton, E.G., Vaughan, G., Methven, J., Coe, H., Brooks, B., Gallagher, M., Longley, I., 2005. Boundary layer structure and decoupling from synoptic scale flow during NAMBLEX. *Atmospheric Chemistry and Physics* 5, 3191–3223.
- Salisbury, G., Rickard, A.R., Monks, P.S., Allan, B.J., Bauguitte, S., Penkett, S.A., Carslaw, N., Lewis, A.C., Creasey, D.J., Heard, D.E., Jacobs, P.J., Lee, J.D., 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.
- Schar, C., Vidale, P.-L., Luthi, D., Frei, C., Harberli, C., Liniger, M.A., Appenzeller, C., 2004. The role of increasing temperature variability in European summer heatwaves. *Nature* 427, 332–336.
- Simpson, D., Guenther, A., Hewitt, C.N., Steinbrecher, R., 1995. Biogenic emissions in Europe. 1. Estimates and uncertainties. *Journal of Geophysical Research* 100, 22875–22890.
- Smith, S.C., Lee, J.D., Bloss, W.J., Johnson, G.P., Heard, D.E., 2005. Concentrations of OH and HO<sub>2</sub> during NAMBLEX: measurements and steady state analysis. *Atmospheric Chemistry and Physics* 5, 12403–12464.
- Stedman, J.R., 2004. The predicted number of air pollution related deaths in the UK during the August 2003 heatwave. *Atmospheric Environment* 38, 1087–1090.
- Stewart, H.E., Hewitt, C.N., Bunce, R.G.H., Steinbrecher, R., Smiatec, G., Schoenemeyer, T., 2003. A highly spatially and temporally resolved inventory for biogenic isoprene and monoterpene emissions: Model description and application to Great Britain. *Journal of Geophysical Research* 108, 4644.
- Stott, P.A., Stone, D.A., Allen, M.R., 2004. Human contribution to the European heatwave of 2003. *Nature* 432, 610.
- Utembe, S.R., Jenkin, M.E., Derwent, R.G., Lewis, A.C., Hopkins, J.R., Hamilton, J.F., 2005. Modelling the ambient distribution of organic compounds during the August 2003 ozone episode in the southern UK. *Faraday Discussions* 130, 311–326.