

Ozone photochemistry during the U.K. heat wave of August 2003.

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Abstract

A wide range of chemical and physical parameters have 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, U.K. indicated significantly elevated levels of primary VOCs, ozone ($>110\text{ppb}$), other photochemical by-products such as PAN, HCHO, and higher oxygenates but not NO_x . Reactive organic tracers in combination with surface Doppler wind radar and back trajectory analysis have been used to establish that initial rapid morning rises in 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 dependant exponentially increasing contribution from biogenic isoprene (max 1.2ppbV). In addition to entrainment of regional air pollution, ozone formation rates within the U.K. boundary layer on the day of observation have been determined using measured peroxy radicals in combination with other chemical data. Under episodic conditions total peroxy radicals in excess 120pptV were observed in late afternoon with strong correlation to a later and higher peak in ozone when compared to non-episodic conditions. During the daytime under episodic conditions alkyl peroxy radical formation was dominated by PAN thermolysis, whose afternoon lifetime averaged only 18.3min , but which was sustained at a concentration greater than 750pptV . Low episodic wind speeds resulted in a relatively small possible spatial footprint for emissions of reactive precursors to PAN, and a strong correlation between isoprene and PAN production rate suggest this species may have contributed to the later afternoon increases seen in surface O_3 .

1. Introduction.

Public association of poor air quality with extremely warm weather is firmly established in the United Kingdom 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 U.K., 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 parts per billion) 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 formation of peroxy radicals 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 increases to more than a few ppb, due to the reaction of OH with NO_2 (which is often in steady state with NO), increasing and terminating the cycle. Thus ozone production should be most efficient at

moderate levels of NO of around 1 ppb, depending on the production rate of HO_x and on the changing partitioning of radicals between HO₂ and RO₂ (Ehhalt, 1999). These are chemical conditions often associated with rural and semi rural locations.

U.K. terrestrial emissions of both nitrogen oxides and volatile organic compounds (VOCs), the key chemical precursors to ozone production, have been reduced with some 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 U.K. ozone events and understand the controlling chemistry 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 control 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 U.K., 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, 2003) through a combination of elevation in ozone and PM₁₀. Put in a national perspective, between 20-40% of all excess U.K. deaths over this heat wave 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 ppb being measured by the U.K. air monitoring network (data available from www.airquality.co.uk) at a number of locations in the S.E. of England. Figure 1 shows distribution of ozone data taken from 76 of the air quality monitoring sites in the U.K. on 6th August. It demonstrates the centering of maximum levels of ozone over Southern England on this day

It is important to understand the chemical and physical processes occurring under such albeit currently rare conditions, as climate models suggest that the occurrence of extreme high temperature periods is likely to significantly increase over the period to 2080 (Schar *et al.*, 2004). The current probability in the U.K. 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. An extrapolation of deaths brought forward from the 2003 example to 2080 frequencies is clearly highly significant. Understanding the complex interplay between the dynamical properties of the atmosphere under high temperature conditions and the chemical and emissions processes occurring within it are important if we are to predict and control air quality under these predicted future climate scenarios.

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 U.K. Derwent and Jenkin, (1991) reported the importance of atmospheric transport in contributing to high U.K. 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 that chemical processing leading to ozone under episodic high temperatures may be substantially different to that which occurs at lower more typical temperatures. This may be a consequence of gas kinetic properties, (e.g. T dependant 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 outside the edge 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. The paper will use observations to determine possible sources of ozone within the boundary layer on day of observation, 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 ($51^{\circ}:44':12''\text{N}$; $0^{\circ}:25':28''\text{E}$), 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 ~ 2 miles. Electricity for the measurement instruments was provided by a diesel powered generator situated ~ 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 O₃, NO, NO₂, CO, C₂ – C₁₀ non methane hydrocarbons (NMHCs), C₂ – C₇ carbonyl compounds, PAN, OH, HO₂ and peroxy radicals. Measurements were also made of a range of photolysis rates including $j(\text{O}^1\text{D})$, $j(\text{NO}_2)$ and $j(\text{HCHO})$ 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 O₃ concentrations was ± 2 ppb. 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/O₃ chemiluminescence analyzer (Thermo Environmental Instruments, Model 42C – trace level), with the instrument sequentially measuring NO and NO_x (NO + NO₂) by use of a heated Molybdenum converter. Detection limit for the instrument was approximately 0.1 ppb for NO and total NO_x. Calibrations for NO and NO₂ were carried out using a gas standard (Air Products) and a resulting uncertainty for NO and NO₂ measurements was estimated to be ± 0.2 ppb. A direct measurement of NO₂ was also made using a tunable diode laser system, and, although there was limited data coverage, it showed good agreement with the converted NO₂ measurement for periods when both instruments were measuring simultaneously. C₂ – C₇ NMHCs and C₂ – C₅ oxygenated volatile organic compounds (*o* – VOCs) including alcohols, aldehydes and ketones were measured using a two-column, gas chromatograph (GC) with flame-ionisation detector (Hopkins *et al.*, 2002). Briefly, a multi-bed, Peltier cooled adsorbent trap, consisting of Carboxen 1000 and Carboxen B, was used to acquire the sample (100 ml min⁻¹ for 10 minutes). Upon injection, the sample was split in an approximately 50:50 ratio between a 50 m aluminium oxide (Al₂O₃) porous layer open tubular (PLOT) column and a 10 m LOWOX column. Eluent from each column was then detected using flame

ionisation detection (FID). Regular calibration of the system was carried out using a standard cylinder mixture at the ppbv level (NPL) containing 27 NMHCs. O – VOC concentrations were calculated using relative detector response factors compared to n-hexane, with response factors calculated from liquid standards. The entire analysis process took around 1 hour, and was fully automated. Detection limits were between 1 and 10 pptv for NMHCs and 10 – 40 pptv for o-VOCs.

Higher molecular weight hydrocarbons (C_6 - C_{10}) were measured using comprehensive gas chromatography (GCXGC), with modulation between the columns enabled by a high-speed switching valve (Hamilton and Lewis, 2003). The column set used provided an initial volatility based separation followed by a secondary polarity based separation. GCXGC instrumentation was based on a HP 6890 Gas Chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a flame ionization detector operating at 100Hz. Analytes were trapped using a similar technique as the lightweight hydrocarbons, with a mixed absorbent bed of Tenax and carbon based materials. Valve switching modulation diverted part of the sample to waste and large air volumes were required to achieve the required sensitivity. Therefore the sampling frequency of the heavy weight VOCs was lower with a 2-hour integrated sample (25 ml min^{-1}) collected every three hours. Daily calibration was performed via direct gaseous sampling of a 74 component Apel Reimer standard, to monitor the performance of the modulator. 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 correlate within 10 %.

Formaldehyde was measured by an instrument using the liquid phase reaction of formaldehyde with acetylacetone (2,4 pentadione) and an amine. This reaction produces α - α' -dimethyl- β - β' -diacetylpyridine, that is excited at 400 nm (Hg-lamp) and the fluorescence is detected at 510 nm. Measurements

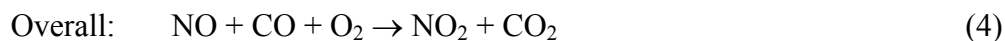
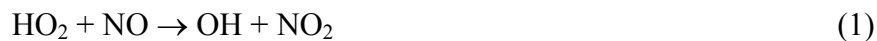
of peroxyacetylnitrate (PAN) were carried out using a custom built two channel GC with electron capture detection (Ai Qualitek, Cambridge U.K.). Calibration of the instrument was performed using gaseous PAN generated by the photolysis of NO with excess acetone, diluted using zero air. The uncertainty of the measurements was found to be less than 5 %, with a time resolution of 90s.

Measurements of OH and HO₂ radicals were made by the University of Leeds using on-resonance, low pressure laser-induced fluorescence (LIF) at 308 nm, through the FAGE (Fluorescence Assay with Gas Expansion) technique (Heard and Pilling, 2003) and references therein). The instrument was based upon the design deployed in previous campaigns, most recently described in Smith *et al.* (2005) (and references therein). In brief, the Leeds FAGE system employs an all solid-state, Nd:YAG pumped Ti:Sapphire laser to generate 308 nm radiation for LIF excitation (see Bloss *et al.* (2003) for a full description of the laser system) which is directed into two low pressure fluorescence cells using fibre optic cables. Thus, using two separate fluorescence cells it is possible to simultaneously detect OH and HO₂ (the latter through chemical conversion to OH *via* addition of NO), by collecting the resultant OH fluorescence, at ~ 308 nm, using gated photomultipliers. Calibrations were carried out on most days of the campaign using the photolysis of water vapour at 185 nm coupled with O₃ actinometry (Smith *et al.*, 2005) with average daytime detection limits of 3.75×10^5 and 2.77×10^6 molecule cm⁻³ for OH and HO₂ respectively. The instrument was housed in an air conditioned sea-container with the fluorescence cells, photomultipliers and gating electronics housed in a weatherproof box on the roof of the container. In order to increase the sampling height the FAGE container was stacked on top of the University of York GC container giving an overall sampling height of ~ 10 m above the ground.

Measurements of peroxy radicals (HO₂ + ΣRO₂) 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.*, 2005). The technique was pioneered by

(Cantrell *et al.*, 1984) and described by (Clemmitshaw *et al.*, 1997; Green *et al.*, 2003; Monks *et al.*, 1998) and uses a dual channel inlet and detection system (as in (Cantrell *et al.*, 1996)).

Briefly, the method relies upon the HO₂ and OH radical-catalysed conversion of NO and CO into CO₂ and NO₂ respectively, through addition of NO and CO into the inlet region *viz.*,



Organic peroxy radicals are readily converted into HO₂ in the presence of NO with varying efficiencies (Ashbourn *et al.*, (1998)). The yield of both CO₂ and NO₂ is equal to CL * ([RO₂] + [HO₂] + [OH]), where CL is the chain length, *i.e.* the number of HO₂/OH inter-conversion cycles that occur before radical termination. The ratio of [HO₂]/[OH] ranges from ~ 50 – 200 in the atmosphere, therefore the PERCA technique effectively measures the sum of inorganic and organic peroxy radicals. The yield of NO₂ is measured using commercial LMA-3 detectors (calibrated daily using NO₂ permeation sources) and this is converted into [HO₂ + ΣRO₂] using Δ[NO₂]/CL. The chain length was calculated on a weekly basis, using a calibration source based upon the photolysis of CH₃I at 253.7 nm to yield CH₃O₂ at varying concentrations (Clemmitshaw *et al.* (1997)). A humidity correction factor equation (using ambient humidity and inlet temperatures) was derived and applied to all PERCA data following Salisbury *et al.* (2002). Using a dual-inlet configuration gives a frequency of raw data capture of 1Hz . Peroxy radical mixing ratios were derived on a one minute basis. The errors on a 1 minute measurement are 35%.

The rates of photolysis of a variety of species were measured using a 2πsr spectral radiometer (Edwards and Monks, 2003). 2πsr filter radiometers were also employed to measure *j*(O¹D) and *j*(NO₂) (Monks *et al.*, 1996). Measurements of wind speed and direction, temperature and relative humidity were also

taken through the campaign. Measurements of NMHCs, *o*-VOCs, CO and met were taken at the top of a 14 m high tower, with all other gas phase measurements sampled at ~ 7 m. Data analysis was aided by 5 day back trajectory calculated every 2 hours using the ECMWF (European Centre for Medium Range Weather Forecast) package supplied by BADC (British Atmospheric Data Centre).

3. Results - Climatology

Time series of meteorology and trace gas measurements from the TORCH campaign are shown in figure 2. Data is presented here for 1st – 30th August 2003, and during this period, the 5 day back trajectory calculations showed the site was subjected to a range of air mass types. From 1st – 3rd August, the air was Atlantic in origin, passing subsequently over the Southern U.K 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 then passing 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 – 8 ms⁻¹ and peak daytime temperatures ranged from 19 – 25°C. The period from the 6th – 10th August 2003 a high pressure weather system was present over the U.K. and much of Western Europe. This period saw very low wind speeds, ranging from 0.5 – 5 ms⁻¹, with local wind direction being typically westerly. Temperatures reached a daily maximum of 26 – 37°C, with the temperatures of > 35°C on 6th, 9th and 10th August, these being particularly unusual for the U.K. The highest ever recorded U.K. air temperature was observed during this period at Faversham, Kent (around 30 miles from the site) at 38.5°C. The period from 13th – 24th August, the air was again Atlantic in origin, passing over the U.K. and arriving at the site in a Westerly / North Westerly direction. Wind speed was generally higher during this period, ranging from 7 – 15 ms⁻¹, with temperatures between 20 and 25°C. From 25th – 30th August, the air was Arctic in Origin, traveling over the North Sea, before arriving at Writtle from a Northerly / North Easterly direction. Wind speeds ranged from 5 – 8 ms⁻¹ during this period, with maximum temperatures between 17 – 20°C.

The most interesting period from the point of view of air pollution is from 5th – 11th August and will be described as the ‘heatwave period’, and is indicated on figure 2. 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 6th – 10th August had been slow moving over the U.K. 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 build to significant levels.

3.1 Ozone / 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 figure 2 and, during the non heatwave period, exhibits a diurnal cycle, typically peaking at 40 – 60 ppbv, around 1-2 hours after solar noon. At night, ozone falls to between 0 – 10 ppbv. This behaviour is very typical of moderately polluted suburban locations. However on 6th – 11th August, the period when maximum daytime temperatures were 27 – 37 °C, peak ozone was observed > 100 ppb, with one minute concentrations measured from the mobile laboratory as high as 150 ppb on 6th August. The nights of 6 - 7th and 10th - 11th August also saw elevated nighttime concentrations of ozone. The very high (> 80 ppb) concentrations on the night of 10th - 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 air mass 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, summarized in figure 3. Similar average ozone concentrations were observed during the early morning, and in both cases, they start to rise just after 08:00. However in 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 NO₂ from TORCH is also plotted in figure 2, 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. During the heatwave period, NO and NO₂ do not exhibit elevated concentrations when compared to non heatwave periods. The average diurnal profile of NO_x 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_x 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 figure 2. Typical ethane and acetylene concentrations of 2500 and 400 pptv respectively are observed throughout the whole of the campaign, with peaks up to 10000 pptv of ethane seen on some days. There is no distinct diurnal cycle in either ethane or acetylene, however both species exhibit generally higher concentrations at night, behaviour that is illustrated in the average diurnal profiles plotted in figure 3. 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 the 6th, 9th and 10th 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. Isoprene behaviour will be discussed further in later sections.

3.3 Other photochemical by-products.

The middle panels on figure 2 show products of photochemical activity 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 double for both species. This behaviour was also seen in other secondary products such as the higher aldehydes and ketones, although not in acetaldehyde. A diverse range of organic nitrate species at elevated concentrations were also seen during the heatwave, although a lack of standards limits the presentation of quantitative data.

The bottom panel of figure 2 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 O^1D from ozone – $j(\text{O}^1\text{D})$. During the heatwave period mixing ratios of peroxy radicals reached 120 pptv during mid-afternoon. The peroxy radicals had an average mixing ratio of 80 pptv at 15:00 GMT over the 5 days of the heatwave over twice that of the average for the rest of the campaign, which peaked at 13:00 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, in TORCH 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 NO₃ and ozone (see for example (Salisbury *et al.*, 2001)).

During the TORCH campaign measurements of [OH] and [HO₂] were made on 23 and 22 days of the campaign respectively, on dates between 27th July - 7th August and 18th - 31st August. No measurements of OH or HO₂ are available over the heat wave period due to technical difficulties with the laser system. Measurements of [OH] show a diurnal cycle with daytime maxima between $1.2 - 7.5 \times 10^6$ molecule cm⁻³. There were six nights on which [OH] of up to 8.5×10^5 were measured (mean night-time detection limit 3.41×10^4 molecule cm⁻³) indicative of significant night-time sources of OH in the polluted air experienced during TORCH. Rate of Production Analyses (ROPA) carried out using the Master Chemical Mechanism (version 3.1) by Emmerson *et al.* 2005, found the main night-time sources of OH to be recycling of HO₂ through reaction with NO, and reaction of O₃ with alkenes. The average [OH] profile shows a rise that starts early in the morning (~ 05:00 GMT) and persists into the evening (~ 18:30 GMT) when levels of $j(\text{O}^1\text{D})$ are not significant, and in fact [OH] appears to track the wider diurnal profile of $j(\text{HONO})$. The average diurnal profile of [HO₂] also tracks that of $j(\text{HCHO})$ at these times providing further evidence to support the photolysis of HONO and HCHO becoming relatively more important to HO_x production when sunlight is of a lower intensity, as both species are photolysed by longer wavelengths of light than O₃ (Alicke *et al.*, 2003; Holland *et al.*, 2003; Martinez *et al.*, 2003). The 24 hour mean [OH] for the entire campaign (derived from hourly means) was found to be 1.38×10^6 molecule cm⁻³. Diurnal profiles in [HO₂] were much less pronounced and in several cases asymmetric about noon with secondary peaks in [HO₂] occurring in the late afternoon / early evening. Noon-time maxima varied between $0.16 - 3.3 \times 10^8$ molecule cm⁻³. There were night-time HO₂ radicals above the daily calculated night-time detection limit on nine nights of the campaign (mean night-time detection limit 1.26×10^6 molecule cm⁻³) with concentrations of between 0.02 and 1.00×10^8 molecule cm⁻³. A peak in NO at ~ 06:00 GMT (attributed to a combination of the collapse in the boundary layer and

morning rush hour traffic) causes a concurrent suppression in HO₂. Despite a rise in the rate of recycling of HO₂ *via* reaction with NO, there is no rise in [OH] as this increased OH production is balanced out by an increased destruction through reaction with NO₂ and other OH sinks that are expelled with NO_x (e.g. VOCs). The 24 hour mean [HO₂] for the entire campaign (derived from hourly averages) was found to be 6.19×10^7 molecule cm⁻³.

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 produced from the photo-oxidation of primary species. Also shown on table 1 for the daytime concentrations, is the product of the average concentration of each species with its OH reactivity. This gives a measure of the contribution with which the hydrocarbon produces free radicals, which in turn lead to the oxidation of NO to NO₂, and eventually to O₃ formation. Total organic OH reactivity is almost double during the heatwave period, compared to the rest of the campaign. In non-heatwave periods the largest contribution to reactivity is from acetaldehyde, contributing 25 % of the total hydrocarbon reactivity, with the total contribution from all oxygenated secondary species being 36 %. The two other largest contributors are Formaldehyde and Isoprene which contribute 16% and 14% of the total reactivity respectively. During the heatwave period, acetaldehyde again contributes the most to total reactivity (~ 25 %). The total from oxygenated species is very similar at 35 %, with formaldehyde also the same at 16%. However the contribution of isoprene to the total reactivity during the heatwave period increases to 20 %. Clearly between heat wave and non-heat wave periods the balance of reactivity between functional group types is broadly similar, but absolute concentrations of organic compounds are generally increased.

The major compositional differences between heat wave and non-heat wave periods may be identified therefore as significantly increased daytime ambient isoprene, ozone, PAN, HCHO and peroxy radicals, and a generally elevated background of anthropogenic VOCs and non-heatwave equivalent levels of NO_x.

4. Discussion

The data series presented in figure 2 shows the increases in a wide range of air pollutants that occurred during the 2003 U.K. heatwave. We believe that these observations are likely to be broadly similar at other rural locations since we do not identify there to be any unique sources or processes occurring at this location.

The exceptionally hot, dry and sunny weather that occurred during the summers of 1976 and 1995, also led to very high levels of ozone in the U.K. 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 ppb at Teddington, Middlesex and from 3rd – 5th July when 254 ppb 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 1986-1995, there was a reduction in the magnitude of the maximum ozone values occurring during summer photochemical episodes. Ozone concentrations during the 1995 heatwave never reached the levels of 1976, but were significantly higher than those reported in previous and subsequent years. Levels reached 90 ppb at rural monitoring sites on several occasions during July and August, with 4 episodes where concentrations reached > 110 ppb. 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 heat wave is not therefore surprising. Given the reductions in emissions of VOCs and NO_x over the past decade it is perhaps unexpected however that peak ozone in 2003 exceeded levels above 100 ppb, since the reduction in the magnitude of such peaks has been considered a generally successful outcome of U.K. emissions reduction policy. It is therefore useful to attempt 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 heat wave 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 very major source of ozone during such anticyclones and that will also hold true also for this case. However the direct (and perhaps unexpected) observation of extremely active chemistry locally in this study, through non-linear reactive 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 U.K., and on the day of observation) generation of ozone, to be added on top of 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 heat wave 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 (UTC). This is shown in data from a Doppler wind radar (Norton *et al.*, 2005) that was deployed at the site. During the night there was evidence of a shallow surface inversion 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. Given the generally low wind speeds ($<5\text{m/s}$) during this period, it is during this entrainment from aloft whereby the regional ozone influence was introduced. The mixing down of highly polluted air is likely to be the primary driver behind the rapid increases in ozone seen during the heatwave morning periods. From a measurement solely of ozone at the surface 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 hours), and so other tracers must be used to make an estimate of this. In the next section we discuss the use of reactive aromatic tracers for this purpose.

4.1 Ratios of aromatic compounds

Typically benzene : toluene (b:t) ratios are 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 is faster than benzene, due to its greater reactivity with the OH radical. The *b:t* ratio has been calculated for the TORCH campaign using the longer time integrated concentrations obtained using GCXGC (3 hr frequency) and is shown in figure 4 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 the behaviour of this ratio during the heatwave period compared to other times.

The OH reactivity of aromatic compounds increases with substitution of the aromatic ring, from benzene ($k_{\text{OH}} = 1.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and toluene ($k_{\text{OH}} = 5.96 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) to the most reactive measured in this study, 1,3,5-trimethyl-benzene (1,3,5-TMB) ($k_{\text{OH}} = 5.75 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The higher aromatics have similar emissions sources to benzene and toluene, but are much more sensitive to changes in OH reactivity and / or transport timescale, since their atmospheric lifetimes are much shorter

Also shown on figure 4 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* are close to the ratio predicted by the National Atmospheric Emissions Inventory (NAEI). This indicates that under Westerly airflow emissions and dilution are the dominant factors controlling abundance measured at Writtle. From the 3rd to 11th of August, the period of high temperatures, the ratio became diurnally varying with *b:1,3,5-TMB* peaking during the afternoon, where [1,3,5-TMB] drops to very low levels. During the nights over this period *b:1,3,5-TMB* returned rapidly to the predicted emission ratio. The implication is that OH chemistry is a more visible factor in controlling the distribution during heatwave periods.

Assuming an arbitrary air mass age of two hours from a remote point source, the OH concentration required to force the change in *b:1,3,5-TMB* ratio from 20:1 to 250:1 can be calculated to be $5 \times 10^6 \text{ molecules cm}^{-3}$ integrated over the previous two hours. This is close to the measured OH concentrations and on first inspection is not unreasonable, however it does not allow for any further local emissions along the air masses trajectory. Emissions close to the end of a trajectory disproportionately force the ratio to low values, so to maintain a 250:1 ratio and counter balance such emissions requires extremely high levels of OH, - this can be calculated to be as high as $1 \times 10^8 \text{ molecules cm}^{-3}$ given diffuse petrochemical and solvent aromatic sources. Any 1,3,5-TMB observed at the site during the daytime of the heat-wave period would be primarily from a small local footprint, as its reactivity was high and windspeeds were low.

A strongly depleted daytime 1,3,5-TMB can therefore only be sustained if either OH is exceptionally high (described above) or there are proportionally reduced emissions of 1,3,5-TMB compared to less reactive species entering the air around Writtle. The diffuse and universal nature of the surface source of aromatics, and the observation of notable close range traffic influence seen in NO_x data, means this change in source type cannot be supported. An effectively isolated observation location is also at odds with exceptionally high concentrations of many other tracers, and so this explanation does not seem reasonable. A more likely description 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, and had no contact with fresh surface emissions for many hours. Hence the air within this region would be fully depleted in 1,3,5-TMB and have a very high *b:1,3,5-TMB* ratio, but not be necessarily depleted in longer lived tracers such as toluene. As air mixes down a high ratio is induced, implying also that air from aloft dominates the aromatic composition over local surface emissions – the opposite to the case seen in strong Westerly flow. We may therefore use the absence of 1,3,5-TMB as a proxy for likely inclusion of regionally produced secondary species such as ozone, and use this ratio change to estimate the possible fraction of ozone entrained from above. This by extension gives some approximation to 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 hours OH processing with no fresh emissions) then a crude estimate can be made of the relative proportions of ‘surface’ and ‘aloft’ air which make up the mixture observed at the site. From the perspective of anthropogenic VOCs this falls in the range of 1 : 10 ± 5 with significant uncertainty introduced due to not only the estimate of the aloft ratio but also in surface emission ratio and OH rate constants. If ozone could be treated as an entity which simply scaled linearly with surface VOC emissions then a similar ratio could be expected for the relative proportions of ‘old’ aloft ozone and versus more

recently produced surface ozone. This is not likely to be the case however as biogenic VOCs, major contributors to O₃ formation, do not follow the same emission pattern as anthropogenic species and this will be discussed in later sections. 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 this 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 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 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 heat wave is not straightforward. The ability to correctly simulate ozone over this heat wave period using a trajectory model was closely tied to the biogenic emissions that were introduced by that model from the surface.

4.2 Measurements of isoprene

Whilst biogenic emissions inventories exist for the U.K. (Simpson *et al.*, 1995) in general it is not considered a geographic region which is strongly influenced by biogenic VOCs. Isoprene is known to be 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 kt C yr⁻¹ (Simpson *et al.*, 1995) which, combined with its short atmospheric lifetime

(approximately 5 hours, assuming an average OH concentration of 5.5×10^5 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 (figure 3) 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. A plot of isoprene concentration versus temperature is shown in figure 5(a) using data collected throughout August 2003 and shows the strongly temperature dependant nature of the relationship.

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, sampled and then analysed off-site using GC-time of flight mass spectrometry. The average data for these observations is given in table 1, and although data is limited, there is a strong indication of monoterpenes elevation in addition to isoprene. The high concentrations of isoprene observed in the late afternoon on episodic days, coupled with their high reactivity and ozone forming potential suggest that ozone may be generated on the day of observation in addition to that which has been mixed down from the regional background during the morning to midday periods. 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. The links between the two species are not necessarily direct however and in the next section we discuss the role of isoprene and other species in controlling peroxy radical abundance and rate of generation of ozone on day of observation.

There is evidence that the emission of additional isoprene over the heat wave 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 ppb in August 2003, and where the relationship becomes clearly temperature rather than vehicle pollution dependant as the dominant source switches from anthropogenic to biogenic (Dollard, 2005).

4.3 Peroxy radicals

Peroxy radicals are key intermediates and chain carriers in the gas phase oxidation of volatile organic compounds, and owing to their short lifetime can give an indication of *in situ* photochemical ozone production. In this section, the chemistry of the peroxy radicals will be explored as an indicator of the local photochemical environment.

In order to delineate the different contributions to the peroxy radical chemistry, a steady state analysis of RO_x production/loss, in which intraconversions among RO_x radicals are not considered, was carried out (Mihele and Hastie, 2003; Penkett *et al.*, 1997). In steady-state the change in peroxy radical concentration can be represented as,

$$\frac{d[RO_x]}{dt} = P_{RO_x} - L_{SR} - L_{NO_2} = 0 \quad (5)$$

the term RO_x includes organic peroxy radicals as well as HO_x, P_{RO_x} is the total RO_x production, L_{SR} the losses owing to self reactions and L_{NO_2} the losses owing to reactions with NO_x. The peroxy-radical production term can be written as

$$P_{RO_x} = 2f \cdot j(O^1D)[O_3](1+\gamma) \quad (6)$$

essentially comprising RO_x production from O₃ photolysis (primary production) and a term γ representing production of RO_x from other sources related as a function of primary production. When $\gamma = 1$, additional sources of RO_x are equal to those from O₃ photolysis. As can be seen from Tables 2 and

3, for the heatwave period, γ values were greater than one for the afternoon period indicating that other sources beyond primary production are necessary to account for the measured peroxy radical mixing ratios and are indeed much more significant than ozone photolysis.

As discussed in section 1, the main photochemical sources of HO_x in a polluted environment are photolysis of ozone, HCHO and HONO (Monks, 2005). Additional sources of RO_x are photolysis of higher aldehydes and thermolysis of PAN and PAN analogues. Table 4 shows the relative significance of four of these sources for which data is available. While HONO was not measured, its contribution to 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 4. Thermolysis of PAN is the largest source of 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 RO_x production respectively. The magnitude of RO_x production from PAN is much greater than that of maximum ozone photolysis for the 6th, 9th, and 10th of August, coinciding with the days when ozone mixing ratios were at their highest.

The dominance of PAN as an afternoon source of RO_x is not surprising considering its extremely short lifetime at temperatures experienced during this heatwave period (figure 6), the PAN lifetime being as low as 7.5 minutes for temperatures of 36°C. In order to sustain such high mixing ratios a very local source is necessary as average wind speed was 5.5 ms^{-1} and average PAN lifetime 18.3 minutes (12:00 – 18:00, 6th – 10th August). Therefore, PAN would need to be produced or recycled within a small footprint of around 6km around the observing location, rather than being a species transported in from

regional sources. Figure 7 shows the correlation between PAN production (calculated assuming PAN is in steady state) and isoprene mixing ratios for the 6th – 9th August although the 10th does not seem to fit this pattern. It is noticeable however that wind speeds were significantly higher on the 10th, resulting in a larger footprint emission and production footprint. The average values for PAN production rate and isoprene for the afternoon period (12:00 – 18:00) display a striking correlation of $R^2 = 0.99$ (excluding the 10th) although the relationship is not necessarily causal. A direct chemical link does however exist between isoprene and PAN through the formation of the CH_3CO_3 radical formed through both methacrolein and methyl vinyl ketone channel in isoprene degradation which can subsequently react with NO_2 . Interestingly acetaldehyde, a key possible precursor to the CH_3CO_3 radical did not exhibit the diurnally varying behaviour seen in the production of PAN. Variability in this species was in line with longer lived tracers of photochemical processing such as methanol and acetone. We conclude that isoprene and its oxidation products were the only measured precursor species to CH_3CO_3 with a temporal profile matching that of PAN / ROx. There are also other PAN type species formed from isoprene although not measured in this study.

Rate of Ozone production

Peroxy radical mixing ratios can be used to investigate the *in situ* production rate of ozone, and by extension estimate O_3 formation which may have occurred on the day of observation. The ozone tendency or net photochemical *in situ* production rate of ozone ($\text{N}(\text{O}_3)$) is a measure of the ozone productivity of an air mass and neglects transport and deposition processes (Monks *et al.*, 2000). $\text{N}(\text{O}_3)$ is made up of a production term, $\text{P}(\text{O}_3)$ minus the loss term, $\text{L}(\text{O}_3)$:

$$\text{N}(\text{O}_3) = k_p[\text{NO}][\text{HO}_2 + \Sigma\text{RO}_2] - \{f.j(\text{O}^1\text{D}) + k_x[\text{OH}] + k_x[\text{HO}_2]\}[\text{O}_3] \quad (7)$$

Where k_p is a combined rate coefficient for the oxidation of NO to NO_2 by all peroxy radicals and $f.j(\text{O}^1\text{D})[\text{O}_3]$ represents the fraction of ozone photolysed to yield O^1D atoms and then OH (with f being

the proportion of O(¹D) atoms which react with H₂O to give OH rather than being collisionally deactivated). The rate constants k_x and k_x are from the ozone loss reactions:



The average P(O₃) for 07:00 to 16:00 for the heatwave period is 42 ppbv h⁻¹ compared to 21 ppbv h⁻¹ for Westerly conditions of 19th–23rd August. Kleinmen *et al.*, (2005), sampled plumes from five American cities and found that in an urban plume under conditions where P(O₃) > 25ppb h⁻¹ there is a potential to transform a typical regional background into a severe ozone episode. Average O₃ mixing ratios for the same section of day for the heatwave and Westerly periods are 72 ppbv and 30 ppbv respectively implying that radical chemistry within the boundary layer is more active during the heatwave than during the cooler period. Using a deposition velocity of 0.5 cm s⁻¹, loss rates at the surface are around 2 ppb hr⁻¹ for 100ppbv O₃ and a 1000m boundary layer height. This is small compared to N(O₃) and indicates that deposition plays a relatively minor role during heatwave conditions. Since boundary layer height and ozone mixing ratio both increase through the day and surface loss can be calculated to remain fairly constant.

As well as being characteristically different from the rest of August, the values of P(O₃) during the heatwave exhibit some variability (Figure 8). The close correlation ($R^2 = 0.93$) of average in situ P(O₃) and the peak O₃ value for each day of the heatwave (Figure 9) are indicative of a link between *in situ* (day of observation) chemistry and final O₃ concentrations and that this is effectively additive to that via regional entrainment. The implication therefore is that vegetation in the U.K. is capable of sustaining a significant boundary layer concentration of isoprene and this in combination with anthropogenic emissions may well provide an additional heatwave source of ozone on top of regional entrainment occurring during to mixing between residual and surface layers. Since biogenic emissions have strong

sensitivities to climate factors the control of the peaks in photochemical ozone during episodes may be complicated by these emissions.

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 measurement period included a period (6th – 10th August) of high pressure over the UK and most of Western Europe that was characterized by low wind speeds (0.5 – 5 ms⁻¹) and exceptionally high U.K. maximum temperatures (26 – 37°C). This period was also characterized by high ozone concentrations, with peak levels > 110ppb observed on each of the five days of the heatwave period. Concentrations of NO and NO₂ did not exhibit significantly elevated concentrations during this heatwave period when compared to the rest of the month of August. Anthropogenic VOCs showed a significant enhancement in concentrations during the heatwave (e.g. ethane and acetylene 1000pptv 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 heat wave. Instantaneous O₃ production rates as high as 100 ppb h⁻¹ have been calculated, where the major source of alkyl peroxy radicals in the afternoon was the thermolysis of PAN. The PAN lifetime during the afternoon periods during the heat wave was on average only 18 mins and as short as 7.5 mins, yet concentrations above 750pptV were sustained. Low wind speeds dictate that production of PAN must be

occurring within a small footprint around the measurement location, and that this PAN is not necessarily a conserved tracer transported with other VOCs. Although PAN has many precursors, the types of VOCs observed in heat wave and non-heat wave periods were somewhat similar, albeit that total VOC reactivity was around double during the episode with proportionally higher concentrations. The distribution of carbonyl to aliphatic to aromatic reactivity remained broadly constant between periods. The most noticeable difference between periods was the strong temperature dependence of ambient isoprene, increasing exponentially with T to a maximum in excess of 1.2 ppbV. The maximum in concentration was coincident in the late afternoon with maximum PAN and O₃, and a strong relationship between ambient isoprene and calculated PAN production rate existed. 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 air mass trajectory arriving in the U.K during an anticyclone may therefore be strongly influenced not only by longer range transport, but also by U.K. biogenic species which have nonlinear emissions, and which have a clear sensitivity to changes in meteorology and climate.

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