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**Volatile organic
compounds above
central London, UK**

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Fluxes and concentrations of volatile organic compounds above central London, UK

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Abstract

Concentrations and fluxes of eight volatile organic compounds (VOCs) were measured during October 2006 from a high telecom tower above central London, as part of the CityFlux contribution to the REPARTEE I campaign. A continuous flow disjunct eddy covariance technique with analysis by proton transfer reaction mass spectrometry was used. Daily averaged VOC mixing ratios were within the range 1–19 ppb for the oxygenated compounds (methanol, acetaldehyde and acetone) and 0.2–1.3 ppb for the aromatics (benzene, toluene and ethylbenzene). Typical VOC fluxes were in the range 0.1–1.0 mg m⁻² h⁻¹. There was a non-linear relationship between VOC fluxes and traffic density for most of the measured compounds. Traffic activity was estimated to account for approximately 70% of the aromatic compound fluxes, whereas non-traffic related sources were found to be more important for methanol and isoprene fluxes. The measured fluxes were comparable to the estimates of the UK national atmospheric emission inventory for the aromatic VOCs and CO. In contrast, fluxes of the oxygenated compounds were about three times larger than inventory estimates. For isoprene and acetonitrile this difference was many times larger. At temperatures over 25°C it is estimated that more than half the isoprene observed in central London is of biogenic origin.

1 Introduction

Volatile organic compounds (VOCs) in ambient air influence local and regional air quality and can also impact upon human health. Consequently, efforts have been made to curtail and better regulate anthropogenic VOC (AVOC) emissions. In Europe, much of this has been achieved through the implementation of the Geneva VOC and Gothenburg multi-pollutant protocols (UNECE, 1991, 1999), which promoted the introduction of 3-way catalytic converters to all newly manufactured road vehicles and forced steps to be taken to reduce evaporative emissions from petroleum products.

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In order to model the effect of VOC emissions on air quality and to quantify the effectiveness of emission control measures accurately it is necessary to compile spatially disaggregated emission inventories. In the UK (as with many other countries) this is done using a “bottom-up” approach to produce a yearly emission estimate for a large number of air pollutants as part of the UK National Atmospheric Emission Inventory (NAEI) activity.

In contrast to the NAEI, micrometeorological flux measurement techniques such as eddy covariance offer a “top down” approach to quantifying emission estimates, giving insight into both spatial and temporal changes in VOC emission from a flux “footprint” and their controls, and they offer the opportunity to identify new sources. To date most VOC flux measurements made with these methods have focussed on emissions of biogenic volatile organic compounds (BVOC) from vegetation canopies such as grassland (Karl et al., 2001; Rinne et al., 2001; Warneke et al., 2002; Ammann et al., 2006; Brunner et al., 2007; Davison et al., 2009) and forests (Karl et al., 2002; Grabmer et al., 2004; Spirig et al., 2005; Lee et al., 2005). However, recent studies have demonstrated that micrometeorological flux measurement techniques can also be extended to the urban canopy, as long as a measurement site with a suitable elevation above street level can be found (Nemitz et al., 2002; Dorsey et al., 2002), and first applications have been made to the measurement of urban VOC fluxes (Velasco et al., 2005; Langford et al., 2009; Park et al., 2009; Velasco et al., 2009).

In this study we use disjunct eddy covariance with continuous flow (DEC_{cf}) to measure emission estimates for eight volatile organic compounds above central London. We compare the results to emission estimates within the most recent (2006) NAEI data base for London. We also analyse these data with respect to traffic density and ancillary measurements of CO fluxes and concentrations.

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2 Experimental

2.1 Measurement site

During the autumn of 2006 (30 September 2006–30 October 2006), micrometeorological measurements of VOC concentrations and fluxes were made over central London. The measurements were conducted as part of the UK CityFlux project, as a contribution to the REgents Park and Tower Environmental Experiment (REPARTEE-I). The aims and objectives of this project are summarised elsewhere (Dall'Osto et al., 2009).

The site selected for the study was the London Telecom Tower (51°31'17.4" N; -0°8'20.04" W), a 188 m high telecommunications tower, which is located in central London. The tower is surrounded by a mixture of commercial and residential buildings, giving the location an urban classification of 2 (Intensely developed high density urban with 2–5 storey, attached or very close-set buildings) according to the criteria of Oke (2006). A more detailed description of this site has been provided by Dall'Osto et al. (2009).

An ultrasonic anemometer (Model R3-50, Gill Instruments, UK) and gas inlet were attached to a mast which extended 3 m above the 12 m tall lattice structure which is erected on the Tower's flat roof. The sample inlet was therefore ~200 m above ground level. Air was pumped down a ~45 m long Teflon tube (3/8" OD) at a flow rate of ~60 l min⁻¹ to the proton transfer reaction mass spectrometer (PTR-MS) which was housed inside the Tower.

2.2 VOC sampling

Concentrations of selected VOCs were measured using an Ionicon (GmbH, Innsbruck, Austria) high sensitivity PTR-MS which was fitted with three Varian turbo-molecular pumps and a stainless steel ringed drift tube (9.6 cm). This instrument has been described in detail elsewhere (Lindinger et al., 1998; de Gouw et al., 2007; Hayward et al., 2002); therefore only a description of the instrument setup and operation are included

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here.

Air for analysis by PTR-MS was purged into the instrument at a flow rate of 0.3 l min^{-1} through a heated Silcosteel inlet line. The instrument was programmed to operate in two modes, SCAN and FLUX. During the first five minutes of every hour the total mass range (m/z 21–146) was scanned to provide basic concentration information on a wide range of hydrocarbons. The PTR-MS was then operated in FLUX mode for two 25 min averaging periods per hour, with the quadrupole scanning through 11 pre-determined masses (dwell time 0.1 s per m/z) in measurement cycles lasting just over 1 s per cycle. The targeted protonated masses and likely contributing compounds were: m/z 33 (methanol), m/z 42 (acetonitrile), m/z 45 (acetaldehyde), m/z 59 (acetone/propanal), m/z 69 (isoprene/furan/alkenes), m/z 79 (benzene), m/z 93 (toluene) and m/z 107 (ethylbenzene/ C_8 aromatics). In addition to these masses, both the primary ion count m/z 21 ($\text{H}_3^{18}\text{O}^+$) and its first cluster m/z 37 ($\text{H}_3^{16}\text{O}^+ \text{H}_2^{16}\text{O}^+$) were recorded. The remaining 5 minutes of each hour were used to measure the instrument background by sampling air which first passed through a platinum catalyst, again in SCAN mode. The catalyst was custom built and consisted of a glass tube packed with platinum catalyst powder, heated to 200°C .

During the study period the PTR-MS operating parameters, drift tube pressure, temperature and voltage were held constant at 2.06 mbar, 45°C and 600 V, respectively, maintaining an E/N ratio of approximately 125 Td. The H_3O^+ primary ion count ranged between $(4\text{--}9)\times 10^6$ ion counts per second (cps) with an average of 7×10^6 cps. Ion counts of m/z 37 ranged between 0.89 and 9.3×10^5 cps with a mean of 3.1×10^5 cps, which represented 4% of the primary ion signal. Typical normalised ion counts ranged between 1 and 210 ncps for the targeted compounds after background subtraction, with instrument sensitivities in the range of 6.4 (acetonitrile) to $8.2 \text{ ncps ppbv}^{-1}$ (benzene).

Gas standards were not available for on-site calibration of the PTR-MS, hence mixing ratios were calculated using the instrument-specific transmission coefficients and reaction rate constants (k) taken from Zhao and Zhang (2004). Despite careful calculation of transmission coefficients, using a range of gas standards under laboratory

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conditions, mixing ratios may be subject to systematic errors, which, in some instances can be as much as a factor of two (de Gouw and Warneke, 2007). In the current study, where possible, VOC mixing ratios were verified against measurements made by a GC-FID, as discussed in more detail in Sect. 3.1.

2.3 Calculation of fluxes

Fluxes of individual VOCs were measured using a continuous flow disjunct eddy covariance technique (DEC_{cf}). This technique has been described in detail by Langford et al. (2009) and Davison et al. (2009). Briefly, a covariance function between vertical wind velocity measurements (w) and VOC mixing ratios (χ) is used to determine the flux for each selected compound (F_χ):

$$F_\chi(\Delta t) = \frac{1}{N} \sum_{i=1}^N w'(i - \Delta t / \Delta t_w) \chi'(i) \quad (1)$$

Here, primes denote the instantaneous fluctuations about the mean vertical wind and VOC concentration (e.g. $\chi' = \chi - \bar{\chi}$), Δt represents the lag time between wind and PTR-MS measurements, Δt_w is the sampling interval of the vertical wind velocity measurements (0.05 s) and N gives the number of disjunct samples (1363) from the PTR-MS during each 25 min averaging period.

The lag time, Δt , was determined using a cross-correlation (c-c) function between w' and χ' within a 25 s flux averaging period. The maximum correlation typically occurred between 6 and 10 s. This agreed closely with the same c-c function applied to CO_2 data recorded by a fast response instrument (Infrared gas analyzer LI-COR 7000) which sub-sampled the same sample air flow directly after the PTR-MS, and the theoretical value of 4 s, calculated from the volume of the inlet line and the flow rate. The precision of each measurement was determined following the criteria specified by Spirig et al. (2005), using the standard deviation of the covariance function at distances far from the peak value to characterise the random noise. Assuming a normal

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distribution, multiplying the standard deviation by 3 gives the measurement precision at the 99.7% confidence interval. This value was used as a proxy for the flux limit of detection and only data that exceeded this threshold are presented here. In addition to VOC measurements, fluxes of CO were measured with a fast-response VUV CO analyser (AeroLaser AL5002) and are described in more detail elsewhere (Phillips et al., 2009a).

2.4 Flux losses

All flux measurement techniques are, to some extent, bandwidth limited and therefore measurement frequency and choice of averaging period become important considerations. During the REPARTEE-I campaign the quadrupole dwell time was set to 0.1 s per m/z , yet the response time of the instrument may be as much as 1 s, resulting in turbulent fluctuations in the <1 Hz frequency range being attenuated during the measurement process. Corrections for such flux losses are available (Horst et al., 1997). However at a measurement height of 200 m, the typical eddy size is sufficiently large that fluctuations in this high frequency range carry only a very minor proportion of the total flux (estimated from Horst, $<2\%$). Therefore no correction was applied here. Conversely, measurements made at this elevation may be subject to attenuation at the lower end of the frequency spectrum as the chosen averaging period may not fully resolve low frequency fluctuations without compromising the stationarity of the measurement.

In order to investigate this effect, sensible heat flux data from the campaign were re-analysed by joining individual 25 min files to create averaging periods of 25, 60, 90, 120 and 150 min (with 5-min gaps). A coordinate rotation was applied to the resulting files which acted as a high pass filter (Finnigan et al., 2003) to the three dimensional wind velocity measurements, ensuring that fluctuations from eddies with a time period greater than that of the averaging period could not contribute to the flux measurement (Moncrieff et al., 2004). The resulting fluxes were then compared back to the average values measured using the standard 25 min averaging periods, which were also rotated

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to ensure the flux was only made up by turbulent fluctuations of 25 min or less.

The results of this are shown in Fig. 1, where the fluxes calculated from the extended averaging period are plotted against the flux constructed by averaging the results from the individual consecutive 25-min averaging periods. Eddies with a time period of between 25 and 60 min increase the flux by 3.1%; similarly eddies with a period of between 1 and 1.5 h increase the flux by 2.6%. Extending the averaging period further to 2.5 h shows a total flux increase of 12.6%, but after this little further increase is observed (not shown). Similar results were observed in heat fluxes measured at Nelson Monument, Edinburgh (E. Nemitz, personal communication) and in CO fluxes measured above Boulder, Colorado (Nemitz et al., 2008).

These findings show that VOC flux measurements made at the Telecom Tower are bandwidth limited with low frequency contributions attenuated due to the choice of averaging period (25 min). Consequently, VOC fluxes measured at this site may be underestimating the true flux by some 10 to 15%. However, increasing the averaging period for the PTR-MS measurements to 2.5 h would have increased the likelihood of non-stationarities affecting the flux measurements. In addition, lower time resolution in the flux measurements contains less information to study the processes affecting the fluxes, which was an important objective of this work. Thus a ~30-min averaging time appears to achieve the right balance.

2.5 Quality assessment of fluxes

A post-processing algorithm was written in LabVIEW which not only re-processed fluxes but also filtered out data files which did not meet specific quality criteria. The algorithm involved the following steps: (i) calculation and optimisation of lag times using a c-c function, (ii) calculation of VOC fluxes, (iii) calculation of flux precision, rejecting files where the peak in the c-c function was below three times the measurement precision, (iv) testing of the mean frictional velocity, rejecting data files where $u_* < 0.15 \text{ m s}^{-1}$ and (v) testing of fluxes for stationarity, rejecting failed data files. The stationarity test applied here and associated data quality rating is described in detail by Foken and

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Wichura et al. (1996) and Velasco et al. (2005).

About 1% of the data were rejected due to lack of stationarity, 25% were removed because of insufficient turbulence ($u_* < 0.15 \text{ m s}^{-1}$) and a further 18% were rejected as fluxes were below the limit of detection. Of the 56% of the data that passed the quality assessment, 91% were ranked as high quality and 9% low quality.

As the urban environment presents a non-ideal terrain for micrometeorological flux measurements, an assessment of the integral turbulent statistics of the vertical wind velocity (σ_w/u_* = standard deviation of the vertical wind velocity normalised by the friction velocity) was carried out, with measured values compared with modelled values, which predict σ_w/u_* for a set of ideal conditions (Foken et al., 2004). Classification of data based on this quality test was outlined by Foken et al. (2004) as part of the FLUXNET programme. According to their criteria over 70% of the current data were rated category 6 or better (suitable for general use) and less than 3% of the data set qualified for rejection. A more detailed analysis of the turbulence characteristics from this site is presented elsewhere (Wood et al., 2009).

2.6 Calculation of the flux footprint

In order to compare measured VOC emissions with the appropriate NAEI grid squares the typical daytime flux footprint for the site was calculated using a simple parameterisation model (Klujan et al., 2004). Although originally developed for dynamically homogenous terrain, this model has been extended to the urban environment with some success (Langford et al., 2009), hence its application here. Typical values of urban meteorology were used to determine footprint estimates under the average conditions encountered during the measurement period. The following parameters were used in the model: standard deviation of vertical wind velocity $\sigma_w = 0.3 \text{ m s}^{-1}$; friction velocity $u_* = 0.45 \text{ m s}^{-1}$; measurement height $z_m = 200 \text{ m}$; roughness length $z_0 = 1.5 \text{ m}$ (1/10th the average building height); and boundary layer height $h = 2000 \text{ m}$ (unstable). The resulting footprint (80% of flux contained within 4.7 km radius) was superimposed onto a map of NAEI 1 × 1 km grid squares and the entrained squares averaged using

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a weighting factor to account for the measured wind direction during the REPARTEE-I campaign.

3 Results and discussion

3.1 VOC concentrations

5 Averaged diurnal concentration plots for each of the eight compounds are shown in Fig. 2 and are summarised in Table 1. During the study period, the largest concentrations of most VOCs were recorded during daytime and the lowest at night, indicating that patterns in emission (peaking at day) had a larger effect on concentrations than boundary layer dynamics. Temporal trends on a weekly time scale were also evident, with VOC concentrations typically 20% higher during weekdays than at weekends. Fur-
10 Furthermore, at weekends, concentrations of some compounds began to increase later in the day, typically around 06:00 [UTC], three or four hours later than was typical Monday to Friday. This is consistent with the temporal pattern in CO₂ concentrations at this site (Helfter et al., 2009). Throughout the measurement period, concentrations of the
15 oxygenated compounds were highest, followed by those of the aromatics and isoprene.

On a day to day basis, each analyte typically followed one of two patterns. The first, characterised by the aromatic compounds (benzene, toluene and ethylbenzene), had two day-time peaks, one occurring around 08:00 and the second, larger peak between 17:00 and 20:00. A third, much less well defined peak, occurring at around
20 13:00 was also evident on certain days, although this tended to be more prominent at weekends. In addition to the aromatics, both acetonitrile and acetaldehyde loosely followed this double-peak trend, whereas acetone and isoprene did not. Instead, for these compounds, only a single midday maximum was observed, followed by a decline in concentration throughout the mid-to late-afternoon and evening.

25 Methanol concentrations were highly variable on both daily and weekly timescales and therefore did not follow either trend. During the first week of measurements,

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methanol mixing ratios increased steadily from 7 ppb, to a maximum of 80 ppb on 08/10/06. A slow decline in concentration was recorded in the subsequent days and, following a short disruption to the measurements between 15–19 October, concentrations returned to the level (7–15 ppb) observed at the start of the campaign. Unlike the other VOCs, strong diurnal trends were not apparent for methanol.

Toluene concentrations also showed longer term variations, with much higher concentrations observed between 1–12 October. During this period the concentration ratio of benzene to toluene (B/T) was 0.07, which is much lower than the range typically observed in urban air (Heeb et al., 2000). This ratio increased to 0.16 between 19–30 October 2006 and toluene concentrations followed those of benzene much more closely.

In order to assess possible analytical interferences of PTR-MS measurements, additional measurements of VOC concentrations were recorded for validation and comparison purposes at a much lower time resolution using a dual column gas chromatograph – flame ionisation detector (GC-FID). This system operated between 19–30 October. Glass sample canisters were pressurized with air taken over 30 min time periods, with 4-hour gaps between samples. Canisters were later analysed offline using a split column GC-FID calibrated with a 74 component hydrocarbon gas standard with individual analytes in the 1–5 ppb range (Apel-Riemer Environmental, Inc.). The results obtained tended to be slightly higher than PTR-MS measurements for compounds in the low C₂–C₃ range, while the heavier hydrocarbons, shown in Fig. 3, such as benzene, toluene and ethylbenzene all showed excellent agreement. This comparison provides independent confirmation that mixing ratios obtained using the specific transmission curve of the PTR-MS were able to yield quantitative results.

Concentrations of benzene, toluene and ethylbenzene were also recorded by the UK Ambient Automatic Hydrocarbon Air Quality Network at their Marylebone road kerb site (e.g. Dumitrean, 2008). This site is 900 m west of the base of the Telecom Tower (Dall’Osto et al., 2009). Comparisons of the trends in concentrations between the two sites were in good agreement for benzene and ethylbenzene with R^2 values of 0.5 and

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0.6 respectively, whereas for toluene, the trend observed at the Tower differed from that seen at street level. Typically, at street level, concentrations of toluene were highest during the day with a broad peak between 07.00 and 17.00 and at their lowest during the night. A comparison of toluene concentrations from the two sites using data obtained between 19–30 October revealed much closer agreement ($R^2=0.58$). The higher concentrations observed by the PTR-MS between 1–12 October were not reflected at the Hydrocarbon Network site, which could be suggestive of the PTR-MS detecting additional compounds at m/z 93, which would overestimate the toluene measurement. Nevertheless, measurements from the Tower may be strongly influenced by air masses originating from outside of the city, whereas at street level, where the sampling location is in close proximity to the primary emission sources, the influence of advected air masses is likely to be negligible.

Despite the good agreement in concentration trends, kerbside measurements were on average twice as high as those observed at the Tower at 200 m height.

3.2 VOC fluxes

Figure 4 illustrates the tendency for fluxes to be on average ~19% lower at weekends than on weekdays. The morning increase in VOC fluxes typically coincided with the increase in traffic which occurred at approximately 06:00 (5 a.m. local time). Yet, on some days, VOC fluxes were not seen until much later, between 07:00 and 08:30. During some nights, due to the elevation of the measurement location, the site became de-coupled from the street-canyon activity and fluxes were only observed as the nocturnal boundary layer broke up in the morning. This phenomenon was most noticeable on the morning of the 23 October and is shown here in relation to the typical traffic activity (2006) in Fig. 5. The “saw-tooth” shaped curve is symptomatic of the venting of nocturnal/early morning emissions, initially trapped in the shallow boundary-layer below the measurement height, and can also be seen in the CO₂ fluxes (Helfter et al., 2009). Thus, the local flux measured with the DECcf approach at the relatively high measurement height of 200 m is not always representative for the surface emission at

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that time. Vertical gradient measurements, required to quantify the storage below the measurement heights, were not available. However, it is expected that the integrated emission over the day nevertheless provides a robust estimate.

Although measurements of boundary layer height (BLH) were not recorded during the REPARTEE-I campaign, estimates of mixed layer depth were taken from the Hysplit model (<http://www.arl.noaa.gov/ready/hysplit4.html>) and compared with flux data. The model shows the nocturnal boundary layer breaking up at around 07:00 and the measurements show the flux to rise shortly after. Although the mixed layer depth estimates suggest a nocturnal boundary layer height of 250 m, some 50 m above the measurement location (200 m), the Hysplit model uses this value as a lower limit and the actual BLH might be significantly lower. Hence the measurement location may be located above the nocturnal boundary layer at night. Lidar measurements made during the subsequent REPARTEE-II campaign near to the Telecom Tower substantiated these observations by showing how the nocturnal boundary layer was stratified resulting in a decoupling of the turbulent fluxes at the tower from the street level emissions (Barlow et al., 2009). It should be noted that an alternative explanation for the higher emissions during the morning compared with the evening rush-hour could be increased emissions associated with cold starts.

Throughout the campaign, the largest observed fluxes were of methanol (average daily flux $0.95 \text{ mg m}^{-2} \text{ h}^{-1}$), followed by toluene ($0.68 \text{ mg m}^{-2} \text{ h}^{-1}$) and acetaldehyde ($0.65 \text{ mg m}^{-2} \text{ h}^{-1}$). The magnitudes of the fluxes were variable from day to day, with much larger fluxes observed on certain days: for example, on Wednesday 11 October emission fluxes in excess of $3 \text{ mg m}^{-2} \text{ h}^{-1}$ were recorded for methanol and acetaldehyde. The average daily fluxes are shown in Table 2, which also shows data from VOC flux studies above Mexico City and Manchester.

Fluxes of acetone and methanol were approximately 1.8 times larger in London than the summer time fluxes measured over the city of Manchester. Similarly, fluxes of both benzene and toluene were between 1.3 and 2.5 times larger in London. This is consistent with the observation of larger organic aerosol emission fluxes above London

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compared with Manchester (Thomas, 2007; Phillips et al., 2009b).

Despite the differences in their relative magnitudes, the diurnal flux profiles are roughly similar for each compound and approximately follow the pattern of traffic activity in the city. The absence of a clear two-peak rush hour pattern is consistent with earlier CO₂ flux measurements made above the city of Edinburgh (Nemitz et al., 2002). One explanation is that rush hour behaviour tends to be more pronounced on commuter roads, thus affecting concentration measurements which are influenced by air masses advected from outside of the city centre. By contrast, in the central, inner city areas (the flux footprint of the tower), traffic density (and other activities) increases steadily throughout the day.

Although the fluxes of VOCs followed a similar pattern, there are also differences. For example, acetone emission rates peak in the morning, whereas emission rates of ethylbenzene peak in the afternoon. Some fluxes remain relatively large into the late evening (benzene, toluene and acetaldehyde), while others decrease more rapidly (acetone and isoprene). This may be due to a change in the source mix in the evening (e.g. larger contribution of residential heating sources; shift of the traffic composition away from HGV; larger fraction of taxi journeys) or a different relative contribution of combustion vs. evaporative sources which respond differently to changes in the meteorological drivers (such as temperature for biological and fugitive sources).

Fluxes of methanol and toluene did not mirror the longer term variations that were observed in measurements of their mixing ratios. This is suggestive of emissions originating from outside the area of the flux footprint being advected over the measurement site, leading to higher concentrations without elevated local fluxes. With an average value of 0.21, the ratio of benzene to toluene flux is much larger than the B/T concentration ratio of 0.08. Ratios of B/T measured from vehicle exhaust are usually in the range of 0.4–0.8 (Heeb et al., 2000). Therefore, the lower values of the flux ratios observed here suggest emissions from traffic were not the only major source of toluene within the city.

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3.3 Ratios of VOC to CO – concentrations and fluxes

Measurements of CO in the urban atmosphere provide a useful marker for anthropogenic combustion emissions. Therefore analysis of the ratios of both concentrations and fluxes of VOCs to CO can be useful in the determination and identification of sources. Average [VOC]/[CO] concentration (ppbv⁻¹/ppbv⁻¹) ratios for this campaign and previous urban studies are presented in Table 3 and the typical diurnal pattern of the ratios are shown in Fig. 6 for each compound.

Ratios of benzene and ethylbenzene with CO concentrations remained relatively constant throughout the daytime, indicating a common source and a similar chemical lifetime. For the remaining compounds, ratios with CO all followed a similar trend, with a higher ratio during the night-time and mid-afternoon. The two troughs in the [VOC]/[CO] ratio coincide with peak traffic flows on the commuter roads outside of the city centre. Explanations for these troughs may include the following: (i) emissions of CO may be elevated in congested traffic situations relative to VOC emissions (Heeb et al., 2000), or (ii) during transport the air is photochemically processed before reaching the tower and therefore the VOCs are depleted in relation to CO, which reacts in the atmosphere more slowly. The most likely explanation, however, is that some of the VOCs have additional sources that are not related to combustion and that make a larger relative contribution outside the rush hour periods.

The average flux ratios of VOC/CO (mole m⁻² h⁻¹/mole m⁻² h⁻¹) differ from concentration ratios, which is an indication that some of the sources contributing to the concentration measurements were located outside the flux footprint. Between the hours of 07:00 and 22:00 the ratio of VOC/CO remains relatively constant, which is suggestive of a common source.

However, during the night time (23:00 to 07:00 UTC) the ratio becomes elevated, with more VOC flux relative to CO flux, peaking at typically 2 to 3 times the daytime values. This increase is likely to be linked to a shift in the source mix during the night, with heating sources and diesel taxis making a larger relative contribution to the emissions.

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In addition, the characteristic times for transport and chemical processing change during night and photochemical processing of the VOCs is strongly suppressed, not just due to the absence of sunlight, but also due to the titration of O_3 by NO at street level. However, it cannot be ruled out that the post-processing of the data also affected the flux ratio. The VOC/CO flux ratio is based on paired measurements when the VOC flux exceeded the calculated limit of detection, which may have resulted in a systematical bias towards higher values.

3.4 VOC flux dependence on traffic activity

Traffic density data recorded on Marylebone Road (2006) were used as a proxy for traffic activity across the whole flux footprint and were compared with the measured VOC fluxes (Fig. 7). These plots indicate a clear relationship with traffic, with an increase in both VOC and CO emissions with increasing volumes of traffic. As the volume of traffic increases, the roads become congested and the average vehicle speed drops from the permissible 50 km h^{-1} (30 mph) on Marylebone road to 34 km h^{-1} at peak times. Emissions of both VOCs and CO from vehicles increase with decreasing vehicle speed (Heeb et al., 2000; Jensen, 1995), therefore the slower average vehicle speed, combined with increased “stop-start” driving conditions, explains the non-linear rise in emissions.

The plots show good correlations between the measured fluxes and traffic activity, yet in places the fit to the data is close to the limit of uncertainty. This is particularly noticeable at vehicle counts of between 300 and 330 and is best illustrated in the plots of acetone and toluene. Vehicle counts in this range typically occurred between 08:00 and 11:00, which coincided with the breakdown of the nocturnal boundary layer and subsequent venting of night time and early morning VOC emissions. Therefore, in reality, these points may have been affected by the hysteresis between flux and traffic counts and may have had a much closer fit to the curve. Conversely, when vehicle counts are at their peak, between 19:00 and 20:00, VOC fluxes fall below the curve. In this instance the deviation from the curve would be consistent with the formation of the

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nocturnal boundary layer.

The intercept of the curve with the zero traffic line was used to estimate the proportion of the flux not attributable to road traffic. For most of the VOCs measured, this figure was around 30% of the peak fluxes, indicating traffic counts to be a very good surrogate for VOC fluxes at this site. Nevertheless, vehicle counts are not the only contributing factor and the average driving speed, driving conditions and ambient air temperature are all likely to influence the relative source strength of VOCs. It should also be noted that non-traffic emissions during the day associated with anthropogenic activities could correlate with traffic and therefore may be masked by the response of the flux to the traffic counts.

For methanol non-vehicle-related emissions were estimated to account for 65% of the total observed flux, while for isoprene this contribution was 47%. Identifying the non-traffic related sources of methanol within the city was not possible due to the large number of potential point and diffuse sources. For isoprene the task is simplified as there are just three dominant sources of isoprene to the atmosphere in the urban environment: direct emissions from vehicles, evaporative emissions from petroleum products and biogenic emissions from plants, where emission rates are both temperature and light dependent (Loreto and Sharkey, 1990). An attempt was made to separate the biogenic fraction of isoprene within the city using 5 years of hydrocarbon data collected between 2001 and 2006 by the Hydrocarbon Network monitoring station situated on Marylebone Road (e.g. Dumitrean, 2008). Scatter plots of isoprene against benzene concentrations were made over a range of ambient air temperatures ($-5-0$, $0-5$... $30-35^{\circ}\text{C}$) (surface temperature measurements obtained from the London Weather Centre – 3.1 km east of Marylebone Road). Benzene is used here as a marker of vehicle emissions. The intercept of the regression line was used to indicate the background concentration of isoprene which was not attributable to direct emissions from vehicles, and the temperature-dependent fraction [%] was calculated using this value as a percentage of the total isoprene present (5th–95th percentile range).

In order to isolate the biogenic fraction from the evaporative fraction, a similar proce-

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5 dure was applied to concentrations of iso-pentane, a compound that shares the same two major sources as benzene and has a similar volatility to isoprene, but importantly has no biogenic component. The results of both analyses are plotted in Fig. 8. Only slight increases in iso-pentane concentrations were found relative to benzene at higher
10 temperatures due to increased evaporative emissions. In contrast, the temperature-dependent fraction of isoprene was large and increased exponentially with temperature. The percentage contribution of biogenic isoprene is thought to be in excess of ~80% at temperatures of 30°C. During the REPARTEE-I campaign the average temperature was 15.9°C which, using the parameterisation from Fig. 8, equates to a 19%
15 contribution of temperature controlled (or biogenic) isoprene. This value is not enough to resolve the 47% non-traffic related sources. Therefore it is likely that other compounds, such as furan and or alkenes are being detected at m/z 69, resulting in an overestimation of isoprene concentrations by the PTR-MS.

3.5 Comparison of measured fluxes with NAEI emission estimates

15 An annual emission estimate for the flux footprint was made using measured VOC fluxes and compared with NAEI emission estimates. Previously this has been done by simply extrapolating average daily flux measurements to give an annual estimate (Langford et al., 2009). Here, we use the equation of the line from Fig. 7 (Sect. 3.4), where VOC fluxes were plotted against traffic density, to produce an emission estimate
20 using traffic data from Marylebone Road for the whole of 2006. As the parameterisation is based on a “snap-shot” of the total yearly fluxes, this method relies heavily on the assumptions that (i) vehicle emissions account for the bulk of the VOC emissions within the city, (ii) the observed traffic density is representative of traffic activity occurring throughout the flux footprint and (iii) that there is little or no seasonal variation in the emission of VOCs. This last assumption has been shown to be untrue for some of the
25 measured VOC with the contribution from fugitive emissions and cold-start emissions changing throughout the year, but no correction has been applied here.

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The traffic density data set was not continuous over the whole year; therefore, missing sections were filled by repeating data from the equivalent lane of traffic. Where no equivalent data were available, data were taken from the previous year's data set, taking care to match both time of day and day of week. In total less than 20% of the traffic data set was filled in this way.

Emission estimates for each of the measured VOCs and CO are shown in Fig. 9 alongside estimates made by the NAEI for the same footprint area. For those VOCs not explicitly included in the NAEI mapping activity, individual emission estimates were made using the total VOC emission map (2006) multiplied by the VOC speciation for 2006 (NAEI Reference: 45321001/0/AO6069/NP).

Measured flux estimates are larger than NAEI estimates in all cases, with the discrepancy ranging from a few percent in the case of benzene to several orders of magnitude for both isoprene and acetonitrile. In general, emission estimates of the aromatic compounds, toluene ($5.28 \text{ t km}^{-2} \text{ yr}^{-1}$), benzene ($1.20 \text{ t km}^{-2} \text{ yr}^{-1}$) and ethylbenzene ($2.2 \text{ t km}^{-2} \text{ yr}^{-1}$), compared most closely with the NAEI and on average were 1.4 times greater. Similarly, fluxes of CO ($329 \text{ t km}^{-2} \text{ yr}^{-1}$) were very close to NAEI estimates with less than 10% difference between the two. This is consistent with the close agreement between the NAEI emissions figure for CO and airborne boundary layer budget measurements (Polson et al., 2009), and the agreement between city-scale CO flux measurements and the NAEI in Edinburgh (Famulari et al., 2009; Phillips et al., 2009a).

The difference between flux derived estimates and NAEI was considerably larger for the oxygenated VOCs, acetaldehyde ($5.28 \text{ t km}^{-2} \text{ yr}^{-1}$), acetone ($4.40 \text{ t km}^{-2} \text{ yr}^{-1}$) and methanol ($8.77 \text{ t km}^{-2} \text{ yr}^{-1}$), whose estimates differed by an average factor of 3.3. These findings reflect results from a similar comparison made in Manchester by Langford et al. (2009) as part of the same CityFlux project. Flux estimates of isoprene ($1.07 \text{ t km}^{-2} \text{ yr}^{-1}$) and acetonitrile ($1.22 \text{ t km}^{-2} \text{ yr}^{-1}$) were many times larger than those predicted by the NAEI. Emissions from the transport sector are not included in the NAEI for either of these two compounds and emissions from nature are not speciated within the inventory, therefore biogenic emissions, which are likely to contribute a sig-

nificant fraction of the total isoprene emission, are not included in these NAEI emission estimates.

4 Conclusions

Traffic within the city has been shown to be the primary source of VOC fluxes to the atmosphere within central London, but its relative contribution varies from compound to compound and also temporally, with changes occurring from hour to hour and in some cases even season to season. It is thought that the relative source strength also varies, with vehicle counts just one of many variables, including air temperature (increased emissions from cold starts vs. increased fugitive emissions), driving conditions (start-stop driving in congested areas), vehicle speed (larger emissions at slower average vehicle speeds) and fleet composition (range of fuel/engine types).

The ambient air temperature has also been shown to play an important role in the emission rates of certain VOCs. Isoprene concentrations in the city, for example, are highly dependent on the ambient air temperature, with biogenic emissions, most probably originating from the large areas of urban parkland within the city, thought to contribute as much as 80% of the total isoprene concentrations recorded at the Marylebone Road monitoring station at temperatures above 30°C. Such information may be significant in aiding our understanding of VOC precursor emissions associated with photochemical pollution episodes

The close agreement between flux measurements and the NAEI for the aromatic VOCs and CO show the “bottom-up” inventory approach to be effective for air pollutants whose emissions are dominated by one or two sources (e.g. road transport or combustion) which are both well understood and accurately characterised within the inventory. For oxygenated compounds such as acetaldehyde or acetone, emissions can originate from a multitude of point and diffuse sources which are difficult to characterise within the inventory, and these appear to be grossly underestimated by the official emission inventory. For many other VOCs, including acetonitrile, major sources

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have yet to be identified and included within the inventory making “top-down” flux measurements essential.

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Table 1. Summary of VOC concentrations and fluxes measured at the Telecom Tower (London) during October 2006.

	Methanol [<i>m/z</i> 33]	Acetonitrile [<i>m/z</i> 42]	Acetaldehyde [<i>m/z</i> 45]	Acetone [<i>m/z</i> 59]	Isoprene [<i>m/z</i> 69]	Benzene [<i>m/z</i> 79]	Toluene [<i>m/z</i> 93]	Ethylbenzene [<i>m/z</i> 107]
Concentrations [ppbv]								
Mean	19.4	0.33	3.57	1.57	0.17	0.14	1.85	0.16
Median	12.3	0.28	3.35	1.49	0.15	0.13	1.30	0.15
5th percentile	5.4	0.19	2.48	1.00	0.08	0.06	0.47	0.06
95th percentile	46.5	0.61	5.29	2.36	0.30	0.26	4.28	0.32
SD	13.7	0.17	0.95	0.47	0.07	0.07	1.26	0.11
N	1065	1072	1065	1067	1048	1067	1058	1027
Fluxes [$\text{mg m}^{-2} \text{h}^{-1}$]								
Mean	0.95	0.25	0.65	0.55	0.13	0.15	0.68	0.28
Median	0.94	0.17	0.60	0.50	0.13	0.15	0.62	0.25
5th percentile	-0.98	-0.08	0.22	0.15	-0.10	-0.10	-0.32	-0.09
95th percentile	2.2	0.82	1.33	1.24	0.26	0.29	1.57	0.63
SD	0.93	0.27	0.38	0.40	0.10	0.11	0.57	0.21
N	512	594	637	641	518	601	589	606

SD: Standard deviation; N: number of 25-min observations.

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Table 2. Average daily VOC fluxes [$\text{mg m}^{-2} \text{h}^{-1}$] measured over a number of urban areas, including Manchester, UK, and Mexico City.

Location	Methanol [<i>m/z</i> 33]	Acetaldehyde [<i>m/z</i> 45]	Acetone [<i>m/z</i> 59]	Benzene [<i>m/z</i> 79]	Toluene [<i>m/z</i> 93]	Ethylbenzene [<i>m/z</i> 107]	Source/Comments
London (Autumn)	0.95	0.65	0.55	0.15	0.68	0.28	This study, DEC _{cf}
Manchester (Summer)	0.54	0.38	0.53	0.12	0.28	–	Langford et al. (2009), DEC
Mexico City	1.04	–	0.4	–	0.83	0.47	Velasco et al. (2005), DEC _{cf}
Mexico City	–	–	–	4.7±2.3	15.5±4.0	–	Karl et al. (2009), airborne DEC _(cf) , average midday fluxes
Mexico City	1.48	–	–	0.40	3.06	1.33	Velasco et al. (2009), DEC _{cf}

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Table 3. Averaged VOC/CO ratios for both concentrations and fluxes.

Compound	London [ppbv/ppbv]		US – Urban [ppbv/ppbv]		London [mole m ⁻² h ⁻¹ /mole m ⁻² h ⁻¹]	
	[VOC]/[CO]	<i>R</i> ^{2**}	[VOC]/[CO]	<i>R</i> ²	VOC/CO	<i>R</i> ^{2**}
Methanol	9.31×10^{-2}	0.01	–	–	8.12×10^{-2}	0.42
Acetonitrile	1.97×10^{-3}	0.85	–	–	7.95×10^{-3}	0.86
Acetaldehyde	2.33×10^{-2}	0.74	–	–	2.44×10^{-2}	0.94
Acetone	1.00×10^{-2}	0.71	–	–	1.45×10^{-2}	0.77
Isoprene	1.00×10^{-3}	0.43	–	–	3.85×10^{-3}	0.64
Benzene	8.57×10^{-4}	0.85	$7.0 \times 10^{-4*}$	0.61*	3.22×10^{-3}	0.93
Toluene	9.79×10^{-3}	0.05	$2.7 \times 10^{-3*}$	0.44*	9.27×10^{-3}	0.90
Ethylbenzene	8.93×10^{-4}	0.94	$4.0 \times 10^{-4*}$	0.30*	3.64×10^{-3}	0.87

* Baker et al. (2008).

** Correlation between average diurnal plots.

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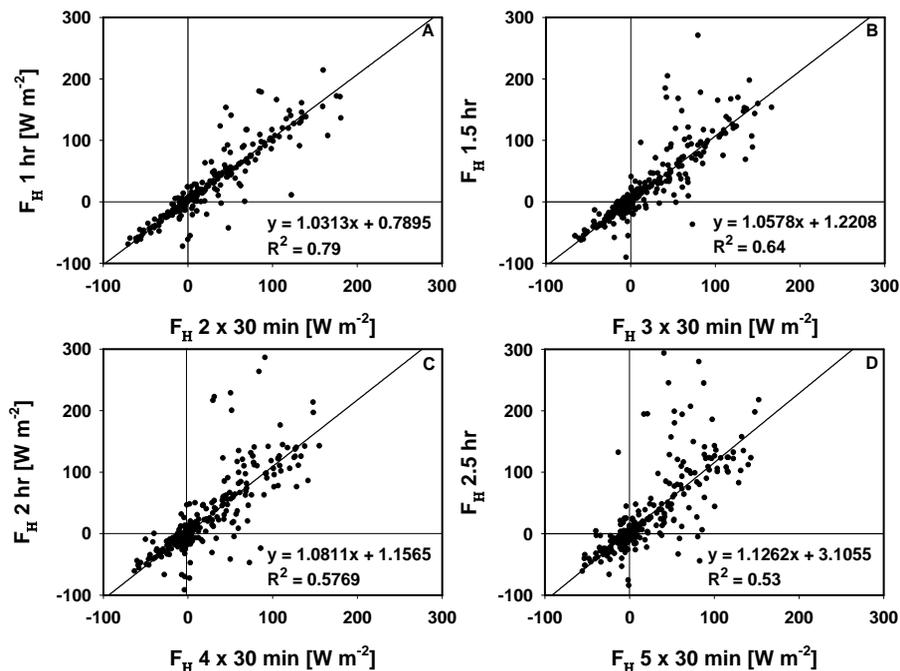


Fig. 1. Fluxes of sensible heat (F_H) measured at the Telecom Tower calculated using averaging periods of 1, 1.5, 2 and 2.5 h and compared with fluxes calculated using the more standard 25 min averaging period.

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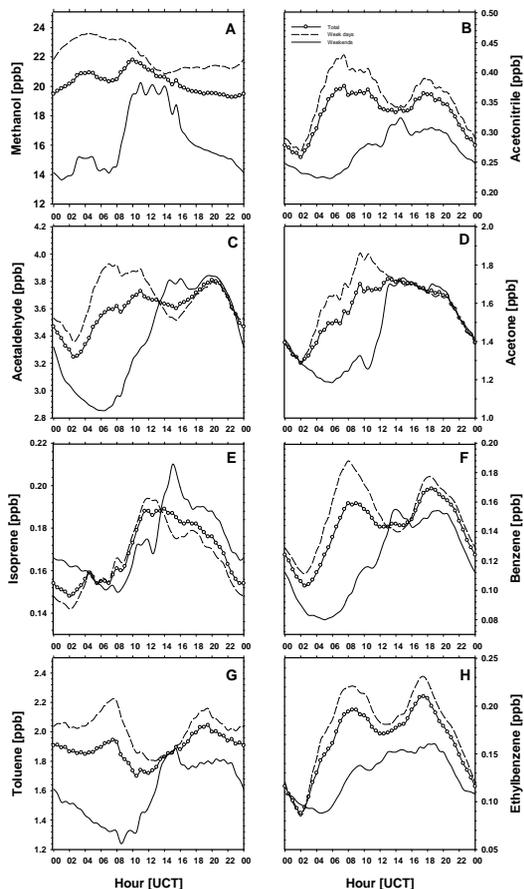


Fig. 2. Average diurnal concentrations of volatile organic compounds measured between 30 September and 30 October 2006. Open circles represent the total average (25 min) concentrations, solid line represents the average weekend concentrations and the dashed line represents average week-day values.

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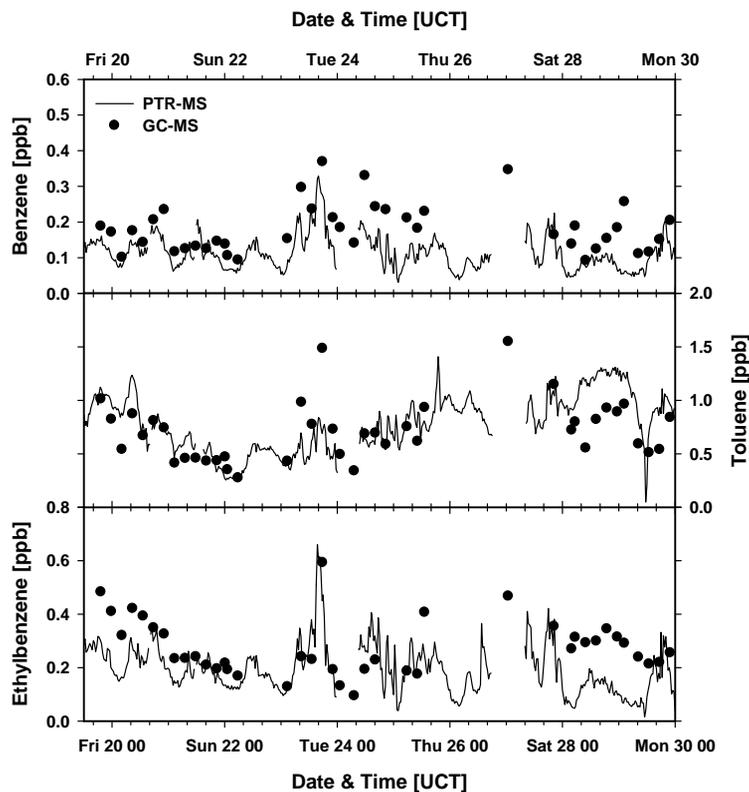


Fig. 3. Mixing ratios of volatile organic compounds obtained by PTR-MS and GC-FID from the Telecom Tower (London) during the REPARTEE-I campaign.

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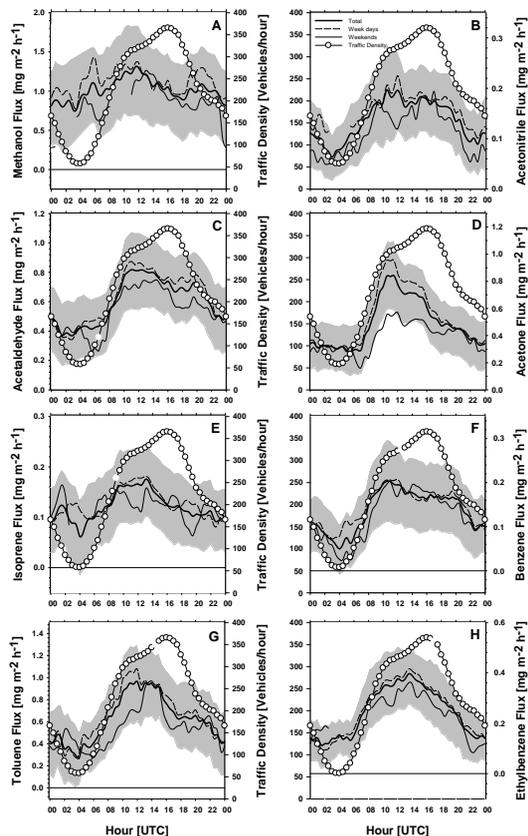


Fig. 4. Average diurnal flux profiles of volatile organic compound fluxes measured during the month of October 2006, from the Telecom Tower, London (UK). Solid bold line represents the total average (25 min) fluxes, solid line denotes the average weekend fluxes, dashed line represents the average week-day fluxes and open circles show the traffic density. Greyed areas represent the measurement precision – see text.

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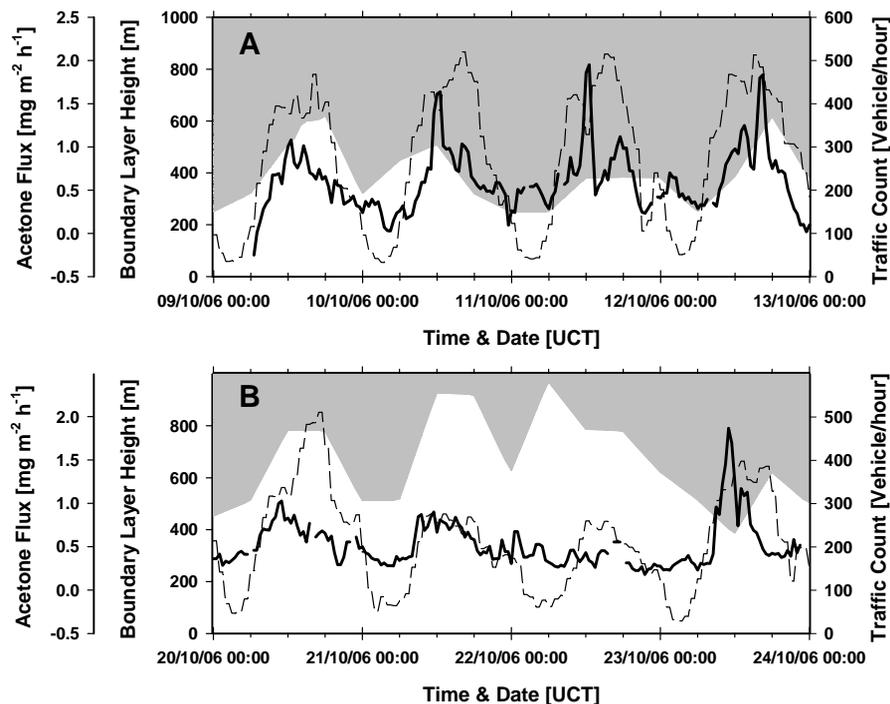


Fig. 5. Graph of acetone fluxes (running mean – solid line) measured during the 2nd (A) and 4th (B) week of the campaign relative to measured vehicle counts (dashed line) for central London (Marylebone Road). The top of the white layer shows the modelled boundary layer height.

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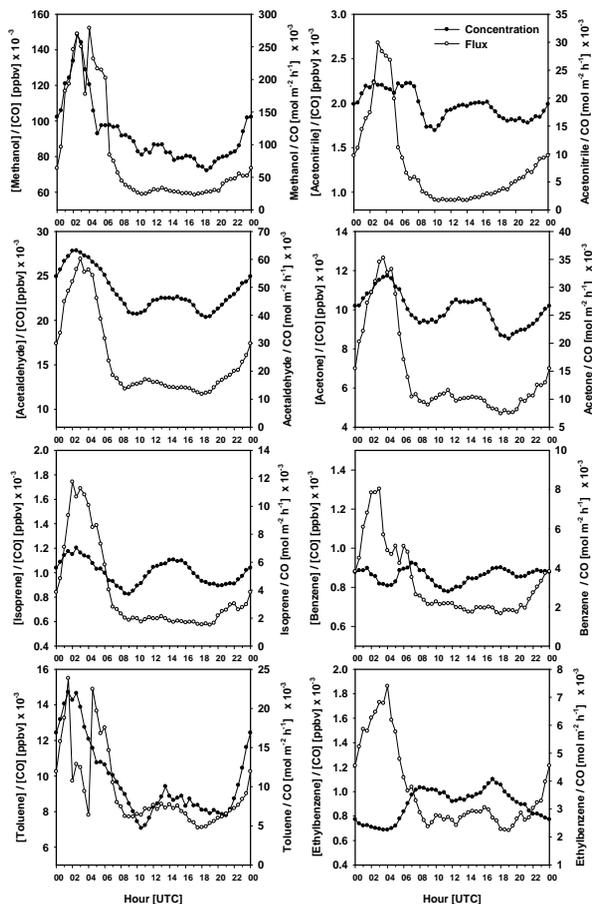


Fig. 6. Ratios of VOC/CO for fluxes ($\text{mole m}^{-2} \text{h}^{-1}/\text{mole m}^{-2} \text{h}^{-1}$) and concentrations ($[\text{ppbv}]/[\text{ppbv}]$) (25 min averaged values) for the period of October 2006, measured from the Telecom Tower, London (UK). Closed circles represent concentration ratios and open circles show flux ratios.

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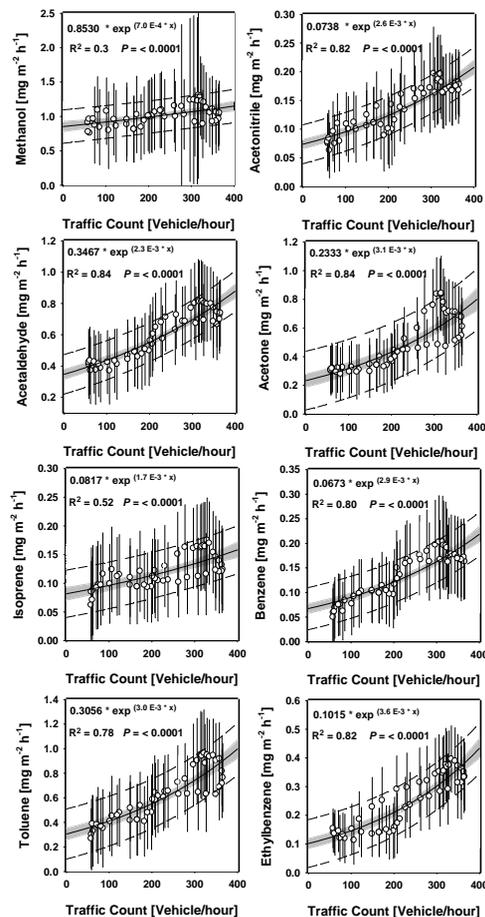


Fig. 7. Scatter plots showing the correlations between VOC flux and measured traffic activity in London city centre (counts – Marylebone Road). Error bars show flux measurement precision, shaded areas show the 95% confidence bands and dashed lines show the 95% prediction bands.

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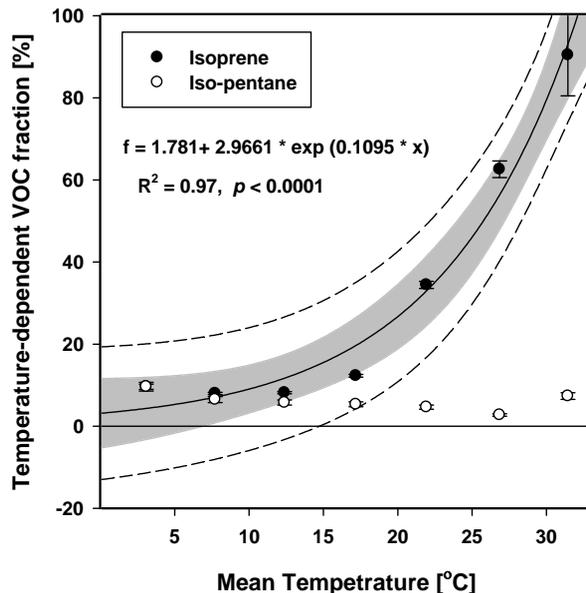


Fig. 8. Temperature dependency of isoprene (closed circles) and iso-pentane (open circles) concentrations, calculated using 5 years of hydrocarbon data collected at the Marylebone Road automatic monitoring station and temperature data from the London weather centre. Error bars show the uncertainty of intercept values for temperature bands $-5-0^{\circ}\text{C}$, $n=114$; $0-5^{\circ}\text{C}$, $n=3405$; $5-10^{\circ}\text{C}$, $n=9539$; $10-15^{\circ}\text{C}$, $n=12176$; $15-20^{\circ}\text{C}$, $n=9340$; $20-25^{\circ}\text{C}$, $n=3171$; $25-30^{\circ}\text{C}$, $n=673$; $30-35^{\circ}\text{C}$, $n=73$.

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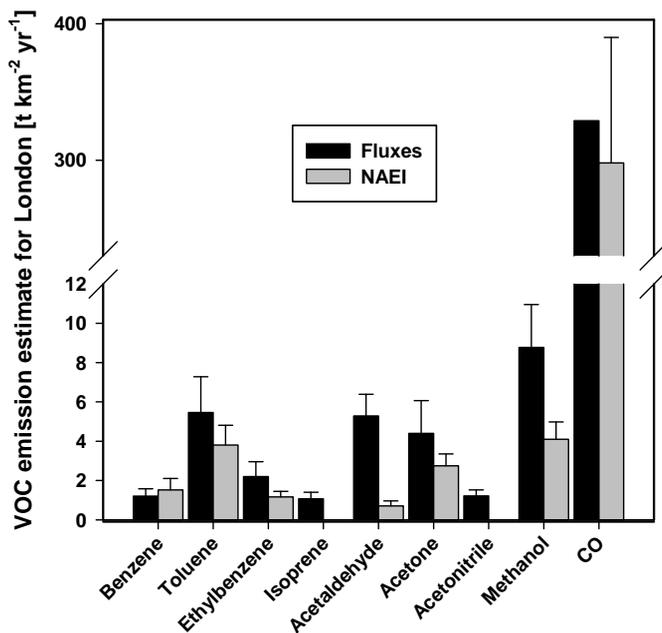


Fig. 9. Measured emission estimates of VOCs and CO from the Telecom Tower flux footprint compared with emission estimates made by the NAEI for the same flux footprint area. NAEI estimates for isoprene and acetonitrile are too small to show up on this scale. Error bars show the standard deviation of averaged NAEI grid squares and the 95% prediction band for the flux parameterisation, where there are no error bars no estimate is given.

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