Seasonal and diurnal trends in concentrations and fluxes of volatile organic compounds in central London

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Authors' responses to reviewers' comments

The authors would like to thank the two reviewers for their astute comments and suggestions, which have helped in improving the revised manuscript.

Responses to the reviewer's comments are below with reviewers' comments in **Bold** followed by a response to each point with the respective revisions to the manuscript in *Italics* unless the changes included the reworking of whole sections. As well as in response to the reviewers' comments, changes have been made throughout to improve the clarity and readability. The manuscript and figures should now be much easier to read and follow. Furthermore, acronyms and formatting have been checked and are now clear and consistent throughout.

The analyses in Section 3.2.2 have been reworked and a new figure (Fig. 8) has been added. In the initial analysis we correlated 30 min averaged CO_2 fluxes with VOC fluxes, including points below the limit of detection (LoD) in the case of VOCs. This resulted in poor correlations as we stated originally. However, we now have realised that it is better to use averaged data which reduces the LoD (see Section 2.3), as has been used for the analyses in Section 3.1.1 and Fig. 3. We now use data points averaged into separate bins according to the CO_2 flux. When we do this we find much better correlations, as stated in the revised manuscript. The text has been modified to make this procedure clearer:

"Good correlations were found between averaged VOC fluxes plotted as a function of averaged CO_2 fluxes, which were measured concurrently at the site ($R^2 = 0.03\text{-}0.81$, $p<0.001$). Traffic-related compounds were initially among the lowest correlations with CO_2 fluxes ($R^2 = 0.03\text{-}0.48$, $p<0.01$). However, when points of peak CO_2 fluxes were removed the correlations with traffic-related VOC fluxes increased significantly to $R^2 = 0.65\text{-}0.91$ ($p<0.001$). Presumably, the initial poor correlations resulted from an additional strong CO_2 source, such as vents from gas-fired boilers in nearby buildings, which have a lower source commonality with aromatic VOCs, i.e. a lower VOC/CO_2 emission ratio than that of traffic emissions for aromatic compounds. The London Atmospheric Emissions Inventory indicates that VOC/CO_2 flux ratios for benzene are higher for traffic emission sources (i.e. 2×10^{-5}) than gas sources (i.e. 0.6×10^{-5}) within the flux footprint (LAEI, 2013). The improved correlations are greater for traffic-related compounds due to the limited range of source types contributing to this group compared with oxygenated/biogenic compounds. The regression coefficient (R^2) of benzene with CO_2 fluxes increased from 0.48 to 0.91, whereas for isoprene fluxes the increase was small, i.e. 0.68 to 0.70 (Figure 8), as isoprene has a range of different sources of which only few are commonly shared sources with CO_2.

The presence of a strong separate CO_2 source within the flux footprint is supported by the high averaged VOC to CO_2 concentration correlations for traffic-related compounds ($R^2 = 0.92\text{-}0.96$, $p<0.001$). This differs from the fluxes, which are influenced only by sources in the flux footprint, where one strong point source with a different emission ratio may have a larger effect on emission rates of one compound but not the other. Concentrations are influenced by advected pollution from outside the flux footprint for both CO_2 and VOCs, where shared emission sources with relatively higher VOC/CO_2 ratios are more widespread. Averaged VOC *to CO_2 concentration correlations were lower with the oxygenated/biogenic compounds (R^2 = <0.71-0.90, $p<0.05$).*

Median VOC/CO_2 flux ratios ranged from 1.7×10^{-5} to 7.7×10^{-5} ($mg\ m^{-2}\ h^{-1}$/ $mg\ m^{-2}\ h^{-1}$) with isoprene and benzene showing low ratios due to their low fluxes, and toluene and C_2-benzenes high ratios. Highest flux ratios for all compounds were with W winds, whereas lowest for biogenic compounds with N and for traffic-related compounds S wind directions. Flux ratios declined towards December as CO_2 fluxes increased and VOC fluxes decreased. Similarly, VOC/CO_2 concentration ratios were between 0.45×10^{-6} and 14.6×10^{-6} (ppb/ppb) with isoprene and benzene representing the lowest and methanol and acetone the highest ratios. Highest concentration ratios were seen in August for oxygenated compounds/isoprene and December for traffic-related species."

Review 1

General comment 1: My main comment concerns the discussion on the influence of boundary layer dynamics: the possible role of atmospheric boundary layer (ABL) dynamics in shaping the diurnal profiles of species concentrations and their difference between summer and winter is mentioned briefly several times throughout the MS (e.g. in section 3.3.1), but not shown. Only in section 3.1.2 it is mentioned that the ABL was on average 1700 m in summer and 900 m in winter. I think you can discuss much more exactly how ABL dynamics have influenced your observations, and show it using the available data. Just some thoughts on the influence of the ABL from looking at the data: In Fig. 1 several concentrations (acetaldehyde, benzene, toluene, C2-benzenes) show a peak just around 8 a.m., which could be due to the emission into a shallow nocturnal ABL. After 8, the ABL quickly grows, clean air is entrained and emissions are diluted, leading to lower concentrations. The second peak in concentrations of aromatics (around 5 p.m.) could be the result of continuing emissions into a collapsing ABL. Finally, during night time, the ABL is shallow, but also the emissions are low, leading to low concentrations. For a good introduction on the ways in which ABL dynamics influence the relation between fluxes and concentrations of chemical species, see for instance Vilà-Guerau de Arellano et al. (2009). It would be very interesting to see correlations between species mixing ratios and ABL height (which is apparently available from LIDAR observations), in addition to the correlations with temperature, PAR and traffic density in Fig 3. This information could also help to strengthen your argument in Sect. 3.1.2 for the role of ABL dynamics in the seasonal variability and your conclusion (p.6625, l. 2-4) that 'many of the spatio-temporal differences in the observed mixing ratios were attributable to emissions and boundary layer dynamics'.

General response 1: A more extensive discussion and description of atmospheric boundary layer effects on VOC concentrations and fluxes is now included throughout Section 3.1, including the suggested reference. The diurnal summer and winter boundary layer heights have been added to Figures 2a and b. Furthermore, correlations of averaged boundary layer height and VOC fluxes and concentrations have been investigated and example plots of averaged isoprene fluxes and concentrations with boundary layer height have been added to Figure 3. Only correlations with boundary layer height during summer are shown due to the larger diurnal changes of boundary layer height in summer than in winter. Boundary layer height measurements were only available for 2-3 weeks in summer and winter 2012, as they were part of the short term intensive observation periods of ClearfLo. The benefit of this flux site is that the low measurement height of the tower means that our measurements are always closely coupled with the surface layer, unlike the previous VOC flux study from the BT Tower in London, which had the problem of becoming decoupled from the surface layer during stable night time conditions due to its high sampling height (Langford et al., 2010b).

<u>General comment 2</u>: Throughout the MS, the term ’diurnal averages’ of VOC fluxes/concentrations are used, which I think is very confusing. To me, a diurnal average flux/concentration means the flux/concentration, as averaged over all observations during one day, so a single value for each day. I think what you mean is the ’average diurnal cycle’ (or ’average diurnal profile’ as you write in the caption of Fig. 2), so the diurnal cycle of the flux/concentration, averaged over multiple days. Please check throughout the MS and use the latter term consistently.

<u>General response 2</u>: The term “*average diurnal profile*” is now used consistently throughout when describing diurnal cycles.

<u>Specific comments:</u>

Comment 1: Title: since large parts of the results section discuss (3.1, 3.1.1) and figures 2 and 4 show diurnal cycles, I would add to the title that you have also looked at diurnal trends. Therefore I would recommend ’Seasonal and diurnal trends in ...’.

Response 1: Title: added “*and diurnal*”.

Comment 2: p. 6603, l. 17-20: the lines about satellite retrievals of VOCs are not necessary for the discussion and could be left out.

Response 2: p. 6603, l. 17-20: This sentence has been removed.

Comment 3: p. 6604, l. 1: Seasonal, diurnal and spatial differences?

Response 3: p. 6604, l. 1: added “*diurnal*”.

Comment 4: p. 6604, l. 1: I would mention both VOC fluxes and concentrations here, since you discuss both.

Response 4: p. 6604, l. 1: added “*and concentrations*”.

Comment 5: p. 6612, l. 22: Is Mexico City the only other city for which flux measurements are available for comparison? You also mentioned papers by Park et al. with flux measurements in Houston, TX. Why not compare those with yours too?

Response 5: p. 6612, l. 22ff: An additional comparison of average fluxes and concentrations with Park et al. 2010 has been added (Section 3.1):

“Most VOC fluxes and concentrations were comparable to or lower than those previously observed in London (Langford et al., 2010b) and other UK cities (Langford et al., 2009), although C_2-benzene fluxes and concentrations, as well as isoprene and benzene concentrations were slightly higher. The discrepancy in isoprene and benzene concentrations is consistent with photochemical loss during transport to the higher measurement height of the previous study. Compared to other cities such as Houston Texas (Park et al., 2010) and Mexico City (Velasco et al., 2005), VOC fluxes and concentrations were lower, apart from C_2-benzenes which were comparable or higher, although it must be noted that C_2-benzenes in this study represent the sum of multiple VOC species. Unlike the other studies cited, Park et al. (2010) use relaxed eddy accumulation to measure VOC fluxes

and hence the data obtained are not directly comparable with measurements made by EC-based methods."

Comment 6: p. 6613, l. 10: If the moments of the peak fluxes coincide with those of a low ABL it is difficult to tell the effects of emissions and ABL dynamics on the concentration apart. Can you check with data on ABL height how exact this coincidence is?
Response 6: p. 6613, l. 10: This was added as part of Response to general comment 1 and now reads:
"The rush hour emission peaks mostly coincide with the boundary layer expansion and collapse and therefore the effect of each factor cannot be separated. The morning concentration peak was slightly higher than the evening peak across traffic-related species even though fluxes tended to be larger during the evening rush hour. Morning emissions enter a shallow nocturnal boundary layer leading to relatively larger concentrations compared with higher afternoon emissions entering a developed boundary layer, leading to relatively lower concentrations. This enhanced dilution effect is found more often during summer when the boundary layer mixing height is higher (Figure 2a). Therefore, the regression analyses below only refer to data from August (cf Section 3.1.2 for comparisons with December). Furthermore, increased photochemical degradation during the day removes VOCs, further contributing to the midday minimum in mixing ratios."

Comment 7: p. 6624, l. 26-27: 'There were observable spatial and temporal variations in relative source impacts at different resolutions such as hour to month.' I find this a too general statement for a conclusion. Can you be more specific?
Response 7: p. 6624 l. 26-27: This has been expanded and changed to:
"There were observable spatial variations in flux rates, which result from the varying spatial distribution of emission types and strengths of emission sources, such as vegetation and traffic. Temporal variations in relative source strengths can be seen in the diurnal and seasonal profiles, reflecting the diurnality and seasonality of some of the driving factors."

Technical comments:

Comment 1: p. 6602, l. 5: after 'proton transfer reaction-mass spectrometer', add '(PTR-MS)', since this acronym is used throughout the text
Response 1: p. 6602, l. 5: added "*(PTR-MS)*".

Comment 2: p. 6602, l. 15: accounted for -> explained
Response 2: p 6602, l. 15: changed sentence to:
"Isoprene, methanol and acetaldehyde fluxes and concentrations in August and September showed high correlations with PAR and temperature, when fluxes and concentrations were largest suggesting that biogenic sources contributed to their fluxes."

Comment 3: p. 6602, l. 17: change into 'Modelled biogenic isoprene fluxes from urban vegetation, using the G95.... ' and remove: ', due to urban vegetation.'
Response 3: p. 6602, l. 17: added "*from urban vegetation"* and removed *"due to urban vegetation*".

Comment 4: p. 6602, l. 25: live -> lives

Response 4: p. 6602, l. 25: changed to “*lives*”.

Comment 5: p. 6603, l. 9: additionally act as a source -> act as an additional source
Response 5: p. 6603 l. 9: changed to “*an additional*”.

Comment 6: p. 6603, l. 11: introduce the acronyms NAEI and LAEI here, where they are first used.
Response 6: p. 6603 l. 11: added “*(LAEI and NAEI)*”

Comment 7: p. 6604, l. 12: m.s.l. -> m.a.s.l.
Response 7: p. 6604 l. 12: added “*m a.s.l.*”

Comment 8: p. 6612, l. 3: diurnal averages -> average diurnal cycles
Response 8: p. 6612 l. 3: changed “*diurnal averages*” to “*Average diurnal cycles*” throughout the manuscript.

Comment 9: p. 6613, l. 8: concentrations for aromatics -> concentrations of aromatics
Response 9: p. 6613 l. 8: changed wording throughout this section.

Comment 10: p. 6615, l. 3-4: were seen with -> were seen between, positive correlations with -> positive correlations between.
Response 10: p. 6615 l. 3-4: changed to “*between*”.

Comment 11: p. 6615, l. 5: pls add a comma between ’temperature’ and ’likely’
Response 11: p. 6615 l. 5: added “,”.

Comment 12: p. 6615, l. 27: Bohnenstengel et al., 2014 -> Bohnenstengel et al., 2015
Response 12: p. 6615 l. 27: changed to “*2015*”.

Comment 13: p. 6616, l. 4: the equation from Langford et al: which equation?
Response 13: p. 6616 l. 4: added “*isoprene temperature response function from figure 9 in*”.

Comment 14: p. 6617, l. 16: add ’from those’ between ’than’ and ’areas’
Response 14: p. 6617 l. 16: added “*from those*”.

Comment 15 and 16: p. 6617, l. 21: add ’that’ before ’compounds’ and “Higher correlations *than what? Than compounds with traffic sources?”*
Response 15 and 16: p. 6617 l. 21-22: changed sentences for clarification:
“Correlations of VOC/VOC fluxes (R^2 = 0.40-0.62, p<0.001) indicated two groups of compounds with good correlations within each group, i.e. compounds related to traffic sources such as aromatics, and oxygenated and biogenic compounds, such as methanol, acetone and isoprene. Correlations of VOC/VOC concentrations (R^2 = 0.13-0.84, p<0.001) showed highest correlations between traffic related compounds (R^2 = 0.45-0.84, p<0.001) and good correlations between the oxygenated and biogenic compounds (R^2 = 0.55-0.69, p<0.001) (Figure 6). High correlations between oxygenated VOCs could indicate source commonality or formation mechanisms that depend on similar environmental factors.”

Comment 17: p. 6618, l. 1: tended -> tend

Response 17: p. 6618 l. 1: changed to “*tend*”.

Comment 18: p. 6618, l. 20: delete ’observed’, since it is mentioned twice in this sentence.
Response 18: p. 6618 l. 20: deleted “*observed*”.

Comment 19: p. 6624, l. 6: What does SNAP stand for?
Response 19: p. 6624 l. 6: added *“(Selected Nomenclature for sources of Air Pollution)”.*

Comment 20: p. 6625, l. 14: however -> but
Response 20: p. 6625 l. 14: changed to “*but*”.

Comment 21: p. 6625, l. 15: Where does ’this’ refer to? This study? The previous line?
Response 21: p. 6625 l. 15: Added “*study*”.

Comment 22: p. 6625, l. 22: there is a typo in the name of the 1st author
Response 22: p. 6625 l. 22: changed to “*Valach*”.

Comment 23: Fig. 1: Can you increase the size of the green dot, so it is easier to find?
Response 23: Fig 1: The size of the green dot has been increased, a label added and the caption updated:
“Map of central London overlaid with the Ordinance Survey grid including the measurement site (KCL) at King’s College (green point) with references to the geography of Greater London and Great Britain.”

Comment 24: Fig. 2: Some use of colours would be very helpful to distinguish between the different lines, like in figure 4. Besides, the axis labels are too small to read without zooming in.
Response 24: Fig. 2: Layout and font size have been increased to improve the clarity, as well as weekdays and weekends are now in colour (red, blue).

Comment 25: Fig. 5: In the caption, first describe the left and then the right panel. Also here, it would be helpful to increase the font size of the axis labels.
Response 25: Fig. 5: The figure size has been increased, as well as captions and order changed.
“Figure 5a. Time series of both measured (grey) and modelled (black) fluxes, as well as PAR and temperature measurements for August and September 2012.

Figure 5b. Correlation between modelled and measured isoprene fluxes (mg m^{-2} h^{-1}*) by wind direction using the G95 algorithm with temperature as a third variable, Ordinary Least Squares (OLS) regression lines, 99th confidence intervals, formulae, and* R^2*-value.”*

Comment 26: Supplementary material: A caption for the figure would be useful. Besides, since the supplement consists of only 1 figure, it would perhaps be more convenient to include it in an appendix to the main paper.
Response 26: A figure caption has been added.

"Figure A1. Sensible heat fluxes (W m^{-2}) measured from the roof tower of the King's College London Strand building calculated using 1 to 2.5 h averaging periods and compared with fluxes calculated using the same 25 min averaging period as used for VOC fluxes."

Review 2

Major comment 1: The suitability of the King College site for monitoring turbulent fluxes needs further assessment. The land cover is very heterogeneous and the buildings morphology does not seem to contribute for measuring fluxes by eddy covariance. The street canyon formed by the own building where the measurements were conducted may enhance the accumulation of freshly emitted VOCs below the urban canopy, particularly during periods of stable atmospheric conditions at night and winter.

Response 1: The KCL site at King's College has been used as a long term CO_2/H_2O flux measurement site and thus site characteristics and suitability for micrometeorological flux measurements have been investigated and described extensively by Kotthaus and Grimmond (2012; 2014a; 2014b). Although the site is not ideal for flux measurements, the cited studies show that representative surface-atmosphere fluxes can be measured at the site without significant bias from the local morphology as long as data are filtered to remove contributions from local micro-sources, e.g. vents and windows, if present. Additionally, they show that results from flux footprint models at the site can provide reasonable information. Some considerations were highlighted such as instrument siting in complex urban areas requiring careful interpretation of measured and modelled data. The relatively low measurement height allows close coupling to the street canyon. The analyses presented here were based on averaged data to reduce some of the uncertainties and used to describe overarching trends. These trends agree with conclusions from previous urban VOC flux studies. This study is the first of its kind to present long term continuous VOC flux measurements by PTR-MS over an urban area and hence provides valuable information on VOC fluxes from central London, despite some minor limitations imposed by the less-than-ideal site morphology. Section 2.1 was expanded to include:

"The sampling point (which we call KCL) is located 37 m west of a sampling point (KSS) that has been used for long-term energy and CO2 flux measurements (Kotthaus and Grimmond, 2012). Although the site is not optimal for micrometeorological flux measurements due to the heterogeneity of the urban canopy, its suitability has been assessed in detail by Kotthaus and Grimmond (2014a; 2014b). This study describes in detail the measurement area and investigates the influence of source area characteristics on long-term radiation and turbulent heat fluxes for the KSS site. They conclude that the site can yield realistic data on surface to atmosphere fluxes."

Kotthaus, S., and Grimmond, C.S.B.: Identification of Micro-scale Anthropogenic CO2, heat and moisture sources – Processing eddy covariance fluxes for a dense urban environment, Atmospheric Environment, 57, 301-316, http://dx.doi.org/10.1016/j.atmosenv.2012.04.024, 2012.

Kotthaus, S., and Grimmond, C.S.B.: Energy exchange in a dense urban environment – Part I: Temporal variability of long-term observations in central London, Urban Climate, 10, 2, 261-280, http://dx.doi.org/10.1016/j.uclim.2013.10.002, 2014a.

Kotthaus, S., and Grimmond, C.S.B.: Energy exchange in a dense urban environment – Part II: Impact of spatial heterogeneity of the surface, Urban Climate, 10, 2, 281-307, http://dx.doi.org/10.1016/j.uclim.2013.10.001, 2014b.

<u>Major comment 2:</u> ***For eddy covariance flux measurements samples are usually collected at 10 Hz (15,000 samples in a period of 25 min). The sampling rate when using the disjunct eddy covariance method is slower. However, a sampling rate of 5.5 sec (273 samples in a period of 25 min) as that used here seems to be extremely slow. The statistical uncertainty of the fluxes caused by a longer time resolution needs to be evaluated. The CO2 flux data discussed in section 3.2.2 may help to assess this issue.***

<u>Response 2</u>: The disjunct sampling increases the random error of the flux but, provided the sampling intervals are less than the integral timescale, this should not introduce a systematic bias. We tested this assumption by simulating disjunct sampling on sensible heat flux data, which were calculated from the continuous data and then compared with the sensible heat fluxes calculated from a disjunct series with a sampling rate of 2 Hz and a sampling interval of 5.5 s. The overall difference between the EC and DEC sensible heat fluxes over the entire measurement period was minimal (0.01 %), therefore no additional corrections have been made to the VOC fluxes. This information was added to Section 2.3:
"The error due to the disjunct sampling was estimated by comparing the sensible heat fluxes calculated from the continuous data series with those calculated from a disjunct data series using a set sampling interval of 5.5 s. The continuous data were averaged to match the sampling frequency of the disjunct data (i.e. 2 Hz). The difference between the eddy covariance and DEC sensible heat fluxes was minimal (0.01 %) and thus no additional corrections were applied."

Specific comments:

Comment 1: P6602, L17. G95 algorithm?
Response 1: p. 6602 l. 17: expanded to "*Guenther et al., (1995)*".

Comment 2: P6603, L12. ...use a "bottom-up" approach based on activity data and emission factors....
Response 2: p. 6603 l. 12: changed to *"… "bottom-up" approach based on activity data and emission factors*".

Comment 3: P6603, L22. This reviewer has serious concerns on the methodology used by Park et al., 2010 & 2011.
Response 3: p. 6603, l. 22: There are very few urban VOC flux measurements and even fewer that use DEC based techniques. Therefore to expand the comparison of VOC fluxes in this study with those in the literature, additional studies using relaxed eddy accumulation (REA) were consulted. REA can be associated with large errors due to the loss of reactive compounds on canister surfaces, but also the potential error from a bias in the vertical wind velocity, as shown by the normalised bias $(\overline{w}/\sigma_w)$. A sentence has been added for further clarification:
"Unlike the other studies cited, Park et al. (2010) use relaxed eddy accumulation to measure VOC fluxes and hence the data obtained are not directly comparable with measurements made by EC-based methods."

Comment 4: P6603, L29. Define PTR-MS.

Response 4: p. 6603 l. 29: expanded to “*proton transfer reaction-mass spectrometry*”.

Comment 5: P6604, L11. Check symbols of seconds, minutes, inches, etc. throughout the text.

Response 5: p. 6604 l. 11: changed to decimal degrees: “*51.511667 N 0.116667 W*”.

Comment 6: P6604, L16. Update classification based on Stewart & Oke (2012).

Response 6: p. 6604 l. 16: Updated site classification, added the reference and changed text to:

“This site is classified as Local Climate Zone (LCZ) Class 2 Compact Midrise according to Stewart and Oke (2012) (i.e. dense mix of midrise buildings (3–9 stories), few or no trees, land cover mostly paved, stone, brick, tile, and concrete construction materials.”

Comment 7: P6604, Section. 2.1. Add fractions of the plan area cover (i.e., building, roads, vegetation, water bodies, etc.).

Response 7: p. 6604, l. 18: Added:

“*Land cover types (in %) were calculated based on the Ordinance Survey map for the 9 km^2 area (Figure 1) encompassing the site and are: roads (37 %), buildings (31 %), other paved areas (14 %), unpaved/ vegetation (11 %), and water bodies (7 %).*”

Comment 8: P6605, L13. Although in following paragraphs the averaging process is described, in a few words mention why periods of 25 min were used instead of periods of 30 min. Periods of 30 min are usually used when measuring fluxes over urban surfaces.

Response 8: As mentioned in Section 2.2 p. 6606 l. 9-11, the hourly duty cycle of the PTR-MS consisted of 5 min zero air measurements, followed by 25 min MID used to calculated fluxes, then a further 5 min mass scan and finally another 25 min MID mode. We present 25 min fluxes as we have no measurements for the initial 5 min of each 30 min period.

Comment 9: P6605, L16-18. Note that emissions in cities respond strongly to human activities, and the behaviour of these follows the local time and not the UTC.

Response 9: Section 2.2, p. 6605, l. 16-18: The time axes of figures all state that local time was used, which has also been added in the text as:

“However, all analyses used local time.”

Comment 10: P6606, L-15-20. Why were data of m/z 33 and m/z 121 not included?

Response 10: *m/z 33* is included, however *m/z* 42 and 121 were not included as the signal was too low and during the measurements their places in the limited duty cycle were subsequently used to investigate other less typically measured masses, none of which showed any useful information.

Comment 11: P6607, L2. Check that all variables are written with italic fonts.

Response 11: p. 6607 l. 2: variables have been checked and are now written with italic font throughout.

Comment 12: P6607, Eq. 1. Fix the fluctuations’ symbols.

Response 12: p. 6607 Eq. 1: fluctuation symbols have been checked and are now correct and consistent throughout.

Comment 13: P6609, Eq. 1. This equation is unreadable.
Response 13: p. 6609, Eq. 1: This equation is clearly presented. It may be that the reviewer is using a non-compatible PDF-viewer. We will check this at the proof-reading stage.

Comment 14: P6609, L20. Ergodicity is a rare/exotic term to indicate that the buildings height and morphology in the monitored district were quite variable. From Wikipedia: "The term ergodic is used to describe a dynamical system which has the same behaviour averaged over time as averaged over the space of all the system's states. In physics the term is used to imply that a system satisfies the ergodic hypothesis of thermodynamics."
Response 14: p. 6609, l. 20-22: The sentence has been changed to:
"The high number of files rejected in the stationarity test is to be expected for eddy covariance measurements over highly heterogeneous canopies, although horizontally averaged canopy morphology recovers some surface homogeneity."

Comment 15: P6610, L7. Do not begin sentences with numbers or acronyms.
Response 15: p. 6610, l. 7: added "*Exactly*".

Comment 16: P6612, L5-10. If daily mean fluxes are presented, it would be better to use units of kg km-2 day-1.
Response 16: p. 6610, l. 3-12: The figures 2a and b show the diurnal profiles of VOC fluxes and mixing ratios, whereas the values represent hourly average fluxes, which are typically given in units of mg m^{-2} h^{-1} (Karl et al., 2004; 2007; 2009; Langford et al., 2009; 2010a; 2010b; Misztal et al., 2011; Rinne et al., 2001; 2002). Both fluxes and concentrations include data from the entire measurement period. For clarification purposes the words "*average diurnal cycles*" are now used throughout to refer to diurnal profiles of VOC emissions and mixing ratios. The units mg m^{-2} h^{-1} are used in table 2 to show the overall average of diurnal profiles, which are in hours of the day. However values are now cited in the main text body in Section 3.1 in units of kg km^{-2} d^{-1} as suggested by the reviewer, as follows:
"Largest median (interquartile range in parenthesis) fluxes per day were from C_2-benzenes and toluene with 7.86 (0.92-21.8) kg km^{-2} d^{-1} and 7.26 (1.83-15.3) kg km^{-2} d^{-1} respectively, followed by oxygenated compounds, i.e. methanol with 6.37 (2.99-10.0) kg km^{-2} d^{-1}, acetaldehyde 3.29 (1.52-5.62) kg km^{-2} d^{-1}, and acetone 5.24 (2.33-9.62) kg km^{-2} d^{-1}. Isoprene and benzene showed smallest median fluxes with 2.14 (0.56-4.85) kg km^{-2} d^{-1} and 1.78 (0.06-4.34) kg km^{-2} d^{-1} respectively."

Comment 17: P6612, L14-15. ... lifetimes and widespread origin including anthropogenic and biogenic sources and photochemistry ...
Response 17: p. 6612 l. 14/15: changed to "*lifetimes and widespread origin including anthropogenic and biogenic sources and photochemistry*".

Comment 18: P6613, L5-7. It may only be true for London and other UK cities.
Response 18: p. 6613, l 5-7: changed to "*central urban areas in UK cities*".

Comment 19: P6614, L23-24. Explain how advected air masses rich in methanol and acetone might affect the local boundary layer meteorology.
Response 19: p. 6614, l. 23-24: This was poorly worded and has been changed to:
"De Gouw et al. (2005) reported that changes in boundary layer meteorology could result in greater effects on observed concentrations of methanol and acetone due to their high background values. The mixing ratios of these compounds are, therefore, dominated by advected pollution rather than the local flux."

Comment 20: P6615, L11-12. Is there an important potential emission source (e.g. petrol station) at the west of the flux tower?
Response 20: p. 6615, l. 11-12: As the Congestion Charge Zone in London limits the number of private vehicles in this area, there are only few petrol stations in the vicinity. The nearest is 1 km to the north and the closest westerly station is 2.5 km away. These petrol stations are outside of the 90 % flux contribution distance and are not likely to have contributed to fluxes. No other significant point sources of this type were identified within the footprint area.

Comment 21: P6617, L3-6. Was turfgrass considered?
Response 21: p. 6617, l. 3-6: added "*total tree leaf area*". Turfgrass was not considered as turf grass species used in the UK do not emit isoprene or emit it at undetectable levels (e.g. Stewart et al., 2003).

Comment 22: P6617, L21. ... for fluxes indicated (What?) ...
Response 22: p. 6617 l. 21-22: This section was poorly phrased and has been changed to improve clarification and consistency:
"Correlations of VOC/VOC fluxes (R2 = 0.40-0.62, p<0.001) indicated two groups of compounds with good correlations within each group, i.e. compounds related to traffic sources such as aromatics, and oxygenated and biogenic compounds, such as methanol, acetone and isoprene. Correlations of VOC/VOC concentrations (R2 = 0.13-0.84, p<0.001) showed highest correlations between traffic-related compounds (R2 = 0.45-0.84, p<0.001) and good correlations between the oxygenated and biogenic compounds (R2 = 0.55-0.69, p<0.001) (Figure 6)."

Comment 23: P6617, L22. Provide examples of such species.
Response 23: p. 6617, l. 22: See part of previous response:
"*i.e. compounds related to traffic sources such as aromatics, and oxygenated and biogenic compounds, such as methanol, acetone and isoprene.*"

Comment 24: P6617, L21-25. This paragraph is difficult to read.
Response 24: p. 6617, l. 21-25: See responses 22 and 23.

Comment 25: P6618, Section 3.2.1. A figure showing scatter plots of benzene versus toluene would be helpful.
Response 25: p. 6618, Section 3.2.1: Phrasing has been improved and two panels have been added to figure 7 showing scatterplots of benzene versus toluene concentrations for the 9th and 12th August respectively. The figure caption now reads:

“Bottom: Scatterplots showing benzene to toluene concentration ratios during the 9th August 2012 (left) and 12th August 2012 (right) with linear regression with 95th confidence interval, regression equation and coefficient (R2).”

Comment 26: P6618, L10. IQR?
Response 26: p. 6618, l.10: added “*and interquartile range*”.

Comment 27: P6618, L14-24. Zavala et al. (2006), Rogers et al. (2006), Velasco et al. (2007) and Karl et al. (2009) reported benzene to toluene ratios for Mexico City. The vehicular fleet and industry from both cities are expected to be considerably different, as well as the benzene to toluene ratio.
Response 27: p. 6618, l. 14-24: The detailed comparison with Mexico City has been removed and only the b/t flux ratios from Karl et al. (2009) have been included to help explain a possible reason for the low observed flux ratios in this study. The comparison with other cities now focuses on European and UK cities. The section has also been rephrased to improve the clarity as follows:
“The observed ratios compared well with those of other European cities, which showed b/t concentration ratios of 0.35 in Zurich (Heeb et al., 2000), 0.57 in Manchester (Langford et al., 2009), 0.57-0.63 in London (Valach et al., 2014), and 0.1 at 190 m above London (Langford et al., 2010b). Traffic related emissions are considered to be an important source of benzene and toluene in London. B/t exhaust emission ratios based on derived yearly emissions in other megacities, such as Mexico City, were found to be 0.4 (Zavala et al., 2006), which agreed well with observed b/t concentration ratios in this study. Airborne flux measurements over Mexico City have shown average b/t flux ratios of 0.31 with lower ratios of 0.07 to 0.1 over industrial areas due to increased toluene emissions from industrial processes (Karl et al., 2009; Velasco et al., 2007). Evaporative emissions from gasoline or direct industrial toluene emissions may have contributed to the lower b/t flux ratios in London. Furthermore, low b/t concentration ratios of 0.26 from diesel emissions have been reported (Corrêa and Arbilla, 2006). The widespread use of diesel fuel in London (buses, taxis and some cars and trains) and diesel emissions from roads which exclude passenger cars, such as Oxford Street (approx. 1.3 km W from the measurement site) or central railway nodes, such as Waterloo Railway Station (1 km to the S), may have affected b/t ratios.“

Comment 28: P6621, L20-22. If this was true, the reported fluxes would not be representative of the monitored district. The measurement height together with the data quality assurance suggests that the flux measurements were properly conducted at the inertial sublayer, where the turbulence and fluxes are relatively homogenous.
Response 28: p. 6621, l. 20-22: The section was poorly worded and has been rewritten as:
“Due to the relatively low measurement height, flux measurements were always closely coupled with the surface layer, unlike measurements by Langford et al. (2010b), which were at times disconnected from the surface layer during stable night time conditions. The flux footprint in this study was relatively small compared with that of measurements previously made a 190 m height from the BT Tower in central London (Langford et al., 2010b).”

Comment 29: P6622, L7-27. This discussion is long and difficult to follow.
Response 29: p. 6622, l. 7-27: This section was poorly phrased. The structure and language have been improved.

"Green areas, as defined on the OS map, comprised 9 % of the total grid area and were evenly distributed across the 9 km^2. Only grid square 1 included a large green area of 23 ha (St. James' Park). The National Forest Inventory England only included 4.4 % green areas within the grid selection (NFI, 2012)."

And:

"The River Thames to the S may have caused the low fluxes associated with S winds (i.e. squares 1, 2 and 3). Contributions of traffic related compound fluxes were statistically significant from the W (i.e. squares 4, 5, and 7), followed by the N (square 8) and E (squares 6 and 9) likely from the nearby heavily trafficked roads (Kingsway, Charing Cross, Strand and Blackfriars areas, respectively). Biogenic compound fluxes were highest from the W and E which coincides with significant nearby green areas within the flux footprint."

Comment 30: P6623, L11. The London Atmospheric Emissions Inventory (LAEI) and the Atmospheric Emissions Inventories (NAEI) ...

Response 30: p. 6623 l. 11: changed to "*London Atmospheric Emissions Inventory (LAEI) and National Atmospheric Emissions Inventories (NAEI)*".

Comment 31: P6623, Section 3.4. Do NAEI and LAEI provide data on the spatial and temporal distribution of the estimated emissions?

Response 31: p. 6623, Section 3.4: Estimates are produced on an annual basis and over a 1 km^2 grid system which coincides with the Ordinance Survey grid. This information was added to the first sentence:

"The London Atmospheric Emissions Inventory (LAEI) and National Atmospheric Emissions Inventories (NAEI) produce yearly emission estimates over the 1 km^2 OS grid for a range of pollutants and emission sources."

Comment 32: P6624, L6. SNAP?

Response 32: p. 6624 l. 6: added *"(Selected Nomenclature for sources of Air Pollution)".*

Comment 33: P6625, L15-17. The article does not discuss the suitability of the King College for turbulent flux measurements. If its suitability has been previously analysed, include the corresponding references.

Response 33: p. 6625, l. 15-17: This issue is addressed in the response to Major comment 1 by this reviewer and references have been added.

Comment 34: P6636, Fig. 1. The green marker is difficult to find. Make it larger.

Response 34: p. 6636, Fig. 1: The size of the green marker has been increased and a label of the site name added.

Comment 35: P6636, Fig. 1. It would be helpful to see the estimated footprint overlaid on the map.

Response 35: p. 6636, Fig. 1: Outlines for X_{max}, 75 %, 90 %, and 99 % of the area contributing to the flux footprint are shown with respective labels. Changes in the figure caption have been made accordingly:

"Map of central London overlaid with the Ordinance Survey grid including the measurement site (KCL) at King's College (green point) with references to the geography of Greater London and Great Britain. Outlines of the areas that contribute the maximum (X_{max}), 75%,

90%, and 99% to the flux footprint using overall median meteorological values are shown in black with their respective labels laid out according to the median wind direction."

Comment 36: P6637, Fig. 2. There is no need of mixing weekdays and weekend's fluxes in one profile. For some species, such as C2-benzenes and toluene, the difference is considerable. Show only the variability (i.e. confidence interval) of weekdays or weekends.

Response 36: p. 6637, Fig. 2: The format used in figure 2 has previously been widely used to show diurnal profiles of pollutant concentrations and fluxes, including by Bigi and Harrison (2010), Langford et al. (2010b), Park et al. (2010), Park et al. (2011), Velasco et al. (2005), Velasco et al. (2009). However, to aid clarity weekend and weekday lines are now in colour (blue and red respectively) to improve the readability and the figure caption has been updated: "*weekdays (red dashed line) and weekends (blue dotted line)*".

Comment 37: P6637, Fig. 2. For panels in section (b) select scales that help to visualize the diurnal characteristics. For example, the scale for benzene should go from 0.20 to 0.40 ppb, instead from 0.00 to 0.45 ppb.

Response 37: p. 6637, Fig. 2: It is conventionally accepted that it is good practice to plot figures with both axes beginning at zero. We retain this format in order to aid comparison with previously published data on VOC mixing ratios, e.g. Bon et al. (2011), Davison et al. (2009), Fraser et al. (1998), Heeb et al. (2000), Karl et al. (2007), Kato et al. (2004), Kim et al. (2001), Langford et al. (2010a), Liu et al. (2015), Misztal et al. (2011), Park et al. (2010), Park et al. (2011), Velasco et al. (2007), von Schneidemesser et al. (2011), Wang et al. (2014), Warneke et al. (2014).

The figure caption was updated to include:

"The mixing ratio axes start from zero apart from that of methanol, which begins at 6.4 ppb due to the high atmospheric background."

Comment 38: P6638, Fig. 3. Check the linear regression of panel (E).

Response 38: p. 6638, Fig. 3: The regression line in panel E has been corrected.

Comment 39: P6639, Fig. 4. What do the bar charts represent? Do they show the mean daily flux/mixing ratio for each monitored month?

Response 39: p. 6639, Fig. 4: Bar charts show hourly fluxes averaged over each month in mg m^{-2} h^{-1}. The figure caption has been expanded with:

"Diurnal profiles by month with confidence intervals and bar charts showing hourly averages for the respective month and representative compound (top) fluxes (mg m^{-2} h^{-1}) (m/z 45, 69 and 79) and (bottom) mixing ratios (ppb) (m/z 59, 69 and 79)."

Comment 40: P6640, Fig. 5. Too many dashed lines in the scatter plots. They are confusing.

Response 40: p. 6640, Fig. 5b: 1:2 and 2:1 lines have been removed.

Comment 41: P6640, Fig. 5. OLS?

Response 41: p. 6640 Fig. 5: caption changed to "*Ordinary Least Squares (OLS)*".

Comment 42: P6640, Fig. 5. Describe first the panels at the left and then the panels at the right.

Response 42: p. 6640, Fig. 5: The caption has been adjusted:
"Figure 5a. Time series of both measured (grey) and modelled (black) fluxes, as well as PAR and temperature measurements for August and September 2012.
Figure 5b. Correlation between modelled and measured isoprene fluxes (mg m^{-2} h^{-1}) by wind direction using the G95 algorithm with temperature as a third variable, Ordinary Least Squares (OLS) regression lines, 99th confidence intervals, formulae, and R^2-value."

Comment 43: P6641, Fig. 6. Scatter plots between fluxes would be more interesting.
Response 43: p. 6641, Fig. 6: Scatterplots between the fluxes show no clear trends, as many fluxes were below the LoD and therefore individual flux points have high uncertainties, hence averaged data have been used throughout in the analyses. However, flux correlations between the same compound pairs as used in the concentration correlations have been added and the figure caption updated:
"Figure 6. Selected scatter plots of representative correlations of VOC/VOC fluxes (top) and mixing ratio (bottom) with temperature as a third variable showing an example of bimodal, strong linear and medium linear correlations as commonly seen in the mixing ratio correlations with R^2-values, 1:1 line, 1:2 and 2:1 lines for the bimodal example in the bottom left panel."

Seasonal and diurnal trends in concentrations and fluxes of volatile organic compounds in~~above~~ central London

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Abstract

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Concentrations and fluxes of seven volatile organic compounds (VOCs) were measured between August and December 2012 at a roof-top site in central London as part of the ClearfLo project (Clean Air for London). VOC concentrations were quantified using a proton transfer reaction-mass spectrometer (PTR-MS) and fluxes were calculated using a virtual disjunct eddy covariance technique (vDEC).~~.~~ The median VOC fluxes, including aromatics, oxygenated compounds and isoprene, ranged from 0.07 to 0.33 mg m^{-2} h^{-1}. Median~~ and~~ mixing ratios were 7.3~~27~~ ppb for methanol ~~(*m/z* 33)~~ and < 1 ppb for the other~~remaining~~ compounds. Strong relationships were observed between the~~most VOC~~ fluxes and concentrations of some VOCs with traffic density, and between the fluxes and concentrations of isoprene and oxygenated compounds ~~but also~~ with photosynthetically active radiation (PAR) and temperature.~~ for the oxygenated compounds and isoprene.~~ An estimated 50-90 % of the fluxes~~%~~ of aromatic VOCs~~fluxes~~ were attributable to traffic activity, which showed little seasonal variation, suggesting that boundary layer effects or possibly advected pollution may be the primary causes of increased concentrations of aromatics in winter. Isoprene~~PAR and temperature-dependent processes accounted for the majority of isoprene~~, methanol and acetaldehyde fluxes and concentrations in August and September showed high correlations with PAR and temperature, when fluxes and concentrations were largest suggesting that biogenic sources contributed to their fluxes.~~.~~ Modelled biogenic isoprene fluxes from urban vegetation using the Guenther et al., (1995)~~G95~~ algorithm agreed well with measured fluxes in August and September.~~, due to urban vegetation.~~ Comparisons of estimated annual benzene emissions from the London and National Atmospheric Emissions Inventories~~Inventory~~ agreed well with measured benzene fluxes. Flux footprint analysis indicated emission sources were localized and that boundary layer dynamics and source strengths were responsible for temporal and spatial VOC flux and concentration variability during the measurement period.

1 Introduction

Currently over 50 % of the global population lives~~live~~ in urban areas and with increasing ~~trends in urbanization and population~~ migration to urban centres, air quality remains a high public health priority. In the European Union, including~~Although~~ in the UK, volatile organic compound (VOC) emissions are subject to control under the European Commission Directive 2008/50/EC and emission reducing technologies have been implemented, yet urban air pollution continues to be a concern. VOCs from both anthropogenic and biogenic sources impact urban air quality and climate through their contribution to tropospheric ozone and aerosol particle formation. Some VOCs including~~are also carcinogens (e.g.~~ benzene and 1,3- butadiene are also carcinogens,~~),~~ which can directly affect human health (Kim et al., 2001). Most VOCs in urban areas are assumed to come from fuel combustion or evaporative emissions (Srivastava et al., 2005; Kansal, 2009). However, in summer, urban vegetation may ~~additionally~~ act as an additional~~a~~ source of VOCs such as methanol, isoprene and monoterpenes even in cities with a temperate climate and little green space, such as London or Manchester (Langford et al., 2009; 2010b).

Emission inventories such as the London and National Atmospheric Emissions Inventories (LAEI and NAEI)~~Inventory~~ use a “bottom-up” approach based on activity data and emission factors to estimate emission rates from pollutant sources. Micrometeorologically-based~~ which are temporally and spatially averaged. Micrometeorological~~ eddy covariance techniques allow a “top-down” approach to quantify fluxes and these measurements can be compared with modelled emission inventory estimates. Such comparisons are essential as “bottom-up” emission~~estimates. Many compounds can have a variety of different sources which have yet to be identified and added to emissions~~ inventories may inadvertently not include specific pollutant sources, or may use unrepresentative emission factors or activity profiles. “Top~~making “top-down” flux measurements vital. Satellite “top~~-down” approaches using Earth observation data from satellites are also available for a~~only~~ few chemicals (Lamsal et al., 2011), but not for primary VOCs. There have been few studies on VOC fluxes in urban areas, and these~~Biogenic isoprene can be indirectly quantified using satellite observations, but is subject to many uncertainties (Palmer et al., 2006). There have been few studies on VOC fluxes in urban areas which~~ have been limited in spatial and temporal extent~~representation~~ (Langford et al., 2009; 2010b; Velasco et al., 2005; 2009; Park et al., 2010; 2011). Due to the high technical demands~~demand~~ of VOC flux measurements, it is difficult to increase spatial coverage or to make measurements~~. However, deploying instrumentation~~ for long periods of time. Making further~~-term~~ measurements of this kind is therefore a high priority in studies of air quality~~provides better understanding of seasonal to annual variability~~.

In this study we present ~~VOC~~ flux and concentration measurements of seven selected volatile organic compounds made over five months in~~above~~ central London using the virtual disjunct eddy covariance method. The aims~~aim~~ of this study were~~was~~ to i) quantify~~:~~

~~i.~~ ~~Quantify~~ VOC fluxes above an urban canopy using proton transfer reaction-mass spectrometry~~PTR-MS~~ and disjunct eddy covariance; ii)
~~ii.~~ investigate seasonal, diurnal and spatial differences in VOC fluxes and concentrations; iii)

~~iii.~~ examine possible major source contributions of speciated VOCs in central London; and iv) compare measured fluxes with those estimated by the London and National Atmospheric Emissions Inventories.

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These observations were made as part of the ClearfLo (Clean air for London) project, which provided integrated short-term and long-term measurements of meteorology, gas phase and particulate pollutants over London and surrounding areas during 2011 and 2012 (Bohnenstengel et al., 2015~~2014~~).

2 Methods

2.1 Measurement site

Micrometeorological flux measurements were made during the period ~~from~~ 7th August - 19th December 2012 from a flux tower located on the roof of a building belonging to King's College, University of London (51.511667 ~~°30'42"~~N 0.116667~~°07'00"~~ W, ground altitude 30 m a.s.l.) on the Strand in central London. Although the site is within the London Congestion Charge Zone (an area encompassing central London requiring road tolls to be paid and hence an area with reduced traffic density~~regularly~~), surrounding roads supported a medium to high traffic volume (annual average of 50000-80000 vehicles per day, (Department for Transport, 2014)) with the River~~river~~ Thames situated 200 m to the south. This site is classified as Local Climate Zone (LCZ) Class 2 Compact Midrise according to Stewart and ~~an~~ Oke (2012) (i.e. dense mix of midrise~~2006) urban class 2 site (intensely developed high density with 2–5 storey, attached or very close-set~~ buildings (3–9 stories), few or no trees, land cover mostly paved,~~made of brick or~~ stone, brick, tile, and concrete construction materials). Land cover types (in %) were calculated based on the Ordinance Survey map for the 9 km^2 area (Figure 1) encompassing the site and are: roads (37 %), buildings (31 %), other paved areas (14 %), unpaved/ vegetation (11 %), and water bodies (7 %).

~~e.g. old city core).~~ The sampling inlet and sonic anemometer were mounted on a triangular mast (Aluma T45-H) at approx. 60.9 m (2.3 times~~x~~ mean building height, z_H) above ground level (a.g.l.). The mean building height was around 25 m and the mast was located on an elevated area in the centre of the roof. A street canyon was located to the NW and an enclosed parking area to the SE, but generally surrounding buildings were of equal height. The sampling point (which we call KCL) is located 37 m~~.), several meters~~ west of a sampling point (~~the~~ KSS) that has been ~~site (i.e. KSSW)~~ used for long-term energy and CO_2 flux measurements (Kotthaus and Grimmond, 2012). Although the site is not optimal for micrometeorological flux measurements due to the heterogeneity of the urban canopy, its suitability has been assessed

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in detail by Kotthaus and Grimmond (2014a; 2014b). This study describes~~The mean building height was around 25 m and the mast was located on an elevated area in the centre of the roof. A street canyon was located directly to the NW and an enclosed parking area to the SE, but generally surrounding buildings were of equal height. Kotthaus and Grimmond (2013) describe~~ in detail the measurement area and investigates~~investigate~~ the influence of source area characteristics on long-term radiation and turbulent heat fluxes for the KSS site. They conclude that the site can yield reasonable data on surface to atmosphere fluxes~~, which is in the same area~~.

The weather in 2012 was somewhat cooler than the ~~(~~1981 to 2010~~)~~ long-term mean for London during summer and autumn, with several cold fronts bringing up to twice as much precipitation and associated winds as average, suppressing pollution levels. However, during~~During~~ the period of the Olympic~~Olympics~~ and Paralympic Games~~Paralympics~~ (27th July – 12th August and 29th August – 9th September 2012) the weather was hot and dry causing sustained pollution peaks. Winter 2012/2013 was generally warmer and drier in London than the 1981-2010 mean (Met Office, 2013).

2.2 Instrumentation and data acquisition

The CSAT3 sonic anemometer (Campbell Scientific) and inlet were faced~~facing~~ toward the predominant wind direction (SW) to minimise flow distortion. Data from the sonic anemometer were logged at a frequency of 10 Hz and flux measurements were calculated using 25 min~~minute~~ averaging periods. The rotation angle theta (θ), used to correct measurements of the vertical wind velocity for minor misalignment of the sonic anemometer, showed no significant disturbance of the turbulence from interactions with the building when plotted against wind direction. Data were recorded in UTC (Universal Time Coordinated),~~)~~ which is one hour earlier than local time in summer and coincident with Greenwich Mean Time in winter. However, all analyses used local time.

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VOC concentrations were measured using a high sensitivity proton transfer reaction-(quadrupole) mass spectrometer (PTR-MS) (Ionicon Analytik GmbH, Innsbruck, Austria) with three Varian turbo-molecular pumps (see for example de Gouw and Warneke, 2007~~(see Lindinger et al., 1998; de Gouw and Warneke, 2007~~; Hayward et al., 2002; Lindinger et al., 1998 for more detailed description of the instrument). Air was drawn through an inlet co-located with the sonic anemometer.~~ on the flux tower approx. 60.9 m a.g.l.~~ Sample air was purged through a ~ 30 m ½” OD (3/8” ID) PTFE tube at a flow rate of 81 L min^{-1} to the PTR-MS, which was housed in a utility room below. The high flow rate ensured turbulent flow was maintained and signal attenuation minimised (Reynolds number, Re = 11177). During the campaign, PTR-MS operating parameters were maintained at 1.95 mbar, 510 V and 50 °C for drift tube pressure, voltage and temperature respectively, to achieve an E/N (E: electric field strength, N: buffer gas number density) ratio of 123 Td (1 Td = 10^{-17} V cm^{2}). This field strength forms a compromise between reagent ion clustering and fragmentation suppression (Hewitt et al., 2003). Further instrument parameters and meteorological conditions are summarized in Table 1. The inlet flow rate into the instrument was ~~held at~~ 0.25-0.3 L min^{-1}.

The logging program was written in LabVIEW (National Instruments, Austin, Texas, USA) and operated the PTR-MS in multiple ion detection (MID) and SCAN modes for VOC concentrations of nine selected masses and a range of the protonated mass spectrum *m/z* 21-206 respectively. The sonic anemometer was not directly interfaced with the LabVIEW logging program, requiring the measurements to be synchronised during post-processing through the use of a cross-correlation function between the vertical wind velocity w and the VOC ion counts c. A valve system controlled the measurement cycle, which consisted ~~consisting~~ of 5 min zero air (ZA), 25 min MID followed by further 5 min SCAN of sample air and 25 min MID mode. During the ZA cycle, air was pumped through a custom-made gas calibration unit (GCU) fitted with a platinum catalyst heated to 200°C to provide instrument background values at ambient humidity. In MID mode the quadrupole scanned nine predetermined protonated masses with a dwell time of 0.5 s each to which the following compounds were ascribed: *m/z* 21 (indirectly quantified *m/z* 19 primary ion count via $[H_3{}^{18}O^+]$), *m/z* 33 (methanol), *m/z* 39 (indirectly quantified *m/z* 37 first cluster $[H_3O^+\ H_2O^+]$), *m/z* 42 (acetonitrile, results not shown), *m/z* 45 (acetaldehyde), *m/z* 59 (acetone/propanal), *m/z* 69 (isoprene/furan), *m/z* 79 (benzene), *m/z* 93 (toluene), *m/z* 107 (C_2-benzenes), and *m/z* 121 (C_3-benzenes, results not shown). The total cycle time was 5.5 s. Secondary electron multiplier (SEM) voltage, as well as O_2^+ (*m/z* 32) and photon "dark counts" (*m/z* 25) signals were monitored weekly.

The PTR-MS cannot distinguish between different compounds with the same integer mass, therefore isobaric interference can occur. For example, *m/z* 107 may result from~~is considered to be the sum of~~ several contributing C_8-aromatics: ethyl benzene, (m+p)-xylene, o-xylene and some benzaldehyde (Warneke et al., 2003). Further interferences at measured *m/z* from additional compounds and fragmentation for this instrument in an urban environment are discussed in Valach et al. (2014). Although the O_2^+ and water cluster ions were kept < 2 % of the primary ion, interferences from ^{17}O~~^{18}O~~$^{+}$ isotopes at *m/z* 33 were taken into account. ~~The sonic anemometer was not directly interfaced with the LabVIEW logging program requiring the measurements to be synchronised during post-processing through the use of a cross-correlation function between the vertical wind velocity *w* and the VOC ion counts *c*.~~

Single point calibrations were performed on-site once a month using a certified multiple component VOC gas standard (Ionimed, ~~since 23rd May 2013~~ part of Ionicon Analytik GmbH, Austria), which was validated by cross-calibration with a second independent VOC standard (Apel Riemer Environmental Inc., CO, USA). Before and after the campaign, multistep calibrations were performed with both standards. Standards were diluted with catalytically converted zero air, since cylinder concentrations were approx. 1 ppm ± 5 % uncertainty (Ionimed Analytik) and 0.5 ppm ± 10 % (Apel Riemer). Error propagation resulted in a total calibration uncertainty of < 20 %. Measured normalised instrument sensitivities (S_N, Table 1) based on Taipale et al. (2008) were used to convert normalised count rates (ncps) of protonated masses (RH^+) to volume mixing ratios (Langford et al., 2010a). Only the o-xylene

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isomer was present in the Ionimed standard, which was used to determine instrument sensitivities for *m/z* 107, but sensitivities agreed well when compared with sensitivities for p-xylene present in the Apel Riemer standard. Any remaining humidity effects on calibrations were previously investigated for this instrument and were found to be within the overall calibration uncertainty (Valach et al., 2014). Detection limits of VOC concentrations (Table 2) were calculated according to Taipale et al. (2008).

2.3 Flux calculations and quality assessment

Fluxes were calculated according to Karl et al. (2002) and Langford et al. (2009; 2010b) using:

$$F = \frac{1}{n}\sum_{i=1}^{n} w'\left(\frac{i-t_{lag}}{\Delta_{tw}}\right) * c'(i), \qquad \text{(Eq. 1)}$$

where w' and c' are the instantaneous fluctuations around the mean vertical wind ($w - \overline{w}$) and mean VOC concentration ($c - \bar{c}$), n is the number of VOC concentration measurements per 25 min averaging period (n = 273), t_{lag} is the lag time between the wind and PTR-MS measurement due to the transit through the sampling line, and Δ_{tw} is the sampling interval of the vertical wind speed measurements of the sonic anemometer (10 Hz = 0.1 s). Langford et al. (in review) recently demonstrated that the method used to determine the time lag becomes important where the signal-to-noise ratio of the analyser is poor, showing that methods that systematically search for a maximum in the cross-correlation function within a given window (MAX method) can bias the calculated fluxes towards more extreme (positive or negative) values. Their study recommends the use of a prescribed lag time determined either through the use of a monitored sample flow rate or by using the typical lag time derived by searching for a maximum. Here the prescribed lag times were determined by fitting a running mean to the time series of daytime lag times calculated using the MAX method for acetone, which had large fluxes and thus the clearest time-lags. Prescribed lag times for all other compounds were set relative to that of acetone, accounting for the offset introduced by the sequential sampling of the PTR-MS.

~~–~~Flux losses due to the attenuation of high and low frequency eddies were estimated for our measurement setup. High frequency flux attenuation was estimated to be on average 11 % using the method of Horst (1997), and a correction was applied. Attenuation from low frequency fluctuations for a 25 min flux period was investigated by re-analysing the sensible heat fluxes for longer averaging periods of 60, 90, 120 and 150 min. The coordinate rotation was applied to the joined files, which acted as a high pass filter to the three wind vectors, confirming that fluctuations of eddies with a longer time period than the averaging time did not contribute to the flux measurement (Moncrieff et al., 2004). The fluxes were compared back to the 25 min average fluxes, which had the coordinate rotation applied before joining, again to ensure only turbulent fluctuations of ≤ 25 min contributed to the flux (Supplementary information Figure A1). Flux losses due to low frequency attenuation were estimated to be < 1.5 % and, therefore, no corrections were deemed necessary. The error due to the disjunct sampling was estimated by comparing the sensible heat fluxes calculated from the continuous data series with those calculated from a disjunct data series using a set sampling interval of 5.5 s. The continuous data were averaged to match the sampling frequency of the disjunct data (i.e. 2 Hz). The difference between the eddy covariance and DEC sensible heat fluxes was minimal (0.01 %) and thus no additional corrections were applied.

Many of the 25 min resolved flux measurements were close to the limit of detection (LoD),~~)~~ based on 1 standard deviation using the method of Spirig et al. (2005), with an average fail rate of 82 %. Various techniques to statistically analyse or replace values below the LoD have been developed (Clarke, 1998). However~~, however~~, they often result in significant bias, either high or low depending on the value substituted, because values tend to be below the LoD when fluxes are indeed small (Helsel and Hirsch, 1992). In this study, our analysis focused on diurnally averaged flux profiles~~fluxes~~ and we decided not to filter out individual flux values on the basis of being < LoD in order to avoid this bias. When averaging the 25 min flux data it is appropriate to also average the LoD which, as shown by Langford et al. (in review), decreases with the square root of the number of samples averaged (*N*). Therefore, although the majority of the individual 25 min flux measurements were below the LoD, their diurnal average profiles~~averages~~ may exceed the LoD for the average and thus still yield important data on the net exchange of VOCs above the city.

$$\overline{LoD} = \frac{1}{N}\sqrt{\sum_{i=1}^{N} LoD^2}.$$ (Eq. 2)

The following describes the additionally applied filter criteria. 25 min flux values with a friction velocity (u_*) < 0.15 m s^{-1} were rejected (3.4 % of total data) due to insufficient turbulence. The stationarity test and data quality rating methods of Foken and Wichura (1996) and Velasco et al. (2005) were used, and 47 % of the data files were rejected on this basis. The high number of files rejected in the stationarity test is to be expected for eddy covariance measurements over highly heterogeneous canopies~~ where ergodicity cannot exist~~, although horizontally averaged canopy morphology recovers some surface~~planar~~ homogeneity. Furthermore, the low measurement height used can cause an increased sensitivity towards canopy roughness features resulting in non-stationarity. Since urban environments are inherently not ideal for micrometeorological flux measurements due to their heterogeneity, integral turbulence characteristics of this site were assessed by comparing the measured standard deviation of the vertical wind velocity (σ_w) normalised by u_* to the parameters of a modelled ideal turbulence (Foken et al., 2004). Results showed that 99.6 % of all the data were rated category six or better and 0.4 % were rejected using the criteria of Foken et al. (2004). This large pass rate gives further confidence that the measurements were not unduly affected by wake turbulence generated from the structure of the building. Erroneous meteorological data (2.6 % of total) were removed around wind directions of 14-15°, due to minor turbulence interferences from the presence of other sensors on the mast. Depending on compound between 40-~~–~~61 % of flux data (N = 1934–~~—~~2949) passed all of the above quality controls. Exactly 2014 h~~hours~~ of concentration data (N = 4834) were obtained. For consistency regression coefficients (R^2) were used throughout.

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The traffic densities used for the analysis were obtained from a nearby site at Marylebone Road (approx. 3 km to the NW) and consisted of hourly vehicle counts covering the period 7th -~~to~~ 22nd August 2012. The major roads of the Strand and the Embankment ~~areas~~ surrounding the measurement site support a comparable traffic volume with an annual average of 50000 - 80000 vehicles per day (Department for Transport, 2014) and diurnal patterns in traffic are likely to be similar across central London.

Photosynthetically active radiation (PAR) and CO_2 measurements used in the analysis were part of the ~~KSS~~ long-term micrometeorological measurements at the same site and covered the period from August to September for PAR and from August to December for CO_2 respectively. Average diurnal profiles were calculated for the boundary layer mixing height, which was measured using three LiDARs located on rooftops within central London during an approx. two week period in summer and winter 2012 (Bohnenstengel et al., 2015).

2.3.1 Flux footprint calculations

Although there are no operational footprint models for urban environments which take the complex topography and spatial variability in building height and surface heat fluxes into account, the analytical footprint model of~~suggested by~~ Kormann and Meixner (2001) has previously been applied in non-homogeneous terrain (Helfter et al., 2011; Neftel et al., 2008). The Kormann-Meixner (KM) model determines the 2D footprint density function explicitly from micrometeorological parameters, which are provided by the eddy covariance measurements, i.e., friction velocity (u_*), ~~Obukhov length (L), horizontal wind velocity at the~~ measurement height ~~(u~~(z_m), Obukhov length (L), horizontal wind velocity at the measurement height ($u(z_m)$), and ~~)),~~ standard deviation of the lateral wind (σ_v). ~~), and measurement height (z_m).~~ The flux footprints were calculated for each 25 min flux period. Neftel et al. (2008) developed a Microsoft Excel based tool, which allows the footprint contributions (%) of user-defined spatial elements to be mapped. In~~, in~~ this case we used a total of nine 1 km^2 grid squares to match the Ordinance Survey (OS) grid (Figure 1), centred on the measurement site.~~).~~ This grid resolution was validated using a simple parameterisation model (Kljun et al., 2004) with

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average diurnal cycle~~average~~ parameters for σ_w, u_*, and boundary layer height (z_i) during the campaign, which calculated the distance of the maximum flux contribution (X_{max}) and the extent of the 90 % flux footprint (X_{90}).

The KM footprint calculation requires the Monin-Obukhov stability parameter (ζ) to be within the interval [-3, 3], where

$$\zeta = \frac{z_m - d}{L}, \qquad \text{(Eq. 3)}$$

with d ($d = ⅔z_H = 16.7$ m) being the displacement height estimated as a fraction of the canopy height (Garrat, 1992). The footprint estimation for cases of extreme stability is of lower quality, but still provides useful information. The vertical turbulent flux $F_c(0,0,z_m)$ measured at the height z_m is related to the corresponding surface flux area $F_c(x,y,0)$ which is upwind of the measurement point, such that

$$F_c(0,0,z_m-d) = \int_{\infty}^{-\infty}\int_{0}^{\infty} F_c(x,y,z_m-d)\Phi(x,y,z_m-d)dxdy\,, \qquad \text{(Eq. 4)}$$

where z_m is the measurement height and the x-~~–~~axis is aligned with the mean horizontal wind direction. $\Phi(x,y,z_m-d)$ is the footprint function and includes a weighting function to describe the influence of a unit point source on the flux from any surface location *(x,y)*. In order to compare VOC fluxes with estimated emissions from the London Atmospheric Emissions Inventory (LAEI), a 9~~the 1~~ km^2 section of the 1 km^2 resolution OS grid system was used, which on average included 90 % of the footprint contribution to all measured fluxes. This area was limited to central London and partially included the following Boroughs: Westminster (squares 1, 4, 5 and 7), Southwark (2, 3 and 6), Camden (8) and the City of London (9) (Figure 1).

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3 Results and Discussion

3.1 Diurnal profiles of VOC fluxes and concentrations

Average diurnal cycles~~Diurnal averages~~ of measured VOC fluxes and mixing ratios are shown in Figure~~Figures~~ 2a and 2b with descriptive statistics for all the data summarized in Table 2. Largest~~Toluene and C_2-benzenes showed the largest~~ median ~~fluxes~~ (interquartile range in parenthesis) fluxes per day were from C_2-benzenes and toluene with 7.86 (~~of~~ 0.92-21.8) kg km~~33 (0.04-0.91) mg m~~$^{-2}$ d~~h~~$^{-1}$ and 7.26 (1.83-15.3) kg km~~0.30 (0.08-0.64) mg m~~$^{-2}$ d~~h~~$^{-1}$ respectively, followed by oxygenated compounds, i.e. methanol with 6.37 (~~(0.27 (0.12-0.42) mg m^{-}~~2.99-10.0) kg km^{-2} d^{-1},~~ h^{-1}),~~ acetaldehyde 3.29 (1.52-5.62) kg km^{-2} d^{-1},~~(0.14 (0.06-0.23) mg m^{-2} h^{-1}),~~ and acetone 5.24 (2.33-9.62) kg km^{-2} d^{-1}.~~(0.22 (0.10-0.40) mg m^{-2} h^{-1}).~~ Isoprene and benzene showed ~~the~~ smallest median fluxes with 2.14 (0.56-4.85) kg km^{-2} d~~0.09 (0.02-0.20) mg m^{-2} h~~$^{-1}$ and 1.78 (0.06-4.34) kg km~~07 (0.002-0.18) mg m~~$^{-2}$ d~~h~~$^{-1}$ respectively. The highest median mixing ratios were of the oxygenated compounds methanol (7.3 (6.8-7.9) ppb), acetone (0.95 (<LoD-1.36) ppb) and acetaldehyde (0.82 (0.59-1.13) ppb), followed by aromatics (C_2-benzenes, toluene and benzene), and isoprene.

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Oxygenated compounds commonly have relatively long atmospheric lifetimes and widespread origin~~sources~~ including anthropogenic and~~,~~ biogenic ~~and some atmospheric~~ sources and photochemistry, resulting in elevated concentrations and less pronounced diurnal profiles (Atkinson, 2000). Most VOC fluxes and concentrations were comparable to or lower than those previously observed in London (Langford et al., 2010b) and other UK cities (Langford et al., 2009), although C_2-benzene fluxes and concentrations, as well as isoprene and benzene concentrations were slightly higher. The discrepancy in isoprene and benzene concentrations is consistent with photochemical loss during transport to the higher measurement height of the previous studies~~study~~. Compared to other cities such as Houston Texas (Park et al., 2010) and Mexico City (Velasco et al., 2005), VOC fluxes and concentrations~~VOC fluxes~~ were lower, apart from C_2-benzenes which were comparable or higher, although it must be noted that C_2-benzenes in this study represent the sum of multiple VOC species. Unlike the other studies cited, Park et al. (2010) use relaxed eddy accumulation to measure VOC fluxes and hence the data obtained are not directly comparable with measurements made by EC-based methods.~~(Velasco et al., 2005).~~

Diurnal profiles of aromatic fluxes and concentrations presented clear double rush hour peaks during the morning and evening (07:00-10:00 and 17:00-20:00 local time). Concentration peaks are thought to be linked to additional advection of traffic-related pollution from larger commuter roads outside of the city centre, as well as boundary layer effects and photochemistry. VOC concentration measurements at canopy height can be affected by boundary layer depth (Vilà-Guerau de Arellano et al., 2009). The rush hour emission peaks mostly coincide with the boundary layer expansion and collapse and therefore the effect of each factor cannot be separated. The morning concentration peak was slightly higher than the evening peak across traffic-related species even though fluxes tended to be larger during the evening rush hour. Morning emissions enter a shallow nocturnal boundary layer leading to relatively larger concentrations compared with higher afternoon emissions entering a developed boundary layer, leading to relatively lower concentrations. This enhanced dilution effect is found more often during summer when the boundary layer mixing height is higher (Figure 2). Therefore, the regression analyses below only refer to data from August (cf Section 3.1.2 for comparisons with winter). Furthermore, increased photochemical degradation during the day removes VOCs, further contributing to the midday minimum in mixing ratios. The diurnal flux profiles of methanol, acetone, isoprene, and to a smaller extent acetaldehyde, showed one large peak just after midday (approx. 13:00 local time), which was only reflected in the concentration profiles of acetone and isoprene. Acetaldehyde concentrations presented a slight double peak similar to mixing ratios of aromatics. Methanol has a relatively long atmospheric lifetime and therefore high background concentrations, hence mixing ratios showed no distinct diurnal profile.

3.1.1 Correlations with possible controlling variables of VOC fluxes and concentrations

Aromatic compound fluxes closely followed the diurnal profile of traffic density with good correlations ($R^2 = 0.51$-0.92, $p<0.05$) and slightly lower fluxes observed on the weekends. In central urban areas in the UK traffic densities — and therefore traffic-related VOC fluxes — increase steadily throughout the day, with discernible peaks during morning, midday and evening (Nemitz et al., 2002), which was also observed in this study. ~~Diurnal profiles of concentrations for aromatics presented clear double rush-hour peaks during the morning and evening (07:00-10:00 and 17:00-20:00 local time), which is thought to be linked to advection from larger commuter roads outside of the city centre, as well as diurnal expansion and contraction of the boundary layer. This suggests that traffic-related emissions were the main contributors to fluxes and mixing ratios of aromatic compounds.~~ Previous studies have shown that the Marylebone Rd traffic count point can be used as a proxy representative of traffic flows throughout central London (Helfter et al., 2011).

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The aforementioned concentration dilution due to boundary layer expansion resulted in negative correlations between boundary layer height and aromatic mixing ratios during August ($R^2 = 0.33$-0.56, $p<0.01$). As aromatic compound fluxes slightly dipped around midday, the mixing ratios were diluted by the deep boundary layer. The above evidence suggests that traffic-related emissions were the main contributors to fluxes and mixing ratios of aromatic compounds. Acetone and isoprene showed peak midday fluxes, which maintained daytime mixing ratios and produced positive correlations with boundary layer height ($R^2 = 0.16$ and 0.59 respectively, $p<0.01$).~~diurnal flux profiles~~ De Gouw et al. (2005) reported that changes in boundary layer meteorology could result in greater effects on observed concentrations of methanol and~~,~~ acetone due to their high background values. The mixing ratios of these compounds are, therefore, likely dominated by advected pollution rather than the local flux. Possibly a combination of boundary layer and photochemical effects were seen with methanol mixing ratios, wherein correlations with mixing height were negative ($R^2 = 0.70$, $p<0.01$), whereas acetone and isoprene fluxes seemed ~~, and isoprene, and~~ to be sufficiently high during

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the day to maintain~~a smaller extent acetaldehyde, showed one large~~ peak ~~just after~~ midday mixing ratios (Figure 3 example of isoprene~~(approx. 13:00 local time~~). Vehicle emissions may have contributed to acetaldehyde and isoprene ~~their~~ levels directly or indirectly (Figure 3 example of isoprene),~~,~~ since ~~flux~~ correlations of ~~acetaldehyde and isoprene~~ fluxes with traffic density were fairly high (R^2 = 0.60 and 0.46 respectively, p<0.05). The~~Their~~ diurnal concentration profile of acetaldehyde to some degree~~profiles~~ mimicked those of traffic-related compounds~~the fluxes with isoprene and acetaldehyde~~ reflecting a slight double peak. ~~Methanol has a relatively long atmospheric lifetime, hence mixing ratios showed no clear diurnal profile.~~

VOC fluxes and concentrations plotted as a function of photosynthetically active radiation (PAR) showed strong daytime (defined as 06:00 to 18:00 local time~~GMT~~) correlations for methanol, acetaldehyde and isoprene fluxes (R^2 = 0.71-0.78, p<0.001) and concentrations (R^2 = 0.~~71-0.78 and 0.~~66-0.83, p<0.001~~01 respectively~~). Plotted as a function of temperature, high correlations with methanol, acetaldehyde and isoprene fluxes were seen (R^2 = 0.75, 0.63, and 0.94, p<0.001 respectively),~~) were seen,~~ whereas only methanol and acetone concentrations showed higher correlations with temperature (R^2 = 0.64 and 0.81, p<0.001 respectively). Methanol fluxes correlated linearly with temperature (R^2 = 0.75, p<0.001), but acetaldehyde and isoprene fluxes ~~had exponential relationships~~ (R^2 = 0.64 and 0.94, p<0.01) ~~for fluxes~~ and mixing ratios (R^2 = 0.45 and 0.55, p<0.01) had exponential relationships with temperature (Figure 3 example of isoprene). The relationships of mixing ratios with PAR and temperature for these compounds improved greatly when ~~excluding~~ night time values were excluded (defined as PAR <100 μmol m^{-2} s^{-1}) and when times~~points~~ of low temperature (< 5 °C) were excluded. This indicates~~), indicating~~ either separate source contributions or effects of boundary layer meteorology in these instances, whereby increased~~. Increased~~ mixing ratios of these compounds with low PAR and temperature ~~are~~ likely result from~~effects of~~ reduced dilution within a shallow boundary layer, e.g., at night or in winter, but also possible contributions of anthropogenic sources such as exhaust emissions, which are largely

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independent of light and temperature. Increases in concentrations due to high PAR and temperature suggest biogenic sources, increased evaporative emissions, and/or secondary atmospheric formation driven by oxidation of precursor hydrocarbons (Singh et al., 1994). Oxygenated compounds have a variety of different source contributions such as tailpipe~~tail pipe~~ emissions, evaporative emissions from fuel and solvents, direct emissions from plants, leaf decomposition, and secondary atmospheric production (Langford et al., 2009 and references therein).

~~-~~Modelling studies have indicated that the contribution of secondary atmospheric formation to VOC concentrations could be more significant, especially in urban areas, during summer, i.e. with high PAR and temperatures (Harley and Cass, 1994; de Gouw et al., 2005)~~.~~.~~ reported that background values could be more important for methanol and acetone concentrations, which could cause changes in boundary layer meteorology to result in greater effects on observed concentrations. Furthermore, acetaldehyde concentrations are more often affected by secondary atmospheric formation. The observed light and temperature responses associated with isoprene fluxes and mixing ratios in August and September can be explained by biogenic sources (cf Section 3.1.3).~~ Acetone fluxes reached a maximum when PAR and temperature were around 1000 µmol m^{-2} s^{-1} and 15-20 °C respectively, before declining, whereas mixing ratios increased exponentially with light and temperature. These observations resemble~~mimic~~ measurements over forest canopies (e.g. Schade and Goldstein, 2001).~~(Schade and Goldstein, 2001).~~ Aromatic compound concentrations and fluxes showed no correlations with PAR. Weak negative correlations were seen between~~with~~ aromatic concentrations and temperature and weakly positive correlations between~~with~~ fluxes and temperature, likely due to increased thermal mixing. The observed light and temperature responses associated with isoprene fluxes and mixing ratios in August and September can be explained by biogenic sources (cf Section 3.1.3).

3.1.2 Seasonal variability of VOC sources and meteorology

Most compounds showed larger fluxes in August and September than in October, November and December, with the exception of acetaldehyde which also showed increased fluxes in December (Figure 4 top~~A~~). Increased acetaldehyde fluxes in December may have resulted from an additional source, such as domestic biomass burning (Andreae and Merlet, 2001; Lipari et al., 1984~~;~~ Andreae and Merlet, 2001), although there are only few residential buildings in this area of London. Only toluene fluxes in September were significantly higher than in other months and benzene fluxes showed no significant seasonal differences. Seasonal variability in fluxes was likely due to increased emissions in summer, especially for compounds with biogenic and secondary atmospheric sources. Average monthly meteorological parameters are summarized in Table 3.

Mixing ratios of aromatics were generally lower in summer and highest in December (Figure 4 bottom~~B~~). This is likely due to less dilution effects in winter when the boundary layer is shallow or from advection of additional sources such as heating, since there was no increase in fluxes. Generally, in summer the boundary layer mixing height is higher and collapses later in the evening which maintains the dilution effect for VOC concentrations. In winter the average boundary layer mixing height is lower. It develops later in the morning and collapses earlier in the afternoon, which could increase overall VOC mixing ratios, but also individual maxima, e.g. during rush hours. Comparing average diurnal profiles of compound mixing ratios with boundary layer height during summer and winter showed that aromatic compound concentrations were associated with negative correlations in summer (cf Section 3.1.1) which became positive during winter (R^2 = 0.10-0.33, p<0.01), while fluxes maintained positive correlations with boundary layer height regardless of season. This suggests boundary layer effects may be an important driver of increased concentrations in winter. Furthermore,~~ and~~ traffic counts for the Congestion Charge Zone in central London indicate lower monthly average vehicle counts in December (Department for Transport~~DfT~~, 2014). Oxygenated compounds and isoprene mixing ratios were highest in summer with the exception of acetone,

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which increased in December likely either from boundary layer effects, reduced photochemical degradation, or advection. Correlations~~Mean daytime maxima~~ of mixing ratios and fluxes with~~diurnal profiles for the~~ boundary layer ~~mixing~~ height ~~measured using three LiDARs located on rooftops within central London~~ were positive for acetone and isoprene during~~between 1700 m in~~ summer and ~~900 m in~~ winter, whereas methanol and acetaldehyde presented negative correlations during summer indicating stronger dilution effects (cf Section 3.1.1).

~~(Bohnenstengel et al., 2014).~~ Increased summer mixing ratios of oxygenated compounds and isoprene indicated a temperature dependent, possibly biogenic source contribution. While biogenic emissions may be advected from outside of the city, the concurrent increase in isoprene fluxes suggests the source to be largely local to the flux footprint. The temperature dependent fraction of observed isoprene mixing ratios, which may include advected pollution, was estimated using the isoprene temperature response function~~equation~~ from Figure 9 in Langford et al. (2010b), which estimated a 30 % and 20 % contribution in August and September respectively. These values were significantly higher than for iso-pentane, a non-biogenic compound available from the Automatic Hydrocarbon Network, to which the same analysis was applied. The temperature dependent component of isoprene in October, November and December showed no significant difference to that of iso-pentane, suggesting the biogenic component was reduced or absent at lower temperatures. High correlations of *m/z* 69 with light and temperature during August and September indicate that isoprene was the likely major component during these months, however the rest of the period the contribution of additional~~other~~ compounds such as furan and other alkenes at that mass may have increased, thereby overestimating the isoprene signal (Yuan et al., 2014).

3.1.3 Modelling the biogenic isoprene contribution in London

An attempt was made to model the biogenic isoprene component during August and September using the light and temperature algorithms of Guenther et al. (1995), hereafter termed G95. The foliar emissions based model calculates VOC fluxes as follows;

$$F = D \times \varepsilon \times \gamma, \qquad \text{(Eq. 5)}$$

where D is the foliar density (kg dry matter m^{-2}), $\boldsymbol{\varepsilon}$ is an ecosystem dependent base emission rate (µg C m^{-2} s^{-1} normalised to a PAR flux of 1000 µmol m^{-2} s^{-1} and leaf temperature of 303.15 K), and γ is a dimensionless activity adjustment factor accounting for the effects of PAR and leaf temperature. Ambient air temperature and PAR measurements were used to calculate the light and temperature controlled parameters C_L and C_T for γ, where~~,~~

$$\gamma = C_L \times C_{T.} \qquad \text{(Eq. 6)}$$

The slope of the linear regression of the measured total isoprene flux and γ provided an emission factor in mg m^{-2} h^{-1}, which was converted to µg g^{-1} h^{-1} by dividing by the foliar density ~~(~~D = 0.~~(~~129 kg~~g~~ m^{-2}). The foliar density was estimated using the total tree leaf area as seen from visible satellite imagery within the flux footprint ~~(approx. 9%)~~ and tree leaf dry weight for representative species commonly planted in the area such as *Platanus x acerifolia* (City of Westminster, 2009), which are also high isoprene emitters (Geron et al., 1994). The resulting base emission rate $\boldsymbol{\varepsilon}$ from the measured fluxes was 6.5 µg g^{-1} h^{-1} which compares well with the figure given in the literature (5 µg g^{-1} h^{-1}) for cities in a cool climate (Guenther et al., 1995). For details~~These estimates are representative~~ of this calculation, see the Supplementary Information B. These estimates are representative of ~~biogenic isoprene fluxes from a highly heterogeneous canopy within~~ the biogenic isoprene fluxes from a highly heterogeneous canopy within~~flux footprint, including both high and low isoprene emitting species as well as low average foliar density due to~~ the flux footprint, including both high and low isoprene emitting species as well as low average foliar density due to the sparse distribution of urban roadside and park trees. Green areas, as defined on the OS map, comprised 9 % of the total grid area and were evenly distributed across the 9 km^2.~~sparse distribution of urban roadside and park trees.~~ Only grid square 1 included a large green area of 23 ha (St. James' Park). The National Forest Inventory (NFI) England only included 4.4 % green areas within the grid selection (NFI, 2012). The NFI excluded individual trees in parks and avenues, which can encompass up to 50 % of trees maintained by the local authority in central London (City of Westminster, 2009).

Figure 5a and b~~5~~ shows that the modelled isoprene fluxes using the calculated base emission rate ~~by wind direction~~ compared well with the measured fluxes by wind direction.~~-~~ Linear regressions from wind directions that have a strong anthropogenic component are lower, e.g. W (R^2 = 0.13, p<0.001), than from those areas dominated by biogenic sources, e.g. SE (R^2 = 0.81, p<0.001) due to~~with~~ the nearby Temple Gardens. Modelled emissions~~fluxes~~ seemingly underestimated observed isoprene fluxes since these included the traffic component, however it appears that biogenic isoprene represents a detectable source contribution in summer.

3.2 VOC/VOC correlations and ratios

Correlations of VOC/VOC ~~correlations for~~ fluxes ~~indicated~~ (R^2 = 0.40-~~ and~~ 0.62, p<0.001) indicated two groups of compounds with good correlations within each group, i.e. compounds related to ~~non-~~traffic sources such as aromatics, and oxygenated and biogenic compounds, such as methanol, acetone and isoprene (Figure 6 top). Correlations of~~had higher correlations.~~ VOC/VOC ~~correlations for~~ concentrations (R^2 =~~between~~ 0.13-0.84, p<0.001) showed highest correlations between traffic-~~-~~related compounds (R^2 =~~between~~ 0.45-0.84, p<0.001) and good correlations between the oxygenated and biogenic compounds ~~and isoprene~~ (R^2 =~~between~~ 0.55-0.69, p<0.001) (Figure 6 bottom). High~~). Higher~~ correlations between oxygenated VOCs could indicate source commonality or formation mechanisms that depend on similar environmental factors. Scatterplots between aromatic compounds and isoprene/oxygenated compounds tend~~tended~~ to show bimodal distributions indicating separate source contributions.~~ (Figure 6, left panel).~~ Using temperature or, to a smaller extent, PAR as a third variable highlights a temperature or light dependency of the second source supporting the existence of additional biogenic and/or atmospheric sources. In the example of isoprene against benzene the relationship changes with temperature from 2:1 to 1:2.

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3.2.1 Benzene to toluene ratios

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Benzene to toluene (b/t) ratios can help identify source types and changes in ratios can indicate the photochemical age of an air mass as toluene reacts at a faster rate with OH in the atmosphere, assuming sufficient OH concentrations to drive the reaction (Warneke et al., 2007). Median (and interquartile range, IQR) b/t flux ratios were 0.21 (0.02-0.43) and median (IQR) b/t concentration ratios were ~~for fluxes and~~ 0.45 (0.39-0.48).~~) for concentrations respectively and are comparable to those reported in the literature (Heeb et al., 2000; Langford et al., 2009; Valach et al., 2014).~~ Individual maxima and minima were seen in the b/t concentration ratios, examples of which are discussed below.

The observed ratios compared well with those of other European cities, which showed b/t concentration ratios of 0.35 in Zurich (Heeb et al., 2000), 0.57 in Manchester (Langford et al., 2009), 0.57-0.63 in London (Valach et al., 2014), and 0.1 at 190 m above London (Langford et al., 2010b). Traffic related emissions are considered to be an important source of benzene and toluene in London. B~~ with a b~~/t exhaust emission ratios~~ratio of 0.4~~ based on derived yearly emissions in other megacities, such as Mexico City, were found to be 0.4 (Zavala et al., 2006), which agreed well with observed b/t concentration ratios in this study.~~(Zavala et al., 2006) and measurements ranging from 0.32 to 0.65 (Rogers et al., 2006).~~ Airborne flux measurements over Mexico City have shown average b/t flux ratios of 0.31 with lower ratios of 0.07 to 0.1 over industrial areas due to increased toluene emissions from industrial processes (Karl et al., 2009; Velasco et al., 2007).~~(Karl et al., 2009; Velasco et al., 2007). Average observed b/t concentration ratios of 0.26 (Karl et al., 2009), 0.25 (Rogers et al., 2006) and 0.20 (Velasco et al., 2007) have been observed in other megacities. Observed b/t concentration ratios agreed with the assumed 0.4 traffic related emission ratio, however b/t flux ratios were lower.~~ Evaporative emissions from gasoline or direct industrial toluene emissions may have contributed to the lower b/t flux ratios in London. Furthermore, low b/t concentration ratios of 0.26 from diesel emissions ~~of 0.26~~ have been reported (Corrêa and Arbilla, 2006).~~(Corrêa and Arbilla, 2006).~~ The widespread use of diesel fuel in London (buses, taxis and some cars and trains) and diesel emissions from roads which exclude passenger cars~~exclusively permitting buses and taxis~~, such as Oxford Street (approx. 1.3 km W from the measurement site) or central railway nodes, such as Waterloo Railway~~Train~~ Station (1 km to the S), may have affected b/t ratios.

~~-~~Wind speed and direction can play a role for b/t concentration ratios by transporting pollution over longer distances allowing more time to react with or exposure to higher OH concentrations, thus increasing the ratio. An example of this (Figure 7) was seen on the 12th August when median (IQR) b/t concentration ratios reached 0.5 (0.45-0.56) with stronger SE winds (mean 3.67 m s^{-1}) possibly advecting pollution from Benelux/Northern Europe, whereas on the 9th August median b/t ratios were 0.34 (0.30-0.38) with low wind speeds (mean 1.28 m s^{-1}) indicating higher contributions of local sources (i.e. 60 % London influence) (Bohnenstengel et al., 2014). On both days OH concentrations above London were around 1.25 x 10^{6} molecules cm^{-3} and b/t flux ratios were not significantly different making pollution advection a likely cause of the observed difference (L. Whalley, personal~~private~~ communication 2014). Calculated back trajectories using the HYSPLIT trajectory model (Hybrid Single Particle Lagrangian Integrated Trajectory Model (Draxler and Rolph, 2014)) were run at 3 h~~-hour~~ intervals starting at ground-level (10 m~~10m~~) from London and propagated 24 h~~24h~~ backwards in time. These agreed with the changes in measured b/t ratios (Figure 7) and during episodes of high b/t ratios indicated that air masses passed over continental Europe within the past day which could have entrained pollution.

~~-~~The median monthly b/t flux ratio during the measurement period stayed between 0.18 and 0.26, which is to be expected since only local fluxes were detected, however the median (IQR) monthly b/t ratio for concentrations steadily increased from 0.41 (0.36-0.47) to 0.62 (0.55-0.70) from August to December. Advected~~Assuming less local photochemical removal during the winter months, as OH concentrations in London are often below the detection limit during winter (Bohnenstengel et al., 2014), this implies advected~~ pollution from mainland Europe may be common in winter or biomass burning may play a greater role in colder months, as this is associated with higher b/t ratios, e.g. 1.67 (Lemieux et al., 2004), due to the different fuel combustion emission profile. Furthermore, OH concentrations in London are often below the detection limit during winter (Bohnenstengel et al., 2015) resulting in less local photochemical removal during the winter months.

Median (IQR) concentration ratios for benzene to C_2-benzenes were 0.31 (0.28-0.33) and toluene to C_2-benenes were 0.72 (0.63-0.81), which both agree with previous values and suggest that these masses are indeed the ascribed traffic-~~-~~related compounds (Heeb et al., 2000; Warneke et al, 2001).

3.2.2 VOC to CO_2 correlations and ratios

Good correlations were found between averaged VOC fluxes plotted as a function of averaged CO_2 fluxes, which were measured concurrently at the site (R^2 = 0.03-0.81, p<0.001).~~Generally, good correlations were found between averaged Correlations of VOC andwith CO_2 fluxes measured concurrently at theon site were low (R^2 = 0.0306-0.8121, p<0.001).~~ Traffic-related compounds were initially ~~), but mostly comparable with values from a previous study in London, which ranged from R^2 = 0.09-0.26 (Harrison et al., 2012). In this study acetaldehyde showed the highest and isoprene was~~ among the lowest correlations with CO_2 fluxes (R^2 = 0.03-0.48, p<0.01). However, when points of peak CO_2 fluxes were removed ~~, which is opposite to~~ the correlations with traffic-related VOC fluxes~~Harrison et al. study. This may indicate in the case of acetaldehyde~~ increased significantly to R^2 = 0.65-0.91 (p<0.001). Presumably, the initial poor correlations resulted from an additional strong CO_2 source, such as vents from gas-fired boilers in nearby buildings, ~~that~~which ~~is not a shared source of~~have a lower source commonality with aromatic VOCs, i.e. a lower VOC/CO_2 emission ratio than that of traffic emissions for aromatic compounds. The London Atmospheric Emissions Inventory indicates that VOC/CO_2 flux ratios for benzene are higher for traffic emission sources (i.e. 2×10^{-5}) than gas sources (i.e. 0.6×10^{-5}) within the flux footprint (LAEI, 2013). The improved correlations ~~is~~are greater ~~and~~ for traffic-related compounds due to the limited range of source types contributing~~ions~~ to this group compared with oxygenated/biogenic compounds. The

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regression coefficient (R^2) of benzene ~~isoprene reduced source commonality~~ with CO_2 fluxes increaseds from 0.48 to 0.91, whereas~~during the respective measurement periods. Concentration correlations were highest~~ for isoprene fluxes the increase was small, i.e. 0.68 to 0.70 (Figure 8), as isoprene has a range of different sources ~~shares~~ of which only few are commonly shared ~~sources~~ with CO_2.

The presence of a strong separate CO_2 source within the flux footprint is supported by the high averaged VOC to CO_2 concentration correlations for traffic-related compounds (R^2 = 0.92-0.96, $p<0.001$). This differs from the fluxes, which are influenced only by sources in the flux footprint, where one strong point source with a different emission ratio may have a larger effect on emission rates of one compound but not the other. Concentrations are influenced by advected pollution from outside the flux footprint for both CO_2 and VOCs, where shared emission sources with relatively higher VOC/CO_2 ratios are more widespread. Averaged VOC to CO_2 concentration correlations ~~were~~were ~~highest for traffic-related compounds (R^2 = 0.92-~~0.96~~traffic related compounds (R^2 = 0.25-0.44, $p<0.001$) and~~ lower for~~with~~ the ~~other~~ oxygenated/biogenic compounds (R^2 = ~~<~~0.71-0.90~~11~~, $p<0.05$). ~~) with acetone showing no significant relationship (p=0.88). Most compound flux and concentration correlations with CO_2 significantly increased towards December (R^2 ≤0.49 and ≤0.86, respectively) reflecting the increased commonality of combustion sources towards winter. Only correlations with C_2-benzene fluxes declined in November and December.~~

Median VOC/CO_2 flux ratios ranged from 1.7 × 10^{-5}~~0.05~~ to 7.7 × 10^{-5} (mg m^{-2} h^{-1}/ mg m^{-2} h^{-1})~~0.26~~ with isoprene and benzene showing low ratios due to their low fluxes, and toluene and C_2-benzenes high ratios. Highest flux ratios for all compounds were with W winds, whereas lowest for biogenic compounds with N and for traffic-~~-~~related compounds S wind directions. Flux ratios declined towards December as CO_2 fluxes increased and VOC fluxes decreased. Similarly, VOC/CO_2 concentration ratios were between 0.45 × 10^{-6} and 14.6 × 10^{-6} (ppb/ppb) with isoprene and benzene representing the lowest and methanol and acetone the highest

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ratios. Highest concentration ratios were seen in August for oxygenated compounds/isoprene and December for traffic-related species.

3.3 Wind direction and flux footprint analysis

Polar Annulus and Polar plots were constructed for VOC fluxes and mixing ratios respectively and representative compounds are shown (Figure 9~~8~~). Polar plots use a generalized additive model (GAM) to interpolate between wind direction and wind speed averaged data points within the OpenAir package in R (see Carslaw and Ropkins, 2012~~Wood, 2006~~; Hastie and Tibshirani, 1990; Wood, 2006).~~Carslaw and Ropkins, 2012).~~ Polar Annulus plots averaged~~average~~ by time of day instead of wind speed ~~and~~ show diurnal variability with wind direction. The majority of the time (83 %) unstable and near neutral conditions prevailed ($\zeta < 0.2$), although the frequency varied between months with 87 %, 89 %, 82 %, 84 % and 69 % during August, September, October, November and December, respectively. Wind directions~~direction~~ with mostly unstable conditions were with W and S winds and near neutral with N or E winds. Mixing ratios were on average highest with low wind speeds (showing a negative correlation) when pollutants accumulate due to reduced mixing, indicating local emissions (Figure 9~~8~~, bottom).

Largest fluxes for all compounds were from the NW with either one daytime peak (e.g. isoprene) or two distinct rush hour peaks (e.g. benzene) (Figure 9~~8~~, top). On average fluxes were largest from the W>E≥N>S (F-statistic =~~between~~ 60.37-~~ and~~ 227.06, p<0.001),~~)~~ because of increased emission rates of specific compound sources. Separated by month, fluxes were largest from W>N>E≥S in August and September, whereas during October, November and December fluxes followed the pattern W>E≥N>S. The flux footprint in this study was relatively small compared with that of measurements previously made at 190 m height from the BT Tower in central London (Langford et al., 2010b). Due to the relatively low measurement height in this study, flux measurements were always closely coupled~~the flux footprint was limited to the immediate surrounding area allowing close coupling~~ with the surface layer, unlike

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measurements by Langford et al. (2010b), which were at times disconnected from the~~ and similar~~ surface layer during stable night time conditions.

~~roughness. ~~The average length of the maximum flux footprint contribution (X_{max}) was around 330 m and 90 % of all the fluxes (X_{90}) originated from within 900 m. The median footprint area was 1.8 km^2. This established that the majority of emission sources contributing to the measured fluxes must have been local. Additionally, the selected emission grid (cf Section 2.3.1 above) encompassed 97 % of the footprint with S and W wind directions, but only 80 % and 84 % during E and N winds. Grid square 5 represented the maximum contribution area since it encompassed the measurement point. Average footprint contributions (mean ± SD) comprised of grid squares 1 (2 % ± 4 %), 2 (5 % ± 7 %), 4 (4 % ± 5 %) and 5 (52 % ± 31 %) during S and W wind conditions, squares 6 (4 % ± 9 %) and 9 (4 % ± 10 %) indicated E wind conditions, and square 8 (18 % ± 27 %) N wind conditions. During October contributions from square 9 increased to 10 % and were more frequent at 30 % in December. Squares 3 (0.6 % ± 2 %) and 7 (0.9 % ± 2 %) provided minimal average contributions.

~~Green areas, as defined on the OS map, within the grid were evenly distributed across the 9 km^2 and comprised 8.8% of the total grid area, half of which was captured by the National Forest Inventory England (NFI, 2012). This definition excluded individual trees in parks and avenues, which can encompass up to 50% of trees maintained by the council in central London (City of Westminster, 2009).~~The River ~~Since footprints were relatively small it is possible that the ~~Thames ~~River ~~to the S may have caused the low fluxes associated with S winds (i.e. squares 1, 2 and 3). Contributions of ~~For ~~traffic-~~-~~related compound fluxes ~~there~~ were statistically significant ~~contributions ~~from the W (i.e. squares 4, 5, and 7), followed by the N (square 8) and E (squares 6 and 9) likely from the nearby heavily trafficked roads (Kingsway, Charing Cross, Strand and Blackfriars areas, respectively). Biogenic compound~~For isoprene, and to some degree methanol and acetaldehyde,~~ fluxes were highest from the W and E which coincides with significant nearby green areas ~~being ~~within the flux~~maximum contributing distance (X_{max}) of the~~ footprint.

~~(300 m).~~ Correlations of fluxes with grid square contributions in the footprint ~~with fluxes~~ can also give information on emission source strengths within the respective grid square (Figure 1).~~emission rates.~~ Generally positive correlations with fluxes across most compounds were seen from the W (squares 4, 5 and 7) confirming that high emission rates~~increased emissions~~ from sources within these grid squares were~~are~~ driving the large~~high~~ fluxes. Strongest correlations of fluxes with contributions from squares 4, 5, and 7 were seen~~, although these were largest (R = 0.40-0.46, p<0.001)~~ during October and November (R^2 = 0.40-0.46, p<0.001),~~,~~ especially for masses associated with biogenic sources (*m/z* 33, 45, 59 and 69). Square 8 showed positive correlations for benzene and only in August for all compounds. Correlations of fluxes with contributions from squares 1, 2, 3, 6 and 9 were negative indicating weaker emission sources in these squares or increased VOC deposition.

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Highest mixing ratios with wind direction were from E>N≥W>S for traffic-~~-~~related compounds, whereas oxygenated compounds/isoprene followed a similar pattern as the fluxes of W≥E>N≥S (F-statistic =~~:~~ 47.49-86.95, p<0.001). Easterly winds in London are often associated with synoptic conditions that bring European Continental air masses to the UK, resulting in higher background concentrations. Furthermore, since the boundary layer was on average more stably stratified and mixing heights were lowest (640 ± 80 m) with E wind conditions, it is likely that pollutant concentrations were allowed to build up resulting in the observed higher concentrations to the E for the more ubiquitous compounds, whereas concentrations of compounds with biogenic contributions additionally had strong sources~~source areas~~ to the W, such as several green areas~~parks~~ (St. James' Park, Hyde Park and Regents Park, total 331 ha).

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3.4 Comparisons with London and National Atmospheric Emissions Inventories

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The London Atmospheric Emissions Inventory (LAEI) and National Atmospheric Emissions Inventory~~Inventories~~ (NAEI) produce yearly~~biannual~~ emission estimates over the 1 km² OS grid for a range of pollutants and emission sources. Total VOC emission estimates are provided, but only benzene and 1,3-butadiene are estimated~~listed~~ separately. Measured emissions were compared with annual estimated emissions for the above OS grid area selection from 2012 for benzene using the LAEI and indirectly speciated VOCs of the NAEI. Using the average flux footprint, the grid square estimates were compared with the scaled flux measurements from the equivalent area (Figure 10).~~.~~

LAEI emission estimates included contributions from major (69 %) and minor roads (4 %), as well as evaporative emissions (27 %) (LAEI, 2012). No data were available on cold start emissions for benzene. The calculated standard errors provided some uncertainty approximation. Measured fluxes compared well with emission estimates, although the LAEI predicted slightly smaller benzene fluxes.~~ (Figure 9).~~ Comparisons of fluxes with wind directions (Section 3.3) agreed well with the LAEI emission estimates for the respective grid squares with highest emissions from squares 4, 5, 7 and 8 (i.e. W and N directions). This comparison assumes that the benzene fluxes during the measurement period were representative of annual emissions with any significant seasonal variation in benzene emission rates captured in this five month period. Section 3.1.2 confirmed that there was little month-to-month variability in the benzene flux.

Using speciated VOC emission contributions (% of total VOC emissions) for 2006 (Bush et al., 2006)~~(NAEI Reference: 45321001/0/AO6069/NP)~~ and emission maps from 2012 for total non-methane VOC emissions, speciated estimates could be compared with observations (Figure 10). The~~9).~~ NAEI includes a wide~~wider~~ range of emission sources divided into 11 SNAP (Selected Nomenclature for sources of Air Pollution) sectors including industrial, commercial and residential processes, transport, waste treatment, solvent use, point sources, agriculture and nature, although the latter two were unavailable for the London urban area. NAEI estimates for benzene exceed the LAEI due to the inclusion of a wider range of sources beyond traffic~~-~~related emissions. Total~~Sum~~ C_2-benzene emission estimates consisted of ethyl benzene, (m+p)-xylene and o-xylene. Benzene and methanol emissions agreed very well, however for all the other compounds estimated emissions were significantly lower than the measured fluxes. Uncertainties related to the measurements, such as isobaric interferences within the PTR-MS could have contributed to measurement overestimation, whereas uncertainties within the modelled emissions ~~estimates~~ and the use of older speciation values may have impacted the estimates. In the case of isoprene, only minimal emissions are assumed, ~~estimated~~ which do not include the biogenic sources that contributed to the measured fluxes. It is also likely that some of the *m/z* 69 signal could be attributed to cyclic alkenes~~alkanes~~, but Section 3.1.3 showed that biogenic isoprene provided a significant contribution during August and September in central London.

4 Conclusion

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Our measurements show that vehicle~~Vehicle~~ emissions are ~~have been shown to be~~ the dominant source of the~~VOC~~ fluxes and concentrations of VOCs in central London, although biogenic sources and secondary atmospheric formation may make~~have provided~~ a significant contribution, particularly in summer for some compounds.~~August and September.~~ There were observable spatial variations in flux rates, which result from the varying spatial distribution of emission types and strengths of emission sources, such as vegetation and traffic. Temporal ~~temporal~~ variations in relative source strengths can be seen in the diurnal and seasonal profiles, reflecting the diurnality and seasonality of some of the driving factors.~~impacts at different resolutions such as hour to month.~~ The measured VOC fluxes mostly originated from an area within a 1 km radius around the measurement site but~~and~~ some instances of pollution advection were seen to affect concentrations at the site. However~~, but~~ many of the spatio-temporal differences in the observed mixing ratios were attributable to changes in emission sources and strengths combined with effects of meteorological conditions. The diurnal and seasonal dynamics of the ~~emissions and~~ boundary layer mixing height are a significant driver of changes in observed VOC concentrations at the site.~~dynamics.~~

The biogenic component of isoprene emissions was modelled using the G95 algorithm and the calculated base emission rate closely matched previous published values for urban areas. Even~~Quantifying the biogenic signal of VOCs~~ in this central urban area~~areas~~ with a temperate climate there is a detectable biogenic component to isoprene emissions. Because of the relative importance~~high percentage~~ of isoprene~~parklands can greatly aid~~ in atmospheric chemistry, its inclusion in~~understanding~~ photochemical pollution models is essential~~precursor emissions and improve predictions of high pollution episodes~~.

Close agreement between the flux footprint contributions and the LAEI for benzene emissions, a compound which is thought to be accurately estimated in the inventory but associated with high measurement uncertainty, gives confidence in the PTR-MS measurements. Good agreement was also seen with methanol estimated from the NAEI, but~~however~~ other compounds were all greatly underestimated in the emissions inventory.

~~-~~This study provides further evidence for the successful implementation of VOC flux measurements in heterogeneous urban landscapes when measurement sites fulfil basic eddy covariance criteria. Further VOC flux observations are essential ~~to help identify major source components~~ for the validation~~a range~~ of “bottom-up” emission~~VOCs which can be included in emissions~~ inventories, especially as the latter are widely used for regulatory and compliance purposes.~~.~~

5 Author contributions

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E. Nemitz and B. Langford planned the measurement campaign, A. Valach with the help of B. Langford and E. Nemitz made the measurements, A. Valach with the help of B. Langford processed the data and completed the analyses. C. N. Hewitt designed the study, obtained funding and supervised the work. A. Valach prepared the manuscript with support from all the co-authors.

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Tables

Table 1. Summary of instrument operating parameters and average meteorological conditions during the measurements in central London, August – December 2012~~– December2012~~.

Parameter	Unit	Mean (range)
Normalised~~Normalized~~ sensitivity (S_N)[a]	ncps ppb^{-1}	11.5 (*m/z* 33), 13.3 (*m/z 45*),10 (*m/z 59*), 4 (*m/z 69*), 3.6 (*m/z 79*), 2.5 (*m/z 93*), 1.5 *(m/z 107)*
Primary ion *(m/z 19)*	Cps	8.31×10^{6} (6.14×10^{6} – 1.15×10^{7})
Water cluster *(m/z 37)*	Cps	1.92×10^{5} (9.15×10^{4} – 3.86×10^{5})
	% of *m/z 19*	2.3 (1.5-3.4)
O_2^+	% of *m/z 19*	<1.45 (1.11-2.01)
Temperature[b]	°C	14.0 (-1.81-30.39)
Relative humidity	%	76 (50-97)
Pressure	mbar	1004.27 (968.71-1023.27)
Wind speed[b]	m s^{-1}	3.35 (0.12-14.96)
Friction velocity (u_*)[b]	m s^{-1}	0.5 (0.01-1.50)
SD of vertical wind speed (σ_w)[b]	m s^{-1}	0.65 (0.15-1.62)

[a] S_N: Normalised~~Normalized~~ sensitivity as calculated using Taipale et al. (2008).

[b] Derived from measurements from the CSAT3 sonic anemometer (Campbell Scientific).

Table 2. Summary of 25 min VOC fluxes and mixing ratios above central London during August-December 2012.

Compound *(m/z)*	Methanol *(m/z 33)*	Acetaldehyde *(m/z 45)*	Acetone *(m/z 59)*	Isoprene *(m/z 69)*	Benzene *(m/z 79)*	Toluene *(m/z 93)*	C_2-benzenes *(m/z 107)*
Fluxes (mg m^{-2} h^{-1})							
Lifetime (OH[a])	12 d	8.8 h	53 d	1.4 h	9.4 d	1.9 d	5.9 h
N	2920	2811	2945	2119	1908	2315	2053
Min.	-2.91	-0.28	-1.74	-0.35	-0.64	-2.31	-3.27
1. quartile	0.12	0.06	0.10	0.02	0.002	0.08	0.04
Median	0.27	0.14	0.22	0.09	0.07	0.30	0.33
Mean	0.29	0.16	0.31	0.13	0.09	0.41	0.54
3. quartile	0.42	0.23	0.40	0.20	0.18	0.64	0.91
Max.	3.36	1.09	2.85	1.16	0.59	4.86	8.63
SD	0.25	0.15	0.34	0.16	0.15	0.53	0.86
Skew	0.86	1.27	2.08	1.18	0.32	1.75	2.33
Kurtosis	20.37	2.85	7.57	2.81	0.76	8.04	14.48
Mixing ratios (ppb)							
N	4834	4834	4834	4834	4834	4834	4834
Min.	5.73	<LoD (0.14)	<LoD (0.02)	<LoD (0.03)	<LoD (0.04)	<LoD (0.05)	<LoD (0.14)
1. quartile	6.82	0.59	<LoD (0.65)	<LoD (0.16)	<LoD (0.18)	<LoD (0.38)	<LoD (0.57)
Median	7.27	0.82	0.95	<LoD (0.22)	<LoD (0.24)	<LoD (0.54)	0.75
Mean	7.53	0.94	1.10	0.25	0.29	<LoD (0.65)	0.87
3. quartile	7.90	1.13	1.36	0.30	0.34	0.77	1.03
Max.	17.06	5.17	6.07	1.86	1.71	5.30	4.96
SD	1.12	0.53	0.66	0.14	0.19	0.45	0.50
Skew	2.21	2.14	1.65	1.97	2.80	3.07	2.79
Kurtosis	7.22	7.83	4.06	7.27	12.37	15.89	12.99
LoD[b]	0.96	0.45	0.66	0.25	0.28	0.66	0.71

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[a] Atmospheric lifetimes with regard to OH for a 12-h daytime average OH concentration of 2.0 x 10^6 molecules cm^{-3} (Atkinson, 2000).

[b] LoD: Limit of detection calculated using Taipale et al. (2008).

Table 3. Summary of site meteorology by month in central London during 2012.

Parameter	Data coverage (%)	Median stability (ζ)	Wind speed (m s^{-1})	Dominant wind direction (%)	Footprint[a] length (m)	Footprint width (
Aug	67	-0.0086	3.3	S (54)	2417	1355
Sep	83	-0.0154	3.2	W (48)	1285	880
Oct	89	-0.0006	3.5	S (29)	2624	1327
Nov	51	-0.0037	3.4	S (53)	2329	1156
Dec	40	0.0047	3.4	N (32)	1804	990

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[a] Calculated two-dimensional description of the oval footprint according to the KM model. Length parameter is the length between the point nearest to the sensor where the crosswind-integrated footprint function reaches 1 % of its maximum value to the point where it drops below 1 % of the maximum value.

Figure captions

Figure 1. Map of central London overlaid with the Ordinance Survey grid including the measurement site (KCL)~~location~~ at King's College (green point) with references to the geography of Greater London and Great Britain. Outlines of the areas that contribute the maximum (X_{max}), as well as 75 %, 90 %, and 99 % to the flux footprint using overall median meteorological values are shown as black contour lines with their respective labels laid out according to the median wind direction.

Figure 2a. Average diurnal profiles in local time for selected VOC fluxes (mg m^{-2} h^{-1}) separated into all days, weekdays (red dashed line) and weekends (blue dotted line) with traffic density (vehicles h^{-1}), detection limit (patterned area), and upper and lower confidence intervals (shaded area). Traffic density (with weekday and weekend) and boundary layer mixing height (for summer and winter) are shown in separate panels. Compounds are: *m/z* 33 (methanol), *m/z* 45 (acetaldehyde), *m/z* 59 (acetone/propanal), *m/z* 69 (isoprene/furan), *m/z* 79 (benzene), *m/z* 93 (toluene), and *m/z* 107 (C_2-benzenes).

Figure 2b. Average diurnal profiles in local time for selected VOC mixing ratios (ppb) separated into all days, weekdays (red dashed line) and weekends (blue dotted line) with detection limit (dotted line), and upper and lower confidence intervals (shaded area). Traffic density (with weekday and weekend) and boundary layer mixing height (for summer and winter) are shown in separate panels. Compounds are: *m/z* 33 (methanol), *m/z* 45 (acetaldehyde), *m/z* 59 (acetone/propanal), *m/z* 69 (isoprene/furan), *m/z* 79 (benzene), *m/z* 93 (toluene), and *m/z* 107 (C_2-benzenes). The mixing ratio axes start from zero apart from that of methanol, which begins at 6.4 ppb due to the high atmospheric background.

Figure 3. Examples, using isoprene, of averaged VOC fluxes (left) and mixing ratios (right) as a function of photosynthetically active radiation (PAR) (µmol m^{-2} s^{-1}), temperature (°C) and traffic density (vehicles h^{-1}) based on 25 min VOC means with linear or exponential regressions, formulae, R^2-values and detection limit (shaded area for fluxes and dashed line for mixing ratios).

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Figure 4. Diurnal profiles by month with confidence intervals and bar charts showing hourly averages for the respective month and~~for~~ representative compound (top~~A~~) fluxes (mg m^{-2} h^{-1}) (m/z 45, 69 and 79) and (bottom~~B~~) mixing ratios (ppb) (m/z 59, 69 and 79). Letters (a-d) indicate statistically significant subgroups using Tukey's HSD (Honest Significant Difference~~honest significant difference~~) post hoc test.

Figure 5a. Time series of both measured (grey) and modelled (black) fluxes, as well as PAR and temperature measurements for August and September 2012.

Figure 5b.~~5~~. ~~*Top:*~~ Correlation between modelled and measured isoprene fluxes (mg m^{-2} h^{-1}) by wind direction using the G95 algorithm with temperature as a third variable, Ordinary Least Squares (OLS) regression lines, 99th confidence intervals, formulae, and R^2-value. ~~*Bottom:* time series of both measured (grey) and modelled (black) fluxes, as well as PAR and temperature measurements for August and September 2012.~~

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Figure 6. Selected scatterplots~~scatter plots~~ of representative correlations of VOC/VOC fluxes (top) and mixing ratio (bottom)~~correlations~~ with temperature as a third variable showing an example of bimodal, strong linear and medium linear correlations as commonly

seen in the mixing ratio correlations with R^2-values, 1:1 line, 1:2 and 2:1 lines for the bimodal example in the bottom left panel.

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Figure 7. Top: 24h back trajectories from the NOAA HYSPLIT trajectory model during selected days in August 2012 corresponding to periods of low (left) and high (right) benzene/toluene concentration ratios. Daily release in 3 h~~3h~~ intervals (10 m height) for 24 h prior. Bottom: Scatterplots showing benzene to toluene concentration ratios during the 9th August 2012 (left) and 12th August 2012 (right) with linear regression with 95th confidence interval, regression equation and coefficient (R^2).

Figure 8. Scatterplots showing averaged flux and concentration regressions of isoprene and benzene as a function of CO_2 fluxes and concentrations based on 25 min VOC means with linear regressions, formulae, R^2-values and detection limit (shaded area for fluxes and dashed line for mixing ratios).

Figure 9.~~**Figure 8.**~~ Polar Annulus and Polar plots for isoprene (*m/z* 69) and benzene (*m/z* 79) VOC fluxes (top) and mixing ratios (bottom) (colour scale) by time of day (top), wind speed (bottom) and wind direction.

Figure 10~~**9**~~. Bar chart showing ~~up-~~scaled comparisons of LAEI and NAEI estimates against measured fluxes in t km^{-2} a^{-1} for speciated VOCs with error bars.