

# 1 Seasonal and diurnal trends in concentrations and fluxes of 2 volatile organic compounds in central London

3  
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5

## 6 **Authors' responses to reviewers' comments**

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

9 Responses to the reviewer's comments are below with reviewers' comments in **Bold** followed  
10 by a response to each point with the respective revisions to the manuscript in *Italics* unless  
11 the changes included the reworking of whole sections. As well as in response to the reviewers'  
12 comments, changes have been made throughout to improve the clarity and readability. The  
13 manuscript and figures should now be much easier to read and follow. Furthermore, acronyms  
14 and formatting have been checked and are now clear and consistent throughout. Also Section  
15 3.2.2 has been expanded.

## 16 17 **Review 1**

18  
19 **General comment 1: My main comment concerns the discussion on the influence of**  
20 **boundary layer dynamics: the possible role of atmospheric boundary layer (ABL)**  
21 **dynamics in shaping the diurnal profiles of species concentrations and their difference**  
22 **between summer and winter is mentioned briefly several times throughout the MS (e.g.**  
23 **in section 3.3.1), but not shown. Only in section 3.1.2 it is mentioned that the ABL was**  
24 **on average 1700 m in summer and 900 m in winter. I think you can discuss much more**  
25 **exactly how ABL dynamics have influenced your observations, and show it using the**  
26 **available data. Just some thoughts on the influence of the ABL from looking at the data:**  
27 **In Fig. 1 several concentrations (acetaldehyde, benzene, toluene, C2-benzenes) show a**  
28 **peak just around 8 a.m., which could be due to the emission into a shallow nocturnal**  
29 **ABL. After 8, the ABL quickly grows, clean air is entrained and emissions are diluted,**  
30 **leading to lower concentrations. The second peak in concentrations of aromatics**  
31 **(around 5 p.m.) could be the result of continuing emissions into a collapsing ABL.**  
32 **Finally, during night time, the ABL is shallow, but also the emissions are low, leading**  
33 **to low concentrations. For a good introduction on the ways in which ABL dynamics**  
34 **influence the relation between fluxes and concentrations of chemical species, see for**  
35 **instance Vilà-Guerau de Arellano et al. (2009). It would be very interesting to see**  
36 **correlations between species mixing ratios and ABL height (which is apparently**  
37 **available from LIDAR observations), in addition to the correlations with temperature,**  
38 **PAR and traffic density in Fig 3. This information could also help to strengthen your**  
39 **argument in Sect. 3.1.2 for the role of ABL dynamics in the seasonal variability and your**  
40 **conclusion (p.6625, l. 2-4) that 'many of the spatio-temporal differences in the observed**  
41 **mixing ratios were attributable to emissions and boundary layer dynamics'.**

42 **General response 1: A more extensive discussion and description of atmospheric boundary**  
43 **layer effects on VOC concentrations and fluxes is now included throughout Section 3.1,**  
44 **including the suggested reference. The diurnal summer and winter boundary layer heights**  
45 **have been added to Figures 2a and b. Furthermore, correlations of averaged boundary layer**  
46 **height and VOC fluxes and concentrations have been investigated and example plots of**

47 averaged isoprene fluxes and concentrations with boundary layer height have been added to  
48 Figure 3. Only correlations with boundary layer height during summer are shown due to the  
49 larger diurnal changes of boundary layer height in summer than in winter. Boundary layer  
50 height measurements were only available for 2-3 weeks in summer and winter 2012, as they  
51 were part of the short term intensive observation periods of ClearfLo. The benefit of this flux  
52 site is that the low measurement height of the tower means that our measurements are always  
53 closely coupled with the surface layer, unlike the previous VOC flux study from the BT Tower  
54 in London, which had the problem of becoming decoupled from the surface layer during stable  
55 night time conditions due to its high sampling height (Langford et al., 2010b).

56  
57 **General comment 2: Throughout the MS, the term 'diurnal averages' of VOC**  
58 **fluxes/concentrations are used, which I think is very confusing. To me, a diurnal**  
59 **average flux/concentration means the flux/concentration, as averaged over all**  
60 **observations during one day, so a single value for each day. I think what you mean is**  
61 **the 'average diurnal cycle' (or 'average diurnal profile' as you write in the caption of**  
62 **Fig. 2), so the diurnal cycle of the flux/concentration, averaged over multiple days.**  
63 **Please check throughout the MS and use the latter term consistently.**

64 **General response 2:** The term "*average diurnal profile*" is now used consistently throughout  
65 when describing diurnal cycles.

66  
67 **Specific comments:**

68  
69 **Comment 1: Title: since large parts of the results section discuss (3.1, 3.1.1) and**  
70 **figures 2 and 4 show diurnal cycles, I would add to the title that you have also looked**  
71 **at diurnal trends. Therefore I would recommend 'Seasonal and diurnal trends in ...'.**

72 Response 1: Title: added "*and diurnal*".

73  
74 **Comment 2: p. 6603, l. 17-20: the lines about satellite retrievals of VOCs are not**  
75 **necessary for the discussion and could be left out.**

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

77  
78 **Comment 3: p. 6604, l. 1: Seasonal, diurnal and spatial differences?**

79 Response 3: p. 6604, l. 1: added "*diurnal*".

80  
81 **Comment 4: p. 6604, l. 1: I would mention both VOC fluxes and concentrations here,**  
82 **since you discuss both.**

83 Response 4: p. 6604, l. 1: added "*and concentrations*".

84  
85 **Comment 5: p. 6612, l. 22: Is Mexico City the only other city for which flux**  
86 **measurements are available for comparison? You also mentioned papers by Park et**  
87 **al. with flux measurements in Houston, TX. Why not compare those with yours too?**

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

90 "*Most VOC fluxes and concentrations were comparable to or lower than those previously*  
91 *observed in London (Langford et al., 2010b) and other UK cities (Langford et al., 2009),*  
92 *although C<sub>2</sub>-benzene fluxes and concentrations, as well as isoprene and benzene*  
93 *concentrations were slightly higher. The discrepancy in isoprene and benzene*  
94 *concentrations is consistent with photochemical loss during transport to the higher*

95 measurement height of the previous study. Compared to other cities such as Houston Texas  
96 (Park et al., 2010) and Mexico City (Velasco et al., 2005), VOC fluxes and concentrations  
97 were lower, apart from C<sub>2</sub>-benzenes which were comparable or higher, although it must be  
98 noted that C<sub>2</sub>-benzenes in this study represent the sum of multiple VOC species. Unlike the  
99 other studies cited, Park et al. (2010) use relaxed eddy accumulation to measure VOC fluxes  
100 and hence the data obtained are not directly comparable with measurements made by EC-  
101 based methods.”

102

103 **Comment 6: p. 6613, l. 10: If the moments of the peak fluxes coincide with those of a**  
104 **low ABL it is difficult to tell the effects of emissions and ABL dynamics on the**  
105 **concentration apart. Can you check with data on ABL height how exact this**  
106 **coincidence is?**

107 Response 6: p. 6613, l. 10: This was added as part of Response to general comment 1 and  
108 now reads:

109 *“The rush hour emission peaks mostly coincide with the boundary layer expansion and*  
110 *collapse and therefore the effect of each factor cannot be separated. The morning*  
111 *concentration peak was slightly higher than the evening peak across traffic-related species*  
112 *even though fluxes tended to be larger during the evening rush hour. Morning emissions*  
113 *enter a shallow nocturnal boundary layer leading to relatively larger concentrations*  
114 *compared with higher afternoon emissions entering a developed boundary layer, leading to*  
115 *relatively lower concentrations. This enhanced dilution effect is found more often during*  
116 *summer when the boundary layer mixing height is higher (Figure 2a). Therefore, the*  
117 *regression analyses below only refer to data from August (cf Section 3.1.2 for comparisons*  
118 *with December). Furthermore, increased photochemical degradation during the day removes*  
119 *VOCs, further contributing to the midday minimum in mixing ratios.”*

120

121 **Comment 7: p. 6624, l. 26-27: 'There were observable spatial and temporal variations**  
122 **in relative source impacts at different resolutions such as hour to month.' I find this a**  
123 **too general statement for a conclusion. Can you be more specific?**

124 Response 7: p. 6624 l. 26-27: This has been expanded and changed to:

125 *“There were observable spatial variations in flux rates, which result from the varying spatial*  
126 *distribution of emission types and strengths of emission sources, such as vegetation and*  
127 *traffic. Temporal variations in relative source strengths can be seen in the diurnal and*  
128 *seasonal profiles, reflecting the diurnality and seasonality of some of the driving factors.”*

129

130 **Technical comments:**

131

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

134 Response 1: p. 6602, l. 5: added “(PTR-MS)”.

135

136 **Comment 2: p. 6602, l. 15: accounted for -> explained**

137 Response 2: p 6602, l. 15: changed sentence to:

138 *“Isoprene, methanol and acetaldehyde fluxes and concentrations in August and September*  
139 *showed high correlations with PAR and temperature, when fluxes and concentrations were*  
140 *largest suggesting that biogenic sources contributed to their fluxes.”*

141

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

144 Response 3: p. 6602, l. 17: added "from urban vegetation" and removed "due to urban  
145 vegetation".

146

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

148 Response 4: p. 6602, l. 25: changed to "lives".

149

150 **Comment 5: p. 6603, l. 9: additionally act as a source -> act as an additional source**

151 Response 5: p. 6603 l. 9: changed to "an additional".

152

153 **Comment 6: p. 6603, l. 11: introduce the acronyms NAEI and LAEI here, where they**  
154 **are first used.**

155 Response 6: p. 6603 l. 11: added "(LAEI and NAEI)"

156

157 **Comment 7: p. 6604, l. 12: m.s.l. -> m.a.s.l.**

158 Response 7: p. 6604 l. 12: added "m a.s.l."

159

160 **Comment 8: p. 6612, l. 3: diurnal averages -> average diurnal cycles**

161 Response 8: p. 6612 l. 3: changed "diurnal averages" to "Average diurnal cycles" throughout  
162 the manuscript.

163

164 **Comment 9: p. 6613, l. 8: concentrations for aromatics -> concentrations of aromatics**

165 Response 9: p. 6613 l. 8: changed wording throughout this section.

166

167 **Comment 10: p. 6615, l. 3-4: were seen with -> were seen between, positive**  
168 **correlations with -> positive correlations between.**

169 Response 10: p. 6615 l. 3-4: changed to "between".

170

171 **Comment 11: p. 6615, l. 5: pls add a comma between 'temperature' and 'likely'**

172 Response 11: p. 6615 l. 5: added ",".

173

174 **Comment 12: p. 6615, l. 27: Bohnenstengel et al., 2014 -> Bohnenstengel et al., 2015**

175 Response 12: p. 6615 l. 27: changed to "2015".

176

177 **Comment 13: p. 6616, l. 4: the equation from Langford et al: which equation?**

178 Response 13: p. 6616 l. 4: added "isoprene temperature response function from figure 9 in".

179

180 **Comment 14: p. 6617, l. 16: add 'from those' between 'than' and 'areas'**

181 Response 14: p. 6617 l. 16: added "from those".

182

183 **Comment 15 and 16: p. 6617, l. 21: add 'that' before 'compounds' and "Higher**  
184 **correlations than what? Than compounds with traffic sources?"**

185 Response 15 and 16: p. 6617 l. 21-22: changed sentences for clarification:

186 "Correlations of VOC/VOC fluxes ( $R^2 = 0.40-0.62$ ,  $p < 0.001$ ) indicated two groups of  
187 compounds with good correlations within each group, i.e. compounds related to traffic  
188 sources such as aromatics, and oxygenated and biogenic compounds, such as methanol,  
189 acetone and isoprene. Correlations of VOC/VOC concentrations ( $R^2 = 0.13-0.84$ ,  $p < 0.001$ )

190 *showed highest correlations between traffic related compounds ( $R^2 = 0.45-0.84$ ,  $p < 0.001$ )*  
191 *and good correlations between the oxygenated and biogenic compounds ( $R^2 = 0.55-0.69$ ,*  
192  *$p < 0.001$ ) (Figure 6). High correlations between oxygenated VOCs could indicate source*  
193 *commonality or formation mechanisms that depend on similar environmental factors.”*

194

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

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

197

198 **Comment 18: p. 6618, l. 20: delete 'observed', since it is mentioned twice in this**  
199 **sentence.**

200 Response 18: p. 6618 l. 20: deleted “observed”.

201

202 **Comment 19: p. 6624, l. 6: What does SNAP stand for?**

203 Response 19: p. 6624 l. 6: added “(Selected Nomenclature for sources of Air Pollution)”.

204

205 **Comment 20: p. 6625, l. 14: however -> but**

206 Response 20: p. 6625 l. 14: changed to “but”.

207

208 **Comment 21: p. 6625, l. 15: Where does 'this' refer to? This study? The previous line?**

209 Response 21: p. 6625 l. 15: Added “study”.

210

211 **Comment 22: p. 6625, l. 22: there is a typo in the name of the 1st author**

212 Response 22: p. 6625 l. 22: changed to “Valach”.

213

214 **Comment 23: Fig. 1: Can you increase the size of the green dot, so it is easier to find?**

215 Response 23: Fig 1: The size of the green dot has been increased, a label added and the  
216 caption updated:

217 *“Map of central London overlaid with the Ordinance Survey grid including the measurement*  
218 *site (KCL) at King’s College (green point) with references to the geography of Greater*  
219 *London and Great Britain.”*

220

221 **Comment 24: Fig. 2: Some use of colours would be very helpful to distinguish**  
222 **between the different lines, like in figure 4. Besides, the axis labels are too small to**  
223 **read without zooming in.**

224 Response 24: Fig. 2: Layout and font size have been increased to improve the clarity, as  
225 well as weekdays and weekends are now in colour (red, blue).

226

227 **Comment 25: Fig. 5: In the caption, first describe the left and then the right panel.**  
228 **Also here, it would be helpful to increase the font size of the axis labels.**

229 Response 25: Fig. 5: The figure size has been increased, as well as captions and order  
230 changed.

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

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

236

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

240 Response 26: A figure caption has been added.

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

244

## 245 **Review 2**

246

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

253

254 Response 1: The KCL site at King’s College has been used as a long term CO<sub>2</sub>/H<sub>2</sub>O flux  
255 measurement site and thus site characteristics and suitability for micrometeorological flux  
256 measurements have been investigated and described extensively by Kotthaus and Grimmond  
257 (2012; 2014a; 2014b). Although the site is not ideal for flux measurements, the cited studies  
258 show that representative surface-atmosphere fluxes can be measured at the site without  
259 significant bias from the local morphology as long as data are filtered to remove contributions  
260 from local micro-sources, e.g. vents and windows, if present. Additionally, they show that  
261 results from flux footprint models at the site can provide reasonable information. Some  
262 considerations were highlighted such as instrument siting in complex urban areas requiring  
263 careful interpretation of measured and modelled data. The relatively low measurement height  
264 allows close coupling to the street canyon. The analyses presented here were based on  
265 averaged data to reduce some of the uncertainties and used to describe overarching trends.  
266 These trends agree with conclusions from previous urban VOC flux studies. This study is the  
267 first of its kind to present long term continuous VOC flux measurements by PTR-MS over an  
268 urban area and hence provides valuable information on VOC fluxes from central London,  
269 despite some minor limitations imposed by the less-than-ideal site morphology. Section 2.1  
270 was expanded to include:

271 *“The sampling point (which we call KCL) is located 37 m west of a sampling point (KSS) that*  
272 *has been used for long-term energy and CO<sub>2</sub> flux measurements (Kotthaus and Grimmond,*  
273 *2012). Although the site is not optimal for micrometeorological flux measurements due to the*  
274 *heterogeneity of the urban canopy, its suitability has been assessed in detail by Kotthaus and*  
275 *Grimmond (2014a; 2014b). This study describes in detail the measurement area and*  
276 *investigates the influence of source area characteristics on long-term radiation and turbulent*  
277 *heat fluxes for the KSS site. They conclude that the site can yield realistic data on surface to*  
278 *atmosphere fluxes.”*

279

280 Kotthaus, S., and Grimmond, C.S.B.: Identification of Micro-scale Anthropogenic CO<sub>2</sub>, heat  
281 and moisture sources – Processing eddy covariance fluxes for a dense urban  
282 environment, Atmospheric Environment, 57, 301-316,  
283 <http://dx.doi.org/10.1016/j.atmosenv.2012.04.024>, 2012.

284 Kotthaus, S., and Grimmond, C.S.B.: Energy exchange in a dense urban environment – Part  
285 I: Temporal variability of long-term observations in central London, Urban Climate, 10, 2,  
286 261-280, <http://dx.doi.org/10.1016/j.uclim.2013.10.002>, 2014a.  
287 Kotthaus, S., and Grimmond, C.S.B.: Energy exchange in a dense urban environment – Part  
288 II: Impact of spatial heterogeneity of the surface, Urban Climate, 10, 2, 281-307,  
289 <http://dx.doi.org/10.1016/j.uclim.2013.10.001>, 2014b.

290

291 **Major comment 2:** *For eddy covariance flux measurements samples are usually*  
292 *collected at 10 Hz (15,000 samples in a period of 25 min). The sampling rate when using*  
293 *the disjunct eddy covariance method is slower. However, a sampling rate of 5.5 sec*  
294 *(273 samples in a period of 25 min) as that used here seems to be extremely slow. The*  
295 *statistical uncertainty of the fluxes caused by a longer time resolution needs to be*  
296 *evaluated. The CO2 flux data discussed in section 3.2.2 may help to assess this issue.*

297

298 **Response 2:** The disjunct sampling increases the random error of the flux but, provided the  
299 sampling intervals are less than the integral timescale, this should not introduce a systematic  
300 bias. We tested this assumption by simulating disjunct sampling on sensible heat flux data,  
301 which were calculated from the continuous data and then compared with the sensible heat  
302 fluxes calculated from a disjunct series with a sampling rate of 2 Hz and a sampling interval of  
303 5.5 s. The overall difference between the EC and DEC sensible heat fluxes over the entire  
304 measurement period was minimal (0.01 %), therefore no additional corrections have been  
305 made to the VOC fluxes. This information was added to Section 2.3:

306 *“The error due to the disjunct sampling was estimated by comparing the sensible heat fluxes*  
307 *calculated from the continuous data series with those calculated from a disjunct data series*  
308 *using a set sampling interval of 5.5 s. The continuous data were averaged to match the*  
309 *sampling frequency of the disjunct data (i.e. 2 Hz). The difference between the eddy*  
310 *covariance and DEC sensible heat fluxes was minimal (0.01 %) and thus no additional*  
311 *corrections were applied.”*

312

313 **Specific comments:**

314

315 **Comment 1: P6602, L17. G95 algorithm?**

316 Response 1: p. 6602 l. 17: expanded to “*Guenther et al., (1995)*”.

317

318 **Comment 2: P6603, L12. ...use a “bottom-up” approach based on activity data and**  
319 **emission factors....**

320 Response 2: p. 6603 l. 12: changed to “... *”bottom-up” approach based on activity data and*  
321 *emission factors”*.”

322

323 **Comment 3: P6603, L22. This reviewer has serious concerns on the methodology**  
324 **used by Park et al., 2010 & 2011.**

325 Response 3: p. 6603, l. 22: There are very few urban VOC flux measurements and even  
326 fewer that use DEC based techniques. Therefore to expand the comparison of VOC fluxes in  
327 this study with those in the literature, additional studies using relaxed eddy accumulation  
328 (REA) were consulted. REA can be associated with large errors due to the loss of reactive  
329 compounds on canister surfaces, but also the potential error from a bias in the vertical wind  
330 velocity, as shown by the normalised bias ( $\bar{w}/\sigma_w$ ). A sentence has been added for further  
331 clarification:

332 *“Unlike the other studies cited, Park et al. (2010) use relaxed eddy accumulation to measure*  
333 *VOC fluxes and hence the data obtained are not directly comparable with measurements*  
334 *made by EC-based methods.”*

335

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

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

338

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

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

342

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

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

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

349

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

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

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

356

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

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

365

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

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

370 *“However, all analyses used local time.”*

371

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

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

377

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



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

381

382 **Comment 12: P6607, Eq. 1. Fix the fluctuations' symbols.**

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

385

386 **Comment 13: P6609, Eq. 1. This equation is unreadable.**

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

389

390 **Comment 14: P6609, L20. Ergodicity is a rare/exotic term to indicate that the buildings**  
391 **height and morphology in the monitored district were quite variable. From Wikipedia:**  
392 **“The term ergodic is used to describe a dynamical system which has the same**  
393 **behaviour averaged over time as averaged over the space of all the system’s states.**  
394 **In physics the term is used to imply that a system satisfies the ergodic hypothesis of**  
395 **thermodynamics.”**

396 Response 14: p. 6609, l. 20-22: The sentence has been changed to:

397 *“The high number of files rejected in the stationarity test is to be expected for eddy*  
398 *covariance measurements over highly heterogeneous canopies, although horizontally*  
399 *averaged canopy morphology recovers some surface homogeneity.”*

400

401 **Comment 15: P6610, L7. Do not begin sentences with numbers or acronyms.**

402 Response 15: p. 6610, l. 7: added “*Exactly*”.

403

404 **Comment 16: P6612, L5-10. If daily mean fluxes are presented, it would be better to**  
405 **use units of kg km<sup>-2</sup> day<sup>-1</sup>.**

406 Response 16: p. 6610, l. 3-12: The figures 2a and b show the diurnal profiles of VOC fluxes  
407 and mixing ratios, whereas the values represent hourly average fluxes, which are typically  
408 given in units of mg m<sup>-2</sup> h<sup>-1</sup> (Karl et al., 2004; 2007; 2009; Langford et al., 2009; 2010a;  
409 2010b; Misztal et al., 2011; Rinne et al., 2001; 2002). Both fluxes and concentrations include  
410 data from the entire measurement period. For clarification purposes the words “*average*  
411 *diurnal cycles*” are now used throughout to refer to diurnal profiles of VOC emissions and  
412 mixing ratios. The units mg m<sup>-2</sup> h<sup>-1</sup> are used in table 2 to show the overall average of diurnal  
413 profiles, which are in hours of the day. However values are now cited in the main text body in  
414 Section 3.1 in units of kg km<sup>-2</sup> d<sup>-1</sup> as suggested by the reviewer, as follows:

415 *“Largest median (interquartile range in parenthesis) fluxes per day were from C<sub>2</sub>-benzenes*  
416 *and toluene with 7.86 (0.92-21.8) kg km<sup>-2</sup> d<sup>-1</sup> and 7.26 (1.83-15.3) kg km<sup>-2</sup> d<sup>-1</sup> respectively,*  
417 *followed by oxygenated compounds, i.e. methanol with 6.37 (2.99-10.0) kg km<sup>-2</sup> d<sup>-1</sup>,*  
418 *acetaldehyde 3.29 (1.52-5.62) kg km<sup>-2</sup> d<sup>-1</sup>, and acetone 5.24 (2.33-9.62) kg km<sup>-2</sup> d<sup>-1</sup>.*  
419 *Isoprene and benzene showed smallest median fluxes with 2.14 (0.56-4.85) kg km<sup>-2</sup> d<sup>-1</sup> and*  
420 *1.78 (0.06-4.34) kg km<sup>-2</sup> d<sup>-1</sup> respectively.”*

421

422 **Comment 17: P6612, L14-15. ... lifetimes and widespread origin including**  
423 **anthropogenic and biogenic sources and photochemistry ...**

424 Response 17: p. 6612 l. 14/15: changed to “*lifetimes and widespread origin including*  
425 *anthropogenic and biogenic sources and photochemistry*”.

426

427 **Comment 18: P6613, L5-7. It may only be true for London and other UK cities.**

428 Response 18: p. 6613, l 5-7: changed to “*central urban areas in UK cities*”.

429

430 **Comment 19: P6614, L23-24. Explain how advected air masses rich in methanol and**  
431 **acetone might affect the local boundary layer meteorology.**

432 Response 19: p. 6614, l. 23-24: This was poorly worded and has been changed to:  
433 “*De Gouw et al. (2005) reported that changes in boundary layer meteorology could result in*  
434 *greater effects on observed concentrations of methanol and acetone due to their high*  
435 *background values. The mixing ratios of these compounds are, therefore, dominated by*  
436 *advected pollution rather than the local flux.*”

437

438 **Comment 20: P6615, L11-12. Is there an important potential emission source (e.g.**  
439 **petrol station) at the west of the flux tower?**

440 Response 20: p. 6615, l. 11-12: As the Congestion Charge Zone in London limits the  
441 number of private vehicles in this area, there are only few petrol stations in the vicinity. The  
442 nearest is 1 km to the north and the closest westerly station is 2.5 km away. These petrol  
443 stations are outside of the 90 % flux contribution distance and are not likely to have  
444 contributed to fluxes. No other significant point sources of this type were identified within the  
445 footprint area.

446

447 **Comment 21: P6617, L3-6. Was turfgrass considered?**

448 Response 21: p. 6617, l. 3-6: added “*total tree leaf area*”. Turfgrass was not considered as  
449 turf grass species used in the UK do not emit isoprene or emit it at undetectable levels (e.g.  
450 Stewart et al., 2003).

451

452 **Comment 22: P6617, L21. ... for fluxes indicated (What?) ...**

453 Response 22: p. 6617 l. 21-22: This section was poorly phrased and has been changed to  
454 improve clarification and consistency:

455 “*Correlations of VOC/VOC fluxes ( $R^2 = 0.40-0.62$ ,  $p < 0.001$ ) indicated two groups of*  
456 *compounds with good correlations within each group, i.e. compounds related to traffic*  
457 *sources such as aromatics, and oxygenated and biogenic compounds, such as methanol,*  
458 *acetone and isoprene. Correlations of VOC/VOC concentrations ( $R^2 = 0.13-0.84$ ,  $p < 0.001$ )*  
459 *showed highest correlations between traffic-related compounds ( $R^2 = 0.45-0.84$ ,  $p < 0.001$ )*  
460 *and good correlations between the oxygenated and biogenic compounds ( $R^2 = 0.55-0.69$ ,*  
461  *$p < 0.001$ ) (Figure 6).”*

462

463 **Comment 23: P6617, L22. Provide examples of such species.**

464 Response 23: p. 6617, l. 22: See part of previous response:

465 “*i.e. compounds related to traffic sources such as aromatics, and oxygenated and biogenic*  
466 *compounds, such as methanol, acetone and isoprene.*”

467

468 **Comment 24: P6617, L21-25. This paragraph is difficult to read.**

469 Response 24: p. 6617, l. 21-25: See responses 22 and 23.

470

471 **Comment 25: P6618, Section 3.2.1. A figure showing scatter plots of benzene versus**  
472 **toluene would be helpful.**

473 Response 25: p. 6618, Section 3.2.1: Phrasing has been improved and two panels have  
474 been added to figure 7 showing scatterplots of benzene versus toluene concentrations for  
475 the 9<sup>th</sup> and 12<sup>th</sup> August respectively. The figure caption now reads:  
476 *“Bottom: Scatterplots showing benzene to toluene concentration ratios during the 9th August*  
477 *2012 (left) and 12th August 2012 (right) with linear regression with 95th confidence interval,*  
478 *regression equation and coefficient (R<sup>2</sup>).”*

479  
480 **Comment 26: P6618, L10. IQR?**

481 Response 26: p. 6618, l.10: added *“and interquartile range”*.

482

483 **Comment 27: P6618, L14-24. Zavala et al. (2006), Rogers et al. (2006), Velasco et al.**  
484 **(2007) and Karl et al. (2009) reported benzene to toluene ratios for Mexico City. The**  
485 **vehicular fleet and industry from both cities are expected to be considerably different,**  
486 **as well as the benzene to toluene ratio.**

487 Response 27: p. 6618, l. 14-24: The detailed comparison with Mexico City has been  
488 removed and only the b/t flux ratios from Karl et al. (2009) have been included to help  
489 explain a possible reason for the low observed flux ratios in this study. The comparison with  
490 other cities now focuses on European and UK cities. The section has also been rephrased to  
491 improve the clarity as follows:

492 *“The observed ratios compared well with those of other European cities, which showed b/t*  
493 *concentration ratios of 0.35 in Zurich (Heeb et al., 2000), 0.57 in Manchester (Langford et*  
494 *al., 2009), 0.57-0.63 in London (Valach et al., 2014), and 0.1 at 190 m above London*  
495 *(Langford et al., 2010b). Traffic related emissions are considered to be an important source*  
496 *of benzene and toluene in London. B/t exhaust emission ratios based on derived yearly*  
497 *emissions in other megacities, such as Mexico City, were found to be 0.4 (Zavala et al.,*  
498 *2006), which agreed well with observed b/t concentration ratios in this study. Airborne flux*  
499 *measurements over Mexico City have shown average b/t flux ratios of 0.31 with lower ratios*  
500 *of 0.07 to 0.1 over industrial areas due to increased toluene emissions from industrial*  
501 *processes (Karl et al., 2009; Velasco et al., 2007). Evaporative emissions from gasoline or*  
502 *direct industrial toluene emissions may have contributed to the lower b/t flux ratios in*  
503 *London. Furthermore, low b/t concentration ratios of 0.26 from diesel emissions have been*  
504 *reported (Corrêa and Arbilla, 2006). The widespread use of diesel fuel in London (buses,*  
505 *taxis and some cars and trains) and diesel emissions from roads which exclude passenger*  
506 *cars, such as Oxford Street (approx. 1.3 km W from the measurement site) or central railway*  
507 *nodes, such as Waterloo Railway Station (1 km to the S), may have affected b/t ratios.”*

508

509 **Comment 28: P6621, L20-22. If this was true, the reported fluxes would not be**  
510 **representative of the monitored district. The measurement height together with the**  
511 **data quality assurance suggests that the flux measurements were properly conducted**  
512 **at the inertial sublayer, where the turbulence and fluxes are relatively homogenous.**

513 Response 28: p. 6621, l. 20-22: The section was poorly worded and has been rewritten as:  
514 *“Due to the relatively low measurement height, flux measurements were always closely*  
515 *coupled with the surface layer, unlike measurements by Langford et al. (2010b), which were*  
516 *at times disconnected from the surface layer during stable night time conditions. The flux*  
517 *footprint in this study was relatively small compared with that of measurements previously*  
518 *made a 190 m height from the BT Tower in central London (Langford et al., 2010b).”*

519

520 **Comment 29: P6622, L7-27. This discussion is long and difficult to follow.**

521 Response 29: p. 6622, l. 7-27: This section was poorly phrased. The structure and language  
522 have been improved.

523 *“Green areas, as defined on the OS map, comprised 9 % of the total grid area and were*  
524 *evenly distributed across the 9 km<sup>2</sup>. Only grid square 1 included a large green area of 23 ha*  
525 *(St. James’ Park). The National Forest Inventory England only included 4.4 % green areas*  
526 *within the grid selection (NFI, 2012).”*

527 And:

528 *“The River Thames to the S may have caused the low fluxes associated with S winds (i.e.*  
529 *squares 1, 2 and 3). Contributions of traffic related compound fluxes were statistically*  
530 *significant from the W (i.e. squares 4, 5, and 7), followed by the N (square 8) and E (squares*  
531 *6 and 9) likely from the nearby heavily trafficked roads (Kingsway, Charing Cross, Strand*  
532 *and Blackfriars areas, respectively). Biogenic compound fluxes were highest from the W and*  
533 *E which coincides with significant nearby green areas within the flux footprint.”*

534

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

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

539

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

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

545 *“The London Atmospheric Emissions Inventory (LAEI) and National Atmospheric Emissions*  
546 *Inventories (NAEI) produce yearly emission estimates over the 1 km<sup>2</sup> OS grid for a range of*  
547 *pollutants and emission sources.”*

548

549 **Comment 32: P6624, L6. SNAP?**

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

551

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

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

557

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

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

561

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

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

567 *“Map of central London overlaid with the Ordinance Survey grid including the measurement*  
568 *site (KCL) at King’s College (green point) with references to the geography of Greater*

569 *London and Great Britain. Outlines of the areas that contribute the maximum ( $X_{max}$ ), 75%,*  
570 *90%, and 99% to the flux footprint using overall median meteorological values are shown in*  
571 *black with their respective labels laid out according to the median wind direction.”*

572

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

577 Response 36: p. 6637, Fig. 2: The format used in figure 2 has previously been widely used  
578 to show diurnal profiles of pollutant concentrations and fluxes, including by Bigi and Harrison  
579 (2010), Langford et al. (2010b), Park et al. (2010), Park et al. (2011), Velasco et al. (2005),  
580 Velasco et al. (2009). However, to aid clarity weekend and weekday lines are now in colour  
581 (blue and red respectively) to improve the readability and the figure caption has been  
582 updated: “weekdays (red dashed line) and weekends (blue dotted line)”.

583

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

587 Response 37: p. 6637, Fig. 2: It is conventionally accepted that it is good practice to plot  
588 figures with both axes beginning at zero. We retain this format in order to aid comparison  
589 with previously published data on VOC mixing ratios, e.g. Bon et al. (2011), Davison et al.  
590 (2009), Fraser et al. (1998), Heeb et al. (2000), Karl et al. (2007), Kato et al. (2004), Kim et  
591 al. (2001), Langford et al. (2010a), Liu et al. (2015), Misztal et al. (2011), Park et al. (2010),  
592 Park et al. (2011), Velasco et al. (2007), von Schneidmesser et al. (2011), Wang et al.  
593 (2014), Warneke et al. (2014).

594 The figure caption was updated to include:

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

597

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

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

600

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

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

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

608

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

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

612

613 **Comment 41: P6640, Fig. 5. OLS?**

614 Response 41: p. 6640 Fig. 5: caption changed to “Ordinary Least Squares (OLS)”.

615

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

618 Response 42: p. 6640, Fig. 5: The caption has been adjusted:

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

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

624

625 **Comment 43: P6641, Fig. 6. Scatter plots between fluxes would be more interesting.**

626 Response 43: p. 6641, Fig. 6: Scatterplots between the fluxes show no clear trends, as  
627 many fluxes were below the LoD and therefore individual flux points have high uncertainties,  
628 hence averaged data have been used throughout in the analyses. However, flux correlations  
629 between the same compound pairs as used in the concentration correlations have been  
630 added and the figure caption updated:

631 *“Figure 6. Selected scatter plots of representative correlations of VOC/VOC fluxes (top) and*  
632 *mixing ratio (bottom) with temperature as a third variable showing an example of bimodal,*  
633 *strong linear and medium linear correlations as commonly seen in the mixing ratio*  
634 *correlations with  $R^2$ -values, 1:1 line, 1:2 and 2:1 lines for the bimodal example in the bottom*  
635 *left panel.”*

1 **Seasonal and diurnal trends in concentrations and fluxes**  
2 **of volatile organic compounds inabove central London**

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## Abstract

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 ClearLo 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<sup>-2</sup> h<sup>-1</sup>. Median and mixing ratios were 7.327 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 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.

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## 41 1 Introduction

42 Currently over 50% of the global population lives in urban areas and with increasing trends  
43 in urbanization and population migration to urban centres, air quality remains a high public  
44 health priority. In the European Union, including ~~Although~~ in the UK, volatile organic compound  
45 (VOC) emissions are subject to control under the European Commission Directive 2008/50/EC  
46 and emission reducing technologies have been implemented, yet urban air pollution continues  
47 to be a concern. VOCs from both anthropogenic and biogenic sources impact urban air quality  
48 and climate through their contribution to tropospheric ozone and aerosol particle formation.  
49 Some VOCs including ~~are also carcinogens (e.g.~~ benzene and 1,3- butadiene are also  
50 carcinogens, which can directly affect human health (Kim et al., 2001). Most VOCs in urban  
51 areas are assumed to come from fuel combustion or evaporative emissions (Srivastava et al.,  
52 2005; Kansal, 2009). However, in summer, urban vegetation may additionally act as an  
53 additional source of VOCs such as methanol, isoprene and monoterpenes even in cities with  
54 a temperate climate and little green space, such as London or Manchester (Langford et al.,  
55 2009; 2010b).

56 Emission inventories such as the London and National Atmospheric Emissions Inventories  
57 (LAEI and NAEI) ~~inventory~~ use a “bottom-up” approach based on activity data and emission  
58 factors to estimate emission rates from pollutant sources. Micrometeorologically-based ~~which~~  
59 ~~are temporally and spatially averaged. Micrometeorological~~ eddy covariance techniques allow  
60 a “top-down” approach to quantify fluxes and these measurements can be compared with  
61 modelled emission inventory estimates. Such comparisons are essential as “bottom-up”  
62 emission estimates. Many compounds can have a variety of different sources which have yet  
63 to be identified and added to emissions inventories may inadvertently not include specific  
64 pollutant sources, or may use unrepresentative emission factors or activity profiles.  
65 “Top making “top-down” flux measurements vital. Satellite “top-down” approaches using Earth  
66 observation data from satellites are also available for only few chemicals (Lamsal et al.,  
67 2011), but not for primary VOCs. There have been few studies on VOC fluxes in urban areas.

68 ~~and these~~ Biogenic isoprene can be indirectly quantified using satellite observations, but is  
69 ~~subject to many uncertainties (Palmer et al., 2006). There have been few studies on VOC~~  
70 ~~fluxes in urban areas which~~ have been limited in spatial and temporal ~~extent~~ representation  
71 (Langford et al., 2009; 2010b; Velasco et al., 2005; 2009; Park et al., 2010; 2011). Due to the  
72 high technical ~~demands~~ demand of VOC flux measurements, it is difficult to increase spatial  
73 coverage ~~or to make measurements. However, deploying instrumentation~~ for long periods of  
74 ~~time. Making further-term~~ measurements of this kind is therefore a high priority in studies of  
75 ~~air quality~~ provides better understanding of seasonal to annual variability.

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

- 79 i. ~~Quantify~~ VOC fluxes above an urban canopy using ~~proton transfer reaction-mass~~  
80 ~~spectrometry PTR-MS~~ and ~~disjunct~~ eddy covariance; ii)
- 81 ii. ~~investigate seasonal, diurnal~~ and spatial differences in VOC fluxes and ~~concentrations;~~  
82 ~~iii)~~
- 83 ~~iii.~~ examine possible major source contributions of speciated VOCs ~~in central London;~~  
84 ~~and iv) compare measured fluxes with those estimated by the London and National~~  
85 ~~Atmospheric Emissions Inventories.~~

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

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## 90 2 Methods

### 91 2.1 Measurement site

92 Micrometeorological flux measurements were made during the period ~~from~~ 7<sup>th</sup> August - 19<sup>th</sup>  
93 December 2012 from a flux tower located on the roof of a building belonging to King's College,  
94 University of London (51.511667 °~~30~~42"N 0.116667°~~07~~00" W, ground altitude 30 m a.s.l.) on  
95 the Strand in central London. Although the site is within the London Congestion Charge Zone  
96 (an area encompassing central London requiring road tolls to be paid and hence an area with  
97 reduced traffic density regularly), surrounding roads supported a medium to high traffic volume  
98 (annual average of 50000-80000 vehicles per day, (Department for Transport, 2014)) with the  
99 ~~River~~ Thames situated 200 m to the south. This site is classified as Local Climate Zone  
100 (LCZ) Class 2 Compact Midrise according to Stewart and Oke (2012) (i.e. dense mix of  
101 midrise2006) urban class 2 site (intensely developed high density with 2–5 storey, attached  
102 or very close-set buildings (3–9 stories), few or no trees, land cover mostly paved, made of  
103 brick or stone, brick, tile, and concrete construction materials). Land cover types (in %) were  
104 calculated based on the Ordnance Survey map for the 9 km<sup>2</sup> area (Figure 1) encompassing  
105 the site and are: roads (37 %), buildings (31 %), other paved areas (14 %), unpaved/  
106 vegetation (11 %), and water bodies (7 %).  
107 ~~e.g. old city core).~~ The sampling inlet and sonic anemometer were mounted on a triangular  
108 mast (Aluma T45-H) at approx. 60.9 m (2.3 ~~times~~ mean building height,  $z_H$ ) above ground  
109 level (a.g.l.). The mean building height was around 25 m and the mast was located on an  
110 elevated area in the centre of the roof. A street canyon was located to the NW and an enclosed  
111 parking area to the SE, but generally surrounding buildings were of equal height. The sampling  
112 point (which we call KCL) is located 37 m, several meters west of a sampling point (the KSS)  
113 that has been site (i.e. KSSW) used for long-term energy and CO<sub>2</sub> flux measurements  
114 (Kotthaus and Grimmond, 2012). Although the site is not optimal for micrometeorological flux  
115 measurements due to the heterogeneity of the urban canopy, its suitability has been assessed

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

124 The weather in 2012 was somewhat cooler than the ~~(1981 to 2010)~~ long-term mean for London  
125 during summer and autumn, with several cold fronts bringing up to twice as much precipitation  
126 and associated winds ~~as average,~~ suppressing pollution levels. ~~However, during~~During the  
127 ~~period of the Olympic~~Olympics and ~~Paralympic Games~~Paralympics (27<sup>th</sup> July – 12<sup>th</sup> August  
128 and 29<sup>th</sup> August – 9<sup>th</sup> September 2012) the weather was hot and dry causing sustained  
129 pollution peaks. Winter 2012/2013 was generally warmer and drier in London than the 1981-  
130 2010 mean (Met Office, 2013).

## 131 2.2 Instrumentation and data acquisition

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

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141 VOC concentrations were measured using a high sensitivity proton transfer reaction-  
142 (quadrupole) mass spectrometer (PTR-MS) (Ionicon Analytik GmbH, Innsbruck, Austria) with  
143 three Varian turbo-molecular pumps [\(see for example de Gouw and Warneke, 2007; see](#)  
144 [Lindinger et al., 1998; de Gouw and Warneke, 2007; Hayward et al., 2002; Lindinger et al.,](#)  
145 [1998](#) for more detailed description of the instrument). Air was drawn through an inlet co-  
146 located with the sonic anemometer ~~on the flux tower approx. 60.9 m a.g.l.~~ Sample air was  
147 purged through a ~ 30 m ½" OD (3/8" ID) PTFE tube at a flow rate of 81 L min<sup>-1</sup> to the PTR-  
148 MS, which was housed in a utility room below. The high flow rate ensured turbulent flow was  
149 maintained and signal attenuation minimised (Reynolds number, Re = 11177). During the  
150 campaign, PTR-MS operating parameters were maintained at 1.95 mbar, 510 V and 50 °C for  
151 drift tube pressure, voltage and temperature respectively, to achieve an *E/N* (*E*: electric field  
152 strength, *N*: buffer gas number density) ratio of 123 Td (1 Td = 10<sup>-17</sup> V cm<sup>2</sup>). This field strength  
153 forms a compromise between reagent ion clustering and fragmentation suppression (Hewitt  
154 et al., 2003). Further instrument parameters and meteorological conditions are summarized in  
155 Table 1. The inlet flow rate into the instrument was ~~held at~~ 0.25-0.3 L min<sup>-1</sup>.

156 -The logging program was written in LabVIEW (National Instruments, Austin, Texas, USA) and  
157 operated the PTR-MS in multiple ion detection (MID) and SCAN modes for VOC  
158 concentrations of nine selected masses and a range of the protonated mass spectrum *m/z*  
159 21-206 respectively. [The sonic anemometer was not directly interfaced with the LabVIEW](#)  
160 [logging program, requiring the measurements to be synchronised during post-processing](#)  
161 [through the use of a cross-correlation function between the vertical wind velocity \*w\* and the](#)  
162 [VOC ion counts \*c\*.](#) A valve system controlled the measurement cycle, ~~which consisted~~  
163 ~~consisting~~ of 5 min zero air (ZA), 25 min MID followed by further 5 min SCAN of sample air  
164 and 25 min MID mode. During the ZA cycle, air was pumped through a custom-made gas  
165 calibration unit (GCU) fitted with a platinum catalyst heated to 200°C to provide instrument  
166 background values at ambient humidity. In MID mode the quadrupole scanned nine  
167 predetermined protonated masses with a dwell time of 0.5 s each to which the following

168 compounds were ascribed:  $m/z$  21 (indirectly quantified  $m/z$  19 primary ion count [via](#)  $[H_3^{18}O^+]$ ),  
169  $m/z$  33 (methanol),  $m/z$  39 (indirectly quantified  $m/z$  37 first cluster  $[H_3O^+ H_2O^+]$ ),  $m/z$  42  
170 (acetonitrile, results not shown),  $m/z$  45 (acetaldehyde),  $m/z$  59 (acetone/propanal),  $m/z$  69  
171 (isoprene/furan),  $m/z$  79 (benzene),  $m/z$  93 (toluene),  $m/z$  107 ( $C_2$ -benzenes), and  $m/z$  121  
172 ( $C_3$ -benzenes, results not shown). The total cycle time was 5.5 s. Secondary electron multiplier  
173 (SEM) voltage, as well as  $O_2^+$  ( $m/z$  32) and photon “dark counts” ( $m/z$  25) signals were  
174 monitored weekly.

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

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

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

### 201 **2.3 Flux calculations and quality assessment**

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

$$203 \quad F = \frac{1}{n} \sum_{i=1}^n w' \left( \frac{i-t_{lag}}{\Delta_{tw}} \right) * c'(i), \quad (\text{Eq. 1})$$

204 where  $w'$  and  $c'$  are the instantaneous fluctuations around the mean vertical wind ( $w - \bar{w}$ ) and  
205 mean VOC concentration ( $c - \bar{c}$ ),  $n$  is the number of VOC concentration measurements per  
206 25 min averaging period ( $n = 273$ ),  $t_{lag}$  is the lag time between the wind and PTR-MS  
207 measurement due to the transit through the sampling line, and  $\Delta_{tw}$  is the sampling interval of  
208 the vertical wind speed measurements of the sonic anemometer (10 Hz = 0.1 s). Langford et  
209 al. (in review) recently demonstrated that the method used to determine the time lag becomes  
210 important where the signal-to-noise ratio of the analyser is poor, showing that methods that  
211 systematically search for a maximum in the cross-correlation function within a given window  
212 (MAX method) can bias the calculated fluxes towards more extreme (positive or negative)  
213 values. Their study recommends the use of a prescribed lag time determined either through  
214 the use of a monitored sample flow rate or by using the typical lag time derived by searching  
215 for a maximum. Here the prescribed lag times were determined by fitting a running mean to  
216 the time series of daytime lag times calculated using the MAX method for acetone, which had  
217 large fluxes and thus the clearest time-lags. Prescribed lag times for all other compounds were  
218 set relative to that of acetone, accounting for the offset introduced by the sequential sampling  
219 of the PTR-MS.

220 –Flux losses due to the attenuation of high and low frequency eddies were estimated for our  
221 measurement setup. High frequency flux attenuation was estimated to be on average 11\_%  
222 using the method of Horst (1997), and a correction was applied. Attenuation from low  
223 frequency fluctuations for a 25 min flux period was investigated by re-analysing the sensible  
224 heat fluxes for longer averaging periods of 60, 90, 120 and 150 min. The coordinate rotation  
225 was applied to the joined files, which acted as a high pass filter to the three wind vectors,  
226 confirming that fluctuations of eddies with a longer time period than the averaging time did not  
227 contribute to the flux measurement (Moncrieff et al., 2004). The fluxes were compared back  
228 to the 25 min average fluxes, which had the coordinate rotation applied before joining, again  
229 to ensure only turbulent fluctuations of  $\leq 25$  min contributed to the flux (Supplementary  
230 information Figure A1). Flux losses due to low frequency attenuation were estimated to be <  
231 1.5\_% and, therefore, no corrections were deemed necessary. [The error due to the disjunct  
232 sampling was estimated by comparing the sensible heat fluxes calculated from the continuous  
233 data series with those calculated from a disjunct data series using a set sampling interval of  
234 5.5 s. The continuous data were averaged to match the sampling frequency of the disjunct  
235 data \(i.e. 2 Hz\). The difference between the eddy covariance and DEC sensible heat fluxes  
236 was minimal \(0.01 %\) and thus no additional corrections were applied.](#)

237 Many of the 25 min resolved flux measurements were close to the limit of detection (LoD),  
238 based on 1 standard deviation using the method of Spirig et al. (2005), with an average fail  
239 rate of 82\_%. Various techniques to statistically analyse or replace values below the LoD have  
240 been developed (Clarke, 1998). ~~However, however~~, they often result in significant bias, either  
241 high or low depending on the value substituted, because values tend to be below the LoD  
242 when fluxes are indeed small (Helsel and Hirsch, 1992). In this study, our analysis focused on  
243 diurnally averaged [flux profiles](#) fluxes and we decided not to filter out individual flux values on  
244 the basis of being < LoD in order to avoid this bias. When averaging the 25 min flux data it is  
245 appropriate to also average the LoD which, as shown by Langford et al. (in review), decreases  
246 with the square root of the number of samples averaged ( $N$ ). Therefore, although the majority



247 of the individual 25 min flux measurements were below the LoD, their diurnal [average](#)  
248 [profilesaverages](#) may exceed the LoD for the average and thus still yield important data on  
249 the net exchange of VOCs above the city.

$$250 \quad \overline{LoD} = \frac{1}{N} \sqrt{\sum_{i=1}^N LoD^2}. \quad (\text{Eq. 2})$$

251 The following describes the additionally applied filter criteria. 25 min flux values with a friction  
252 velocity ( $u_*$ )  $< 0.15 \text{ m s}^{-1}$  were rejected (3.4 % of total data) due to insufficient turbulence. The  
253 stationarity test and data quality rating methods of Foken and Wichura (1996) and Velasco et  
254 al. (2005) were used, and 47% of the data files were rejected on this basis. The high number  
255 of files rejected in the stationarity test is to be expected for eddy covariance measurements  
256 over [highly heterogeneous](#) canopies ~~where ergodicity cannot exist~~, although horizontally  
257 averaged canopy morphology recovers some [surfaceplanar](#) homogeneity. Furthermore, the  
258 low measurement height [used](#) can cause an increased sensitivity towards canopy roughness  
259 features resulting in non-stationarity. Since urban environments are [inherently](#) not ideal for  
260 micrometeorological flux measurements [due to their heterogeneity](#), integral turbulence  
261 characteristics of this site were assessed by comparing the measured standard deviation of  
262 the vertical wind velocity ( $\sigma_w$ ) normalised by  $u_*$  to the parameters of a modelled ideal  
263 turbulence (Foken et al., 2004). Results showed that 99.6 % of all the data were rated category  
264 six or better and 0.4 % were rejected using the criteria of Foken et al. (2004). This large pass  
265 rate gives further confidence that the measurements were not unduly affected by wake  
266 turbulence generated from the structure of the building. Erroneous meteorological data (2.6 %  
267 of total) were removed around wind directions of 14-15°, due to minor turbulence interferences  
268 from the presence of other sensors on the mast. Depending on compound between 40-61  
269 % of flux data ( $N = 1934$  ~~—~~ 2949) passed all of the above quality controls. [Exactly 2014 hhours](#)  
270 of concentration data ( $N = 4834$ ) were obtained. For consistency regression coefficients ( $R^2$ )  
271 were used throughout.

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272 The traffic densities used for the analysis were obtained from a nearby site at Marylebone  
273 Road (approx. 3 km to the NW) and consisted of hourly vehicle counts covering the period 7<sup>th</sup>  
274 ~~to~~ 22<sup>nd</sup> August 2012. The major roads of the Strand and the Embankment ~~areas~~ surrounding  
275 the measurement site support a comparable traffic volume with an annual average of 50000 -  
276 80000 vehicles per day (Department for Transport, 2014) and diurnal patterns in traffic are  
277 likely to be similar across central London.

278 Photosynthetically active radiation (PAR) and CO<sub>2</sub> measurements used in the analysis were  
279 part of the ~~KSS~~ long-term micrometeorological measurements at the same site and covered  
280 the period from August to September for PAR and ~~from August~~ to December for CO<sub>2</sub>  
281 respectively. Average diurnal profiles were calculated for the boundary layer mixing height,  
282 which was measured using three LiDARs located on rooftops within central London during an  
283 approx. two week period in summer and winter 2012 (Bohnenstengel et al., 2015).

### 284 2.3.1 Flux footprint calculations

285 Although there are no operational footprint models for urban environments which take the  
286 complex topography and spatial variability in building height and surface heat fluxes into  
287 account, the analytical footprint model ~~of suggested by~~ Kormann and Meixner (2001) has  
288 previously been applied in non-homogeneous terrain (Helfter et al., 2011; Neftel et al., 2008).

289 The Kormann-Meixner (KM) model determines the 2D footprint density function explicitly from  
290 micrometeorological parameters, which are provided by the eddy covariance measurements,

291 i.e., friction velocity ( $u_*$ ), ~~Obukhov length ( $L$ ), horizontal wind velocity at the measurement~~  
292 ~~height ( $u(z_m)$ , Obukhov length ( $L$ ), horizontal wind velocity at the measurement height ( $u(z_m)$ ),~~  
293 ~~and  $\sigma_v$ )~~ standard deviation of the lateral wind ( $\sigma_v$ ), ~~and measurement height ( $z_m$ ).~~ The flux

294 footprints were calculated for each 25 min flux period. Neftel et al. (2008) developed a  
295 Microsoft Excel based tool, which allows the footprint contributions (%) of user-defined spatial

296 elements to be mapped. ~~In, in~~ this case we used a total of nine 1 km<sup>2</sup> grid squares to match  
297 the Ordnance Survey (OS) grid (Figure 1), ~~centred on the measurement site.~~ This grid

298 resolution was validated using a simple parameterisation model (Kljun et al., 2004) with

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299 [average](#) diurnal [cycleaverage](#) parameters for  $\sigma_w$ ,  $u^*$ , and boundary layer height ( $z_i$ ) during the  
300 campaign, which calculated the distance of the maximum flux contribution ( $X_{max}$ ) and the  
301 extent of the 90 % flux footprint ( $X_{90}$ ).

302 The KM footprint calculation requires the Monin-Obukhov stability parameter ( $\zeta$ ) to be within  
303 the interval [-3, 3], where

$$304 \quad \zeta = \frac{z_m - d}{L}, \quad (\text{Eq. 3})$$

305 with  $d$  ( $d = \frac{1}{3}z_H = 16.7$  m) being the displacement height estimated as a fraction of the canopy  
306 height (Garrat, 1992). The footprint estimation for cases of extreme stability is of lower quality,  
307 but still provides useful information. The vertical turbulent flux  $F_c(0,0,z_m)$  measured at the  
308 height  $z_m$  is related to the corresponding surface flux area  $F_c(x,y,0)$  which is upwind of the  
309 measurement point, such that

$$310 \quad F_c(0,0,z_m - d) = \int_{-\infty}^{\infty} \int_0^{\infty} F_c(x,y,z_m - d) \Phi(x,y,z_m - d) dx dy, \quad (\text{Eq. 4})$$

311 where  $z_m$  is the measurement height and the  $x$ -axis is aligned with the mean horizontal wind  
312 direction.  $\Phi(x,y,z_m - d)$  is the footprint function and includes a weighting function to describe  
313 the influence of a unit point source on the flux from any surface location  $(x,y)$ . In order to  
314 compare VOC fluxes with estimated emissions from the London Atmospheric Emissions  
315 Inventory (LAEI), [a 9 km<sup>2</sup> section of the 1 km<sup>2</sup> resolution OS grid system was used](#) which  
316 on average included 90% of the footprint contribution to all measured fluxes. This area was  
317 limited to central London and partially included the following Boroughs: Westminster (squares  
318 1, 4, 5 and 7), Southwark (2, 3 and 6), Camden (8) and the City of London (9) (Figure 1).

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## 319 3 Results and Discussion

### 320 3.1 Diurnal profiles of VOC fluxes and concentrations

321 ~~Average diurnal cycles~~Diurnal averages of measured VOC fluxes and mixing ratios are shown  
322 in ~~Figure~~Figures 2a and 2b with descriptive statistics for all the data summarized in Table 2.  
323 ~~Largest Toluene and C<sub>2</sub>-benzenes showed the largest~~ median fluxes (interquartile range in  
324 parenthesis) ~~fluxes per day were from C<sub>2</sub>-benzenes and toluene with 7.86 (of 0.92-21.8) kg~~  
325 ~~km<sup>33</sup> (0.04-0.91) mg m<sup>-2</sup> dh<sup>-1</sup> and 7.26 (1.83-15.3) kg km<sup>0.30</sup> (0.08-0.64) mg m<sup>-2</sup> dh<sup>-1</sup>~~  
326 respectively, followed by oxygenated compounds, i.e. methanol ~~with 6.37 ((0.27 (0.12-0.42)~~  
327 ~~mg m<sup>2.99</sup>-10.0) kg km<sup>2</sup> d<sup>-1</sup> h<sup>-1</sup>),~~ acetaldehyde ~~3.29 (1.52-5.62) kg km<sup>2</sup> d<sup>-1</sup> (0.14 (0.06-0.23)~~  
328 ~~mg m<sup>-2</sup> h<sup>-1</sup>),~~ and acetone ~~5.24 (2.33-9.62) kg km<sup>2</sup> d<sup>-1</sup> (0.22 (0.10-0.40) mg m<sup>-2</sup> h<sup>-1</sup>)~~. Isoprene  
329 and benzene showed ~~the~~ smallest median fluxes with ~~2.14 (0.56-4.85) kg km<sup>2</sup> d<sup>-1</sup> (0.09 (0.02-~~  
330 ~~0.20) mg m<sup>-2</sup> h<sup>-1</sup> and 1.78 (0.06-4.34) kg km<sup>07</sup> (0.002-0.18) mg m<sup>-2</sup> dh<sup>-1</sup> respectively. The~~  
331 highest median mixing ratios were of the oxygenated compounds methanol (7.3 (6.8-7.9) ppb),  
332 acetone (0.95 (<LoD-1.36) ppb) and acetaldehyde (0.82 (0.59-1.13) ppb), followed by  
333 aromatics (C<sub>2</sub>-benzenes, toluene and benzene), and isoprene.

334 -Oxygenated compounds commonly have relatively long atmospheric lifetimes and  
335 widespread ~~origins~~sources including anthropogenic ~~and~~ biogenic ~~and some atmospheric~~  
336 ~~sources~~ and photochemistry, resulting in elevated concentrations and less pronounced diurnal  
337 profiles (Atkinson, 2000). Most VOC fluxes and concentrations were comparable to or lower  
338 than those previously observed in London (Langford et al., 2010b) and other UK cities  
339 (Langford et al., 2009), although C<sub>2</sub>-benzene fluxes and concentrations, as well as isoprene  
340 and benzene concentrations were slightly higher. The discrepancy in isoprene and benzene  
341 concentrations is consistent with photochemical loss during transport to the higher  
342 measurement height of the previous ~~studies~~study. Compared to ~~other cities such as Houston~~  
343 ~~Texas (Park et al., 2010) and Mexico City (Velasco et al., 2005), VOC fluxes and~~  
344 ~~concentrations~~VOC fluxes were lower, apart from C<sub>2</sub>-benzenes ~~which were comparable or~~

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345 [higher, although it must be noted that C<sub>2</sub>-benzenes in this study represent the sum of multiple](#)  
346 [VOC species. Unlike the other studies cited, Park et al. \(2010\) use relaxed eddy accumulation](#)  
347 [to measure VOC fluxes and hence the data obtained are not directly comparable with](#)  
348 [measurements made by EC-based methods. \(Velasco et al., 2005\).](#)

349 [Diurnal profiles of aromatic fluxes and concentrations presented clear double rush hour peaks](#)  
350 [during the morning and evening \(07:00-10:00 and 17:00-20:00 local time\). Concentration](#)  
351 [peaks are thought to be linked to additional advection of traffic-related pollution from larger](#)  
352 [commuter roads outside of the city centre, as well as boundary layer effects and](#)  
353 [photochemistry. VOC concentration measurements at canopy height can be affected by](#)  
354 [boundary layer depth \(Vilà-Guerau de Arellano et al., 2009\). The rush hour emission peaks](#)  
355 [mostly coincide with the boundary layer expansion and collapse and therefore the effect of](#)  
356 [each factor cannot be separated. The morning concentration peak was slightly higher than the](#)  
357 [evening peak across traffic-related species even though fluxes tended to be larger during the](#)  
358 [evening rush hour. Morning emissions enter a shallow nocturnal boundary layer leading to](#)  
359 [relatively larger concentrations compared with higher afternoon emissions entering a](#)  
360 [developed boundary layer, leading to relatively lower concentrations. This enhanced dilution](#)  
361 [effect is found more often during summer when the boundary layer mixing height is higher](#)  
362 [\(Figure 2\). Therefore, the regression analyses below only refer to data from August \(cf Section](#)  
363 [3.1.2 for comparisons with winter\). Furthermore, increased photochemical degradation during](#)  
364 [the day removes VOCs, further contributing to the midday minimum in mixing ratios. The](#)  
365 [diurnal flux profiles of methanol, acetone, isoprene, and to a smaller extent acetaldehyde,](#)  
366 [showed one large peak just after midday \(approx. 13:00 local time\), which was only reflected](#)  
367 [in the concentration profiles of acetone and isoprene. Acetaldehyde concentrations presented](#)  
368 [a slight double peak similar to mixing ratios of aromatics. Methanol has a relatively long](#)  
369 [atmospheric lifetime and therefore high background concentrations, hence mixing ratios](#)  
370 [showed no distinct diurnal profile.](#)

371 **3.1.1 Correlations with possible controlling variables of VOC fluxes and concentrations**

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

384 The ~~above mentioned concentration dilution due to boundary layer expansion resulted in~~  
385 ~~negative correlations between boundary layer height and aromatic mixing ratios during August~~  
386 ~~( $R^2 = 0.33-0.56$ ,  $p < 0.01$ ). As aromatic compound fluxes slightly dipped around midday, the~~  
387 ~~mixing ratios were diluted by the deep boundary layer. The above evidence suggests that~~  
388 ~~traffic-related emissions were the main contributors to fluxes and mixing ratios of aromatic~~  
389 ~~compounds. Acetone and isoprene showed peak midday fluxes, which maintained daytime~~  
390 ~~mixing ratios and produced positive correlations with boundary layer height ( $R^2 = 0.16$  and~~  
391 ~~0.59 respectively,  $p < 0.01$ ).~~ ~~diurnal flux profiles.~~ De Gouw et al. (2005) reported that changes  
392 in boundary layer meteorology could result in greater effects on observed concentrations of  
393 methanol ~~and~~ acetone ~~due to their high background values. The mixing ratios of these~~  
394 ~~compounds are, therefore, likely dominated by advected pollution rather than the local flux.~~  
395 ~~Possibly a combination of boundary layer and photochemical effects were seen with methanol~~  
396 ~~mixing ratios, wherein correlations with mixing height were negative ( $R^2 = 0.70$ ,  $p < 0.01$ ),~~  
397 ~~whereas acetone and isoprene fluxes seemed, and isoprene, and to be sufficiently high during~~

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

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407 VOC fluxes and concentrations plotted as a function of photosynthetically active radiation  
408 (PAR) showed strong daytime (defined as 06:00 to 18:00 ~~local time~~ GMT) correlations for  
409 methanol, acetaldehyde and isoprene fluxes ( $R^2 = 0.71-0.78$ ,  $p < 0.001$ ) and concentrations ( $R^2$   
410 ~~= 0.71-0.78 and 0.66-0.83~~,  $p < 0.001-0.04$  respectively). Plotted as a function of temperature, high  
411 correlations with methanol, acetaldehyde and isoprene fluxes ~~were seen~~ ( $R^2 = 0.75$ ,  $0.63$ , and  
412  $0.94$ ,  $p < 0.001$  respectively), ~~were seen~~, whereas only methanol and acetone concentrations  
413 showed higher correlations with temperature ( $R^2 = 0.64$  and  $0.81$ ,  $p < 0.001$  respectively).  
414 Methanol fluxes correlated linearly with temperature ( $R^2 = 0.75$ ,  $p < 0.001$ ), but acetaldehyde  
415 and isoprene ~~fluxes had exponential relationships~~ ( $R^2 = 0.64$  and  $0.94$ ,  $p < 0.01$ ) ~~for fluxes~~ and  
416 mixing ratios ( $R^2 = 0.45$  and  $0.55$ ,  $p < 0.01$ ) ~~had exponential relationships~~ with temperature

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417 (Figure 3 example of isoprene). The relationships of mixing ratios with PAR and temperature  
418 for these compounds improved greatly when ~~excluding~~ night time values ~~were excluded~~  
419 (defined as  $PAR < 100 \mu\text{mol m}^{-2} \text{s}^{-1}$ ) and ~~when time points~~ of low temperature ( $< 5 \text{ }^\circ\text{C}$ ) ~~were~~  
420 ~~excluded. This indicates~~, ~~indicating~~ either separate source contributions or effects of  
421 boundary layer meteorology in these instances, ~~whereby increased~~ ~~increased~~ mixing ratios  
422 of these compounds with low PAR and temperature ~~are likely~~ ~~result from~~ ~~effects of~~ reduced  
423 dilution within a shallow boundary layer, e.g., at night or in winter, but also possible  
424 contributions of anthropogenic sources such as exhaust emissions, which are largely

425 independent of light and temperature. Increases in concentrations due to high PAR and  
426 temperature suggest biogenic sources, increased evaporative emissions, and/or secondary  
427 atmospheric formation driven by oxidation of precursor hydrocarbons (Singh et al., 1994).

428 Oxygenated compounds have a variety of different source contributions such as ~~tailpipe~~  
429 ~~pipe~~ emissions, evaporative emissions from fuel and solvents, direct emissions from plants,  
430 leaf decomposition, and secondary atmospheric production (Langford et al., 2009 and  
431 references therein).

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



### 450 3.1.2 Seasonal variability of VOC sources and meteorology

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

461 Mixing ratios of aromatics were generally lower in summer and highest in December (Figure  
462 4 [bottomB](#)). This is likely due to less dilution effects in winter when the boundary layer is  
463 shallow or from advection of additional sources such as heating, since there was no increase  
464 in fluxes. [Generally, in summer the boundary layer mixing height is higher and collapses later](#)  
465 [in the evening which maintains the dilution effect for VOC concentrations. In winter the](#)  
466 [average boundary layer mixing height is lower. It develops later in the morning and collapses](#)  
467 [earlier in the afternoon, which could increase overall VOC mixing ratios, but also individual](#)  
468 [maxima, e.g. during rush hours. Comparing average diurnal profiles of compound mixing ratios](#)  
469 [with boundary layer height during summer and winter showed that aromatic compound](#)  
470 [concentrations were associated with negative correlations in summer \(cf Section 3.1.1\) which](#)  
471 [became positive during winter \( \$R^2 = 0.10-0.33\$ ,  \$p < 0.01\$ \), while fluxes maintained positive](#)  
472 [correlations with boundary layer height regardless of season. This suggests boundary layer](#)  
473 [effects may be an important driver of increased concentrations in winter. Furthermore, and](#)  
474 traffic counts for the Congestion Charge Zone in central London indicate lower monthly  
475 average vehicle counts in December ([Department for Transport, 2014](#)). Oxygenated  
476 compounds and isoprene mixing ratios were highest in summer with the exception of acetone,

477 which increased in December likely either from boundary layer effects, reduced photochemical  
478 degradation, or advection. ~~Correlations~~ ~~Mean daytime maxima~~ of ~~mixing ratios and fluxes~~  
479 ~~with diurnal profiles for the~~ boundary layer ~~mixing height measured using three LiDARs located~~  
480 ~~on rooftops within central London~~ were ~~positive for acetone and isoprene during between 1700~~  
481 ~~m in summer and 900 m in winter,~~ whereas methanol and acetaldehyde presented negative  
482 ~~correlations during summer indicating stronger dilution effects (cf Section 3.1.1).~~  
483 ~~(Bohnenstengel et al., 2014).~~ Increased summer mixing ratios of oxygenated compounds and  
484 isoprene indicated a temperature dependent, possibly biogenic source contribution. While  
485 biogenic emissions may be advected from outside of the city, the concurrent increase in  
486 isoprene fluxes suggests the source to be largely local to the flux footprint. The temperature  
487 dependent fraction of observed isoprene mixing ratios, which may include advected pollution,  
488 was estimated using the ~~isoprene temperature response function equation~~ from ~~Figure 9 in~~  
489 Langford et al. (2010b), which estimated a 30\_% and 20\_% contribution in August and  
490 September respectively. These values were significantly higher than for iso-pentane, a non-  
491 biogenic compound ~~available from the Automatic Hydrocarbon Network~~, to which the same  
492 analysis was applied. The temperature dependent component of isoprene in October,  
493 November and December showed no significant difference to that of iso-pentane, suggesting  
494 the biogenic component was reduced or absent at lower temperatures. High correlations of  
495  $m/z$  69 with light and temperature during August and September indicate that isoprene was  
496 the likely major component during these months, however the rest of the period the  
497 contribution of ~~additional ether~~ compounds such as furan and other alkenes at that mass may  
498 have increased, thereby overestimating the isoprene signal (Yuan et al., 2014).

### 499 3.1.3 Modelling the biogenic isoprene contribution in London

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

503 
$$F = D \times \varepsilon \times \gamma, \quad (\text{Eq. 5})$$

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

509 
$$\gamma = C_L \times C_T. \quad (\text{Eq. 6})$$

510 The slope of the linear regression of the measured total isoprene flux and  $\gamma$  provided an  
511 emission factor in  $\text{mg m}^{-2} \text{h}^{-1}$ , which was converted to  $\mu\text{g g}^{-1} \text{h}^{-1}$  by dividing by the foliar density  
512 ( $D = 0.129 \text{ kg g}^{-1} \text{ m}^{-2}$ ). The foliar density was estimated using the total [tree](#) leaf area as seen  
513 from visible satellite imagery within the flux footprint (~~approx. 9%~~) and [tree](#) leaf dry weight for  
514 representative species commonly planted in the area such as *Platanus x acerifolia* (City of  
515 Westminster, 2009), which are also high isoprene emitters (Geron et al., 1994). The resulting  
516 base emission rate  $\varepsilon$  from the measured fluxes was  $6.5 \mu\text{g g}^{-1} \text{h}^{-1}$  which compares well with  
517 the figure given in the literature ( $5 \mu\text{g g}^{-1} \text{h}^{-1}$ ) for cities in a cool climate (Guenther et al., 1995).

518 ~~For details~~[These estimates are representative of this calculation, see the Supplementary](#)  
519 [Information B. These estimates are representative of biogenic isoprene fluxes from a highly](#)  
520 [heterogeneous canopy within the biogenic isoprene fluxes from a highly heterogeneous](#)  
521 [canopy within flux footprint, including both high and low isoprene emitting species as well as](#)  
522 [low average foliar density due to the flux footprint, including both high and low isoprene](#)  
523 [emitting species as well as low average foliar density due to the sparse distribution of urban](#)  
524 [roadside and park trees. Green areas, as defined on the OS map, comprised 9 % of the total](#)  
525 [grid area and were evenly distributed across the 9 km<sup>2</sup>, sparse distribution of urban roadside](#)  
526 [and park trees. Only grid square 1 included a large green area of 23 ha \(St. James' Park\). The](#)  
527 [National Forest Inventory \(NFI\) England only included 4.4 % green areas within the grid](#)  
528 [selection \(NFI, 2012\). The NFI excluded individual trees in parks and avenues, which can](#)

529 [encompass up to 50 % of trees maintained by the local authority in central London \(City of](#)  
530 [Westminster, 2009\)](#).

531 Figure [5a and b5](#) shows that the modelled isoprene fluxes using the calculated base emission  
532 rate ~~by wind direction~~ compared well with the measured fluxes [by wind direction](#). Linear  
533 regressions from wind directions that have a strong anthropogenic component are lower, e.g.  
534 W ( $R^2 = 0.13$ ,  $p < 0.001$ ), than [from those](#) areas dominated by biogenic sources, e.g. SE ( $R^2 =$   
535  $0.81$ ,  $p < 0.001$ ) ~~due to~~ the nearby Temple Gardens. Modelled ~~emissions fluxes~~ seemingly  
536 underestimated observed isoprene fluxes since these included the traffic component, however  
537 it appears that biogenic isoprene represents a detectable source contribution in summer.

### 538 3.2 VOC/VOC correlations and ratios

539 ~~Correlations of VOC/VOC~~ ~~correlations for~~ fluxes ~~indicated~~ ( $R^2 = 0.40$  ~~and~~  $0.62$ ,  $p < 0.001$ )  
540 ~~indicated two groups of~~ compounds with [good correlations within each group, i.e. compounds](#)  
541 [related to non-traffic sources such as aromatics, and oxygenated and biogenic compounds,](#)  
542 [such as methanol, acetone and isoprene \(Figure 6 top\). Correlations of](#) ~~had higher correlations.~~  
543 VOC/VOC ~~correlations for~~ concentrations ( $R^2$  ~~=between~~  $0.13$ - $0.84$ ,  $p < 0.001$ ) showed highest  
544 correlations between traffic-~~related~~ compounds ( $R^2$  ~~=between~~  $0.45$ - $0.84$ ,  $p < 0.001$ ) and [good](#)  
545 [correlations](#) between the oxygenated [and biogenic](#) compounds ~~and isoprene~~ ( $R^2$  ~~=between~~  
546  $0.55$ - $0.69$ ,  $p < 0.001$ ) (Figure 6 [bottom](#)). ~~High~~ ~~Higher~~ correlations between oxygenated VOCs  
547 could indicate source commonality or formation mechanisms that depend on similar  
548 environmental factors. Scatterplots between aromatic compounds and isoprene/oxygenated  
549 compounds ~~tended~~ to show bimodal distributions indicating separate source  
550 contributions. ~~(Figure 6, left panel)~~. Using temperature or, to a smaller extent, PAR as a third  
551 variable highlights a temperature or light dependency of the second source supporting the  
552 existence of additional biogenic and/or atmospheric sources. In the example of isoprene  
553 against benzene the relationship changes with temperature from 2:1 to 1:2.

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### 3.2.1 Benzene to toluene ratios

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 0.45 (0.39-0.48) 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

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581 trains) and diesel emissions from roads ~~which exclude passenger cars exclusively permitting~~  
582 ~~buses and taxis~~, such as Oxford Street (approx. 1.3 km W from the measurement site) or  
583 central railway nodes, such as Waterloo ~~Railway Train~~ Station (1 km to the S), may have  
584 affected b/t ratios.

585 -Wind speed and direction can play a role for b/t concentration ratios by transporting pollution  
586 over longer distances allowing more time ~~to react with~~ or exposure to higher OH  
587 concentrations, thus increasing the ratio. An example of this (~~Figure 7~~) was seen on the 12<sup>th</sup>  
588 August when median (IQR) b/t concentration ratios reached 0.5 (0.45-0.56) with stronger SE  
589 winds (mean 3.67 m s<sup>-1</sup>) possibly advecting pollution from Benelux/Northern Europe, whereas  
590 on the 9<sup>th</sup> August median b/t ratios were 0.34 (0.30-0.38) with low wind speeds (mean 1.28 m  
591 s<sup>-1</sup>) indicating higher contributions of local sources (i.e. 60% London influence)  
592 (Bohnenstengel et al., 2014). On both days OH concentrations above London were around  
593 1.25 x 10<sup>6</sup> molecules cm<sup>-3</sup> and b/t flux ratios were not significantly different making pollution  
594 advection a likely cause of the observed difference (~~L. Whalley, personal/private~~  
595 ~~communication 2014~~). Calculated back trajectories using the HYSPLIT trajectory model  
596 (Hybrid Single Particle Lagrangian Integrated Trajectory Model (Draxler and Rolph, 2014))  
597 were run at 3 ~~h-hour~~ intervals starting at ground-level (~~10 m/40m~~) from London and propagated  
598 ~~24 h/24h~~ backwards in time. These agreed with the changes in measured b/t ratios (Figure 7)  
599 and during episodes of high b/t ratios indicated that air masses passed over continental  
600 Europe within the past day which could have entrained pollution.

601 -The median monthly b/t flux ratio ~~during the measurement period~~ stayed between 0.18 and  
602 0.26, which is to be expected since only local fluxes were detected, however the median (IQR)  
603 monthly b/t ratio for concentrations steadily increased from 0.41 (0.36-0.47) to 0.62 (0.55-  
604 0.70) from August to December. ~~Advected Assuming less local photochemical removal during~~  
605 ~~the winter months, as OH concentrations in London are often below the detection limit during~~  
606 ~~winter (Bohnenstengel et al., 2014), this implies advected~~ pollution from mainland Europe may  
607 be common in winter or biomass burning may play a greater role in colder months, as this is

608 associated with higher b/t ratios, e.g. 1.67 (Lemieux et al., 2004), due to the different fuel  
609 combustion emission profile. Furthermore, OH concentrations in London are often below the  
610 detection limit during winter (Bohnenstengel et al., 2015) resulting in less local photochemical  
611 removal during the winter months.

612 Median (IQR) concentration ratios for benzene to C<sub>2</sub>-benzenes were 0.31 (0.28-0.33) and  
613 toluene to C<sub>2</sub>-benzenes were 0.72 (0.63-0.81), which both agree with previous values and  
614 suggest that these masses are indeed the ascribed traffic-related compounds (Heeb et al.,  
615 2000; Warneke et al, 2001).

### 616 3.2.2 VOC to CO<sub>2</sub> correlations and ratios

617 Generally, good correlations were found between averaged ~~Correlations of VOC and with~~ CO<sub>2</sub>  
618 fluxes measured concurrently at the site were low ( $R^2 = 0.0306-0.8124$ ,  $p < 0.001$ ). ~~Traffic-~~  
619 related compounds were ), but mostly comparable with values from a previous study in  
620 London, which ranged from  $R^2 = 0.09-0.26$  (Harrison et al., 2012). In this study acetaldehyde  
621 showed the highest and isoprene was among the lowest correlations with CO<sub>2</sub> fluxes ( $R^2 =$   
622 0.03-0.48,  $p < 0.01$ ). However, when points of peak CO<sub>2</sub> fluxes were removed, which is  
623 opposite to the correlations with traffic-related VOC fluxes Harrison et al. study. This may  
624 indicate in the case of acetaldehyde increased significantly to  $R^2 = 0.65-0.91$  ( $p < 0.001$ ).  
625 Presumably, the initial poor correlations resulted from an additional strong CO<sub>2</sub> source that is  
626 not a shared source of aromatic VOCs. The improved correlation is greater and for traffic-  
627 related compounds due to the limited range of source contributions to this group compared  
628 with oxygenated/biogenic compounds. The regression coefficient ( $R^2$ ) of benzene isoprene  
629 reduced source commonality with CO<sub>2</sub> fluxes increases from 0.48 to 0.91, whereas during the  
630 respective measurement periods. Concentration correlations were highest for isoprene fluxes  
631 the increase was small, i.e. 0.68 to 0.70 (Figure 8), as isoprene shares only few common  
632 sources with CO<sub>2</sub>. Averaged VOC to CO<sub>2</sub> concentration correlations were highest for traffic-  
633 related compounds ( $R^2 = 0.92-0.96$  traffic related compounds ( $R^2 = 0.25-0.44$ ,  $p < 0.001$ ) and  
634 lower for with the other compounds ( $R^2 = < 0.71-0.9044$ ,  $p < 0.05$ ), with acetone showing no

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635 significant relationship ( $p=0.88$ ). Most compound flux and concentration correlations with  $\text{CO}_2$   
636 significantly increased towards December ( $R^2 \leq 0.49$  and  $\leq 0.86$ , respectively) reflecting the  
637 increased commonality of combustion sources towards winter. Only correlations with  $\text{C}_2$ -  
638 benzene fluxes declined in November and December.

639 Median VOC/ $\text{CO}_2$  flux ratios ranged from  $1.7 \times 10^{-6}$  to  $7.7 \times 10^{-5}$  ( $\text{mg m}^{-2} \text{h}^{-1} / \text{mg m}^{-2} \text{h}^{-1}$ )  
640 with isoprene and benzene showing low ratios due to their low fluxes, and toluene and  
641  $\text{C}_2$ -benzenes high ratios. Highest flux ratios for all compounds were with W winds, whereas  
642 lowest for biogenic compounds with N and for traffic-related compounds S wind directions.  
643 Flux ratios declined towards December as  $\text{CO}_2$  fluxes increased and VOC fluxes decreased.  
644 Similarly, VOC/ $\text{CO}_2$  concentration ratios were between  $0.45 \times 10^{-6}$  and  $14.6 \times 10^{-6}$  (ppb/ppb)  
645 with isoprene and benzene representing the lowest and methanol and acetone the highest  
646 ratios. Highest concentration ratios were seen in August for oxygenated compounds/isoprene  
647 and December for traffic-related species.

### 648 3.3 Wind direction and flux footprint analysis

649 Polar Annulus and Polar plots were constructed for VOC fluxes and mixing ratios respectively  
650 and representative compounds are shown (Figure 98). Polar plots use a generalized additive  
651 model (GAM) to interpolate between wind direction and wind speed averaged data points  
652 within the OpenAir package in R (see Carslaw and Ropkins, 2012; Wood, 2006; Hastie and  
653 Tibshirani, 1990; Wood, 2006; Carslaw and Ropkins, 2012). Polar Annulus plots  
654 averaged by time of day instead of wind speed and show diurnal variability with wind  
655 direction. The majority of the time (83%) unstable and near neutral conditions prevailed ( $\zeta <$   
656 0.2), although the frequency varied between months with 87%, 89%, 82%, 84% and 69%  
657 during August, September, October, November and December, respectively. Wind  
658 directions with mostly unstable conditions were with W and S winds and near neutral  
659 with N or E winds. Mixing ratios were on average highest with low wind speeds (showing a  
660 negative correlation) when pollutants accumulate due to reduced mixing, indicating local  
661 emissions (Figure 98, bottom).



662 -Largest fluxes for all compounds were from the NW with either one daytime peak (e.g.  
663 isoprene) or two distinct rush hour peaks (e.g. benzene) (Figure 98, top). On average fluxes  
664 were largest from the W>E>N>S (F-statistic ~~between 60.37 and 227.06~~,  $p < 0.001$ ) because  
665 of increased emission rates of specific compound sources. Separated by month, fluxes were  
666 largest from W>N>E>S in August and September, whereas during October, November and  
667 December fluxes followed the pattern W>E>N>S. ~~The flux footprint in this study was relatively~~  
668 ~~small compared with that of measurements previously made at 190 m height from the BT~~  
669 ~~Tower in central London (Langford et al., 2010b).~~ Due to the relatively low measurement height  
670 ~~in this study, flux measurements were always closely coupled~~ ~~the flux footprint was limited to~~  
671 ~~the immediate surrounding area allowing close coupling~~ with the surface layer, ~~unlike~~  
672 ~~measurements by Langford et al. (2010b), which were at times disconnected from the and~~  
673 ~~similar~~ surface ~~layer during stable night time conditions.~~

674 ~~roughness.~~ The average length of the maximum flux footprint contribution ( $X_{max}$ ) was around  
675 330 m and 90% of all the fluxes ( $X_{90}$ ) originated from within 900 m. The median footprint area  
676 was 1.8 km<sup>2</sup>. This established that the majority of emission sources contributing to the  
677 measured fluxes must have been local. Additionally, the selected emission grid (cf Section  
678 2.3.1 above) encompassed 97% of the footprint with S and W wind directions, but only 80%  
679 and 84% during E and N winds. Grid square 5 represented the maximum contribution area  
680 since it encompassed the measurement point. Average footprint contributions (mean  $\pm$  SD)  
681 comprised of grid squares 1 (2%  $\pm$  4%), 2 (5%  $\pm$  7%), 4 (4%  $\pm$  5%) and 5 (52%  $\pm$  31%)  
682 during S and W wind conditions, squares 6 (4%  $\pm$  9%) and 9 (4%  $\pm$  10%) indicated E wind  
683 conditions, and square 8 (18%  $\pm$  27%) N wind conditions. During October contributions from  
684 square 9 increased to 10% and were more frequent at 30% in December. Squares 3 (0.6%  
685  $\pm$  2%) and 7 (0.9%  $\pm$  2%) provided minimal average contributions.

686 ~~Green areas, as defined on the OS map, within the grid were evenly distributed across the 9~~  
687 ~~km<sup>2</sup> and comprised 8.8% of the total grid area, half of which was captured by the National~~  
688 ~~Forest Inventory England (NFI, 2012). This definition excluded individual trees in parks and~~

689 ~~avenues, which can encompass up to 50% of trees maintained by the council in central~~  
690 ~~London (City of Westminster, 2009). The River Since footprints were relatively small it is~~  
691 ~~possible that the Thames River to the S may have~~ caused the low fluxes associated with S  
692 winds (i.e. squares 1, 2 and 3). ~~Contributions of For traffic-related compound fluxes there~~  
693 were statistically significant ~~contributions~~ from the W (i.e. squares 4, 5, and 7), followed by the  
694 N (square 8) and E (squares 6 and 9) likely from the nearby heavily trafficked roads (Kingsway,  
695 Charing Cross, Strand and Blackfriars areas, respectively). ~~Biogenic compound For isoprene,~~  
696 ~~and to some degree methanol and acetaldehyde,~~ fluxes were highest from the W and E ~~which~~  
697 ~~coincides with significant nearby green areas being within the flux maximum contributing~~  
698 ~~distance ( $X_{max}$ ) of the footprint.~~  
699 ~~(300 m).~~ Correlations of ~~fluxes with~~ grid square contributions in the footprint ~~with fluxes~~ can  
700 also give information on ~~emission source strengths within the respective~~ grid square (Figure  
701 1). ~~emission rates.~~ Generally positive correlations with fluxes across most compounds were  
702 seen from the W (squares 4, 5 and 7) confirming that ~~high emission rates increased emissions~~  
703 from ~~sources within~~ these grid squares ~~were~~ driving the ~~large~~ high fluxes. ~~Strongest~~  
704 ~~correlations of fluxes with contributions from squares 4, 5, and 7 were seen, although these~~  
705 ~~were largest ( $R = 0.40-0.46$ ,  $p < 0.001$ ) during October and November ( $R^2 = 0.40-0.46$ ,~~  
706  ~~$p < 0.001$ ),~~ especially for masses associated with biogenic sources ( $m/z$  33, 45, 59 and 69).  
707 Square 8 showed positive correlations for benzene and only in August for all compounds.  
708 ~~Correlations of fluxes with contributions from squares 1, 2, 3, 6 and 9 were negative indicating~~  
709 ~~weaker emission sources in these squares or increased VOC deposition.~~  
710 Highest mixing ratios with wind direction were from  $E > N \geq W > S$  for traffic-related compounds,  
711 whereas oxygenated compounds/isoprene followed a similar pattern as the fluxes of  
712  $W \geq E > N \geq S$  (F-statistic  $= 47.49-86.95$ ,  $p < 0.001$ ). Easterly winds in London are often  
713 associated with synoptic conditions that bring European Continental air masses to the UK,  
714 resulting in higher background concentrations. Furthermore, since the boundary layer was on  
715 average more stably stratified ~~and mixing heights were lowest ( $640 \pm 80$  m)~~ with E wind

716 conditions, it is likely that pollutant concentrations were allowed to build up resulting in the  
717 observed higher concentrations to the E for the more ubiquitous compounds, whereas  
718 concentrations of compounds with biogenic contributions additionally had strong  
719 ~~source~~~~source areas~~ to the W, such as several ~~green areas~~~~parke~~ (St. James' Park, Hyde Park  
720 and Regents Park, total 331 ha).

### 721 **3.4 Comparisons with London and National Atmospheric Emissions**

#### 722 **Inventories**

723 The London ~~Atmospheric Emissions Inventory~~ (LAEI) and National Atmospheric Emissions  
724 ~~Inventory~~~~inventories~~ (NAEI) produce ~~yearly~~~~biannual~~ emission estimates ~~over the 1 km<sup>2</sup> OS~~  
725 ~~grid~~ for a range of pollutants and emission sources. Total VOC emission estimates are  
726 provided, but only benzene and 1,3-butadiene are ~~estimated~~~~listed~~ separately. Measured  
727 emissions were compared with annual estimated emissions for the above OS grid area  
728 ~~selection~~ from 2012 for benzene using the LAEI and indirectly speciated VOCs of the NAEI.  
729 Using the average flux footprint, the grid square estimates were compared with the scaled flux  
730 measurements from the equivalent area ~~(Figure 10)~~.

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

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742 Using speciated VOC emission contributions (% of total VOC emissions) for 2006 ([Bush et al.,](#)  
743 [2006](#))([NAEI Reference: 45321001/0/AO6069/NP](#)) and emission maps from 2012 for total non-  
744 methane VOC emissions, speciated estimates could be compared with observations (Figure  
745 [10](#)). ~~The~~ NAEI includes a ~~wider~~ range of emission sources divided into 11 SNAP  
746 ([Selected Nomenclature for sources of Air Pollution](#)) sectors including industrial, commercial  
747 and residential processes, transport, waste treatment, solvent use, point sources, agriculture  
748 and nature, although the latter two were unavailable for the London urban area. NAEI  
749 estimates for benzene exceed the LAEI due to the inclusion of a wider range of sources  
750 beyond traffic-related emissions. ~~TotalSum~~ C<sub>2</sub>-benzene emission estimates consisted of ethyl  
751 benzene, (m+p)-xylene and o-xylene. Benzene and methanol emissions agreed very well,  
752 however for all the other compounds estimated emissions were significantly lower than the  
753 measured fluxes. Uncertainties related to the measurements, such as isobaric interferences  
754 within the PTR-MS could have contributed to measurement overestimation, whereas  
755 uncertainties within the [modelled](#) emissions ~~estimates~~ and the use of older speciation values  
756 may have impacted the estimates. In the case of isoprene, only minimal emissions are  
757 [assumed, estimated](#) which do not include the biogenic sources that contributed to the  
758 measured fluxes. It is also likely that some of the *m/z* 69 signal could be attributed to cyclic  
759 [alkenesalkanes](#), but Section 3.1.3 showed that biogenic isoprene provided a significant  
760 contribution during August and September in central London.

## 4 Conclusion

~~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

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787 agreement was also seen with methanol estimated from the NAEI, ~~but~~ however other  
788 compounds were all greatly underestimated in the emissions inventory.

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

## 795 5 Author contributions

796 E. Nemitz and B. Langford planned the measurement campaign, A. Valach with the help of B.  
797 Langford and E. Nemitz made the measurements, A. Valach with the help of B. Langford  
798 processed the data and completed the analyses. [C. N. Hewitt designed the study, obtained](#)  
799 [funding and supervised the work. A. Valach](#) prepared the manuscript with support from all the  
800 co-authors.

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## 801 6 Acknowledgements

802 This work was funded by the UK Natural Environment Research Council (NERC) through the  
803 ClearLo project (Clean Air for London; NERC grant NE/H003169/1) and the National  
804 Capability function of the Centre for Ecology & Hydrology. Amy Valach thanks NERC for a  
805 PhD studentship. ~~Further thanks to~~ David Carslaw (King's College London) ~~and for the back~~  
806 ~~trajectory data,~~ the NOAA Air Resources Laboratory (ARL) ~~provided for the provision of the~~  
807 HYSPLIT ~~back trajectories transport and dispersion model,~~ Lisa Whalley (University of Leeds)  
808 ~~provided the for~~ OH data, Sue Grimmond (University of Reading), Simone Kotthaus  
809 (University of Reading), and the urban meteorology research group at King's College London  
810 ~~provided for~~ site access, meteorology and CO<sub>2</sub> data. [E. House, M. Shaw, W. J. Acton and B.](#)  
811 [Davison provided technical assistance.](#)

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1035 **Tables**

1036 Table 1. Summary of instrument operating parameters and average meteorological conditions during the  
 1037 measurements in central London, August – [December 2012](#)–~~December2012~~.

Parameter	Unit	Mean (range)
<a href="#">NormalisedNormalized</a> sensitivity ( $S_N$ ) <sup>a</sup>	ncps ppb <sup>-1</sup>	11.5 ( <i>m/z</i> 33), 13.3 ( <i>m/z</i> 45), 10 ( <i>m/z</i> 59), 4 ( <i>m/z</i> 69), 3.6 ( <i>m/z</i> 79), 2.5 ( <i>m/z</i> 93), 1.5 ( <i>m/z</i> 107)
Primary ion ( <i>m/z</i> 19)	Cps	8.31×10 <sup>6</sup> (6.14 ×10 <sup>6</sup> – 1.15×10 <sup>7</sup> )
Water cluster ( <i>m/z</i> 37)	Cps	1.92×10 <sup>5</sup> (9.15 ×10 <sup>4</sup> – 3.86×10 <sup>5</sup> )
	% of <i>m/z</i> 19	2.3 (1.5-3.4)
O <sub>2</sub> <sup>+</sup>	% of <i>m/z</i> 19	<1.45 (1.11-2.01)
Temperature <sup>b</sup>	°C	14.0 (-1.81-30.39)
Relative humidity	%	76 (50-97)
Pressure	mbar	1004.27 (968.71-1023.27)
Wind speed <sup>b</sup>	m s <sup>-1</sup>	3.35 (0.12-14.96)
Friction velocity ( <i>u</i> ) <sup>b</sup>	m s <sup>-1</sup>	0.5 (0.01-1.50)
SD of vertical wind speed ( $\sigma_w$ ) <sup>b</sup>	m s <sup>-1</sup>	0.65 (0.15-1.62)

1038 <sup>a</sup> $S_N$ : [NormalisedNormalized](#) sensitivity as calculated using Taipale et al. (2008).

1039 <sup>b</sup>Derived from measurements from the CSAT3 sonic anemometer (Campbell Scientific).

1040 Table 2. Summary of 25 min VOC fluxes and mixing ratios above central London during August-December 2012.

Compound ( <i>m/z</i> )	Methanol ( <i>m/z</i> 33)	Acetaldehyde ( <i>m/z</i> 45)	Acetone ( <i>m/z</i> 59)	Isoprene ( <i>m/z</i> 69)	Benzene ( <i>m/z</i> 79)	Toluene ( <i>m/z</i> 93)	C <sub>2</sub> -benzenes ( <i>m/z</i> 107)
<i>Fluxes (mg m<sup>-2</sup> h<sup>-1</sup>)</i>							
Lifetime (OH <sup>a</sup> )	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
<i>Mixing ratios (ppb)</i>							
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 <sup>b</sup>	0.96	0.45	0.66	0.25	0.28	0.66	0.71

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1041 <sup>a</sup>Atmospheric lifetimes with regard to OH for a 12-h daytime average OH concentration of 2.0 x 10<sup>6</sup> molecules  
1042 cm<sup>-3</sup> (Atkinson, 2000).

1043 <sup>b</sup>LoD: Limit of detection calculated using Taipale et al. (2008).

1044

1045 Table 3. Summary of site meteorology by month in central London during 2012.

Parameter	Data coverage (%)	Median stability ( $\zeta$ )	Wind speed ( $\text{m s}^{-1}$ )	Dominant wind direction (%)	Footprint <sup>a</sup> length (m)	Footprint width (m)
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

1046 <sup>a</sup>Calculated two-dimensional description of the oval footprint according to the KM model. Length  
 1047 parameter is the length between the point nearest to the sensor where the crosswind-integrated  
 1048 footprint function reaches 1% of its maximum value to the point where it drops below 1% of the  
 1049 maximum value.

1050 **Figure captions**

1051 **Figure 1.** Map of central London overlaid with the Ordinance Survey grid including the  
1052 measurement [site \(KCL\) location](#) at King's College (green point) with references to the  
1053 geography of Greater London and Great Britain. [Outlines of the areas that contribute the](#)  
1054 [maximum \( \$X\_{max}\$ \), as well as 75 %, 90 %, and 99 % to the flux footprint using overall median](#)  
1055 [meteorological values are shown as black contour lines with their respective labels laid out](#)  
1056 [according to the median wind direction.](#)

1057 **Figure 2a.** Average diurnal profiles in local time for selected VOC fluxes ( $\text{mg m}^{-2} \text{h}^{-1}$ )  
1058 separated into all days, weekdays ([red dashed line](#)) and weekends ([blue dotted line](#)) with  
1059 traffic [density](#) (vehicles  $\text{h}^{-1}$ ), detection limit (patterned area), and upper and lower confidence  
1060 intervals (shaded area). [Traffic density \(with weekday and weekend\) and boundary layer](#)  
1061 [mixing height \(for summer and winter\) are shown in separate panels.](#) Compounds are:  $m/z$   
1062 33 (methanol),  $m/z$  45 (acetaldehyde),  $m/z$  59 (acetone/propanal),  $m/z$  69 (isoprene/furan),  
1063  $m/z$  79 (benzene),  $m/z$  93 (toluene), and  $m/z$  107 ( $\text{C}_2$ -benzenes).

1064 **Figure 2b.** Average diurnal profiles in local time for selected VOC mixing ratios (ppb)  
1065 separated into all days, weekdays ([red dashed line](#)) and weekends ([blue dotted line](#)) with  
1066 detection limit (dotted line), and upper and lower confidence intervals (shaded area). [Traffic](#)  
1067 [density \(with weekday and weekend\) and boundary layer mixing height \(for summer and](#)  
1068 [winter\) are shown in separate panels.](#) Compounds are:  $m/z$  33 (methanol),  $m/z$  45  
1069 (acetaldehyde),  $m/z$  59 (acetone/propanal),  $m/z$  69 (isoprene/furan),  $m/z$  79 (benzene),  $m/z$   
1070 93 (toluene), and  $m/z$  107 ( $\text{C}_2$ -benzenes). [The mixing ratio axes start from zero apart from](#)  
1071 [that of methanol, which begins at 6.4 ppb due to the high atmospheric background.](#)

1072 **Figure 3.** Examples, using isoprene, of averaged VOC fluxes (left) and mixing ratios (right)  
1073 as a function of photosynthetically active radiation (PAR) ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ), temperature ( $^{\circ}\text{C}$ )  
1074 and traffic density (vehicles  $\text{h}^{-1}$ ) based on 25 min VOC means with linear or exponential  
1075 regressions, formulae,  $R^2$ -values and detection limit (shaded area for fluxes and dashed line  
1076 for mixing ratios).

1077 **Figure 4.** Diurnal profiles by month with confidence intervals and bar charts [showing hourly](#)  
1078 [averages for the respective month and for](#) representative compound ([topA](#)) fluxes ( $\text{mg m}^{-2} \text{h}^{-1}$ )  
1079 ( $m/z$  45, 69 and 79) and ([bottomB](#)) mixing ratios (ppb) ( $m/z$  59, 69 and 79). Letters (a-d)  
1080 indicate statistically significant subgroups using Tukey's HSD ([Honest Significant](#)  
1081 [Difference/honest significant difference](#)) post hoc test.

1082 **Figure 5a.** [Time series of both measured \(grey\) and modelled \(black\) fluxes, as well as PAR](#)  
1083 [and temperature measurements for August and September 2012.](#)

1084 **Figure 5b.5-Top:** Correlation between modelled and measured isoprene fluxes ( $\text{mg m}^{-2} \text{h}^{-1}$ )  
1085 by wind direction using the G95 algorithm with temperature as a third variable, [Ordinary](#)  
1086 [Least Squares \(OLS\)](#) regression lines, 99<sup>th</sup> confidence intervals, formulae, and  $R^2$ -value.  
1087 **Bottom:** [time series of both measured \(grey\) and modelled \(black\) fluxes, as well as PAR](#)  
1088 [and temperature measurements for August and September 2012.](#)

1089 **Figure 6.** Selected [scatterplots/scatter plots](#) of representative [correlations of VOC/VOC](#)  
1090 [fluxes \(top\) and mixing ratio \(bottom\) correlations](#) with temperature as a third variable  
1091 showing an example of bimodal, strong linear and medium linear correlations [as commonly](#)

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1092 [seen in the mixing ratio correlations](#) with  $R^2$ -values, 1:1 line, 1:2 and 2:1 lines for the bimodal  
1093 example in the [bottom](#) left panel.

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1094 **Figure 7.** [Top](#): 24h back trajectories from the NOAA HYSPLIT trajectory model during  
1095 selected days in August 2012 corresponding to periods of low (left) and high (right)  
1096 benzene/toluene concentration ratios. Daily release in ~~3 h~~ intervals (10 m height) for 24 h  
1097 prior. [Bottom](#): [Scatterplots showing benzene to toluene concentration ratios during the 9<sup>th</sup>](#)  
1098 [August 2012 \(left\) and 12<sup>th</sup> August 2012 \(right\) with linear regression with 95<sup>th</sup> confidence](#)  
1099 [interval, regression equation and coefficient \( \$R^2\$ \).](#)

1100 [Figure 8.](#) [Scatterplots showing averaged flux and concentration regressions of isoprene and](#)  
1101 [benzene as a function of CO<sub>2</sub> fluxes and concentrations based on 25 min VOC means with](#)  
1102 [linear regressions, formulae,  \$R^2\$ -values and detection limit \(shaded area for fluxes and](#)  
1103 [dashed line for mixing ratios\).](#)

1104 [Figure 9.](#)~~Figure 8.~~ Polar Annulus and Polar plots for isoprene ( $m/z$  69) and benzene ( $m/z$   
1105 79) VOC fluxes (top) and mixing ratios (bottom) (colour scale) by time of day (top), wind  
1106 speed (bottom) and wind direction.

1107 **Figure 109.** Bar chart showing ~~up~~-scaled comparisons of LAEI and NAEI estimates against  
1108 measured fluxes in  $t\ km^{-2}\ a^{-1}$  for speciated VOCs with error bars.