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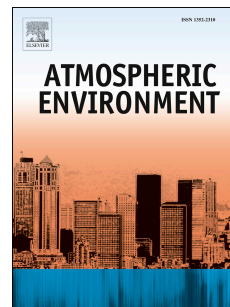
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Concentrations of selected volatile organic compounds at kerbside and background sites in central London

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Abstract

Ground-level concentrations of nine volatile organic compounds (VOCs) were measured using a proton transfer reaction-mass spectrometer (PTR-MS) in central London at an urban background (North Kensington, NK, during 16th - 25th Jan 2012) and a kerbside site (Marylebone Rd, MRd, during 25th Jan - 7th Feb 2012) as part of the winter intensive observation period of the ClearLo project. Site comparisons indicated that VOC concentrations at the urban background site were significantly lower than at the kerbside site (ratio MRd/NK of 2.3). At the kerbside site PTR-MS measurements of aromatics (benzene, toluene, C₂- and C₃-benzenes) were compared with the gas chromatography – flame ionization detector data from the UK Government’s Automatic Hydrocarbon Network. Very good qualitative agreement was observed between the two methods ($r = 0.90 - 0.91$, $p < 0.001$, $N = 260$), although there was a significant offset between the instruments. This was partly due to issues with humidity dependent background measurements, but possibly also from isobaric interference of other compounds and their fragments, giving a positive bias to the PTR-MS data. Most compounds showed strong indications of traffic-related sources with double rush hour peaks in diurnal profiles and high correlations with known traffic-related compounds ($r = 0.68 - 0.97$ at NK, $0.48 - 0.87$ at MRd, $p < 0.001$, $N_{NK} = 2202-2227$, $N_{MRd} = 2705-2720$) and CO ($r = 0.80-0.96$ at NK, $0.65-0.84$ at MRd, p

31 <0.001, $N_{NK} = 223$, $N_{MRd} = 256-274$). Polar plots agreed with statistical analysis of wind direction
32 dependency and identification of potential emission sources was attempted.

33 **1 Introduction**

34 Anthropogenic sources of volatile organic compounds (VOCs) are of particular importance in urban
35 areas due to the intensity of fossil fuel combustion and the relative paucity of biogenic sources in
36 cities. A wide range of VOCs are emitted directly by the evaporation of fuels and solvents, as unburnt
37 fuel and as partially oxidized compounds from combustion processes, mostly vehicle emissions
38 (Kansal, 2009). Some VOCs can directly affect human health (e.g. benzene, which is a known
39 carcinogen) while others contribute to the formation of ozone and aerosol particles in the
40 atmosphere (Derwent, 1995). Both have detrimental effects on human health and the environment
41 (Kim et al., 2001). In winter elevated VOC concentrations are observed due to the shallow daytime
42 boundary layer with limited dilution and mixing. In the UK, VOC emissions are subject to control
43 under European Commission Directive 2008/50/EC. Monitoring networks such as the Automatic
44 Hydrocarbon Network (AHN) provide a running annual mean concentration for a suite of pollutants.
45 Emissions are estimated as part of the National Atmospheric Emission Inventory (NAEI) activity
46 (Yardley et al., 2012).

47 A wide range of studies focus on VOC concentrations and air quality in cities around the world using
48 diverse measuring techniques (Baker et al., 2008; Jobson et al., 2010). Due to the variety of emission
49 sources, meteorological conditions, and often short atmospheric lifetimes of the compounds, VOC
50 volume mixing ratios can be associated with large variability. Slow response instruments have
51 identified seasonal and diurnal patterns of urban VOC concentrations (Kim et al., 2001), however
52 only fast response instruments have been shown to record this short term variability.

53 The aim of this study was to:

- 54 I. Quantify a suite of VOCs at an urban background and a kerbside site in winter and;
- 55 II. Compare VOC volume mixing ratios from fast response PTR-MS measurements with the GC-
56 FID measurements from the Automatic Hydrocarbon Network.

57 This study was part of the winter intensive observation period of the Clean Air for London project
58 (ClearfLo, www.clearflo.ac.uk), aimed to research boundary layer pollution over London in 2011-
59 2012 (Bohnenstengel et al., in review). Here we report measurements of nine VOC species measured
60 at high temporal resolution at a kerbside and a background site in central London (16th January - 7th
61 February 2012).

62 2 Methods

63 2.1 Measurement sites and meteorology

64 Details of both the North Kensington (NK) background and Marylebone Rd (MRd) kerbside sites are
65 compared (Supplementary content Table A1). Air was pumped through a PTFE inlet (and PTFE filter
66 at MRd) attached to 1/4" OD PTFE tubing to a high sensitivity proton transfer reaction-mass
67 spectrometer (PTR-MS; Ionicon Analytik GmbH, Innsbruck, Austria).

68 Meteorological measurements were co-located with the inlet at NK (Figure 1 and Supplementary
69 content Table A1). The mean UK temperature in January was 6.0 °C, i.e. 1.3 °C above the 1971-2000
70 average (UK Met Office, 2012), although February experienced low temperatures and snowfall,
71 which is uncommon in London.

72 2.2 VOC sampling

73 VOC mixing ratios were measured on-line using a PTR-MS (de Gouw and Warneke, 2007; Lindinger
74 et al., 1998). The instrument was operated in multiple ion detection (MID) and mass scan (SCAN)
75 modes (Supplementary content A1). In MID mode the quadrupole mass spectrometer scanned
76 through 11 pre-determined masses, to which the following compounds were ascribed: m/z 21
77 (indirect quantification of m/z 19 primary ion count $[\text{H}_3\text{O}^+]$ via isotopologue $[\text{H}_3^{18}\text{O}^+]$), m/z 33
78 (methanol), m/z 39 (indirectly quantified m/z 37 first cluster $[\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}^+]$), m/z 42 (acetonitrile), m/z
79 45 (acetaldehyde) m/z 59 (acetone/propanal), m/z 69 (cycloalkanes/isoprene), m/z 79 (benzene),
80 m/z 93 (toluene), m/z 107 (C_2 -benzenes) and m/z 121 (C_3 -benzenes).

81 The UK national Automatic Hydrocarbon Network (AHN) station at MRd measures 29 different
82 hydrocarbons using a gas chromatography-flame ionization detector (GC-FID, AutoSystem XL;
83 PerkinElmer Inc., USA). This method complies with standards set out by the European Air Quality
84 Directive (Broadway and Tipler, 2008). A 40 min continuous sampling period provides hourly means
85 (Supplementary content A2).

86 PTR-MS measures in unit mass resolution and a fragment may derive from several parent
87 compounds, therefore each detected mass may relate to one or more compounds. Where possible,
88 measurements should be verified by more specific analytical techniques, such as GC-FID.
89 Unfortunately, only benzene, toluene, some C_2 - and C_3 -benzenes were verified by the AHN.

90 2.3 Quality analyses and data handling

91 The PTR-MS was calibrated over a range of concentrations using a certified multi-component VOC
92 gas standard (Ionimed Analytik GmbH, Austria). The measured instrument sensitivities were then
93 used to convert normalized count rates of RH^+ to volume mixing ratios (Langford et al., 2010a). The

94 instrument background was quantified using a platinum catalyst and subtracted from the ambient
95 measurements. Since the background was determined for dry air, corrections for humidity effects on
96 some compounds had to be applied and were associated with large uncertainties (Supplementary
97 content B).

98 A low pass filter was applied to smooth the data and reduce instrumental noise. Spearman's rank
99 correlation coefficients and Wilcoxon rank sum tests were used in statistical analyses due to the data
100 distributions.

101 **3 Results & Discussion**

102 **3.1 VOC concentrations**

103 VOC concentrations measured by the PTR-MS at the North Kensington (NK) background site (Figure
104 2a) and at the Marylebone Rd (MRd) kerbside site (Figure 2b) are summarized in Table 1a and 1b. At
105 both sites methanol, acetaldehyde and acetone, all oxygenated compounds, were the most
106 abundant. Methanol has a variety of biogenic, anthropogenic and atmospheric sources (Cady-Pereira
107 et al., 2012). Acetone has some biogenic contributions but solvents and tailpipe emissions were
108 most likely the main sources (de Gouw et al., 2005; Reissell et al., 1999; Warneke et al., 1999). Both
109 have a low photochemical reactivity with OH resulting in longer atmospheric lifetimes, which also
110 contributed to the relatively high mixing ratios. The compounds with the lowest mixing ratios at both
111 sites were acetonitrile and cycloalkanes/isoprene. Although these are emitted from vehicle exhaust,
112 their volume mixing ratios were much lower than other traffic-related compounds. The isoprene
113 component of m/z 69 was estimated at 22% and presumably from traffic as the biogenic component
114 was absent due to the season (Borbon et al., 2001). Comparison with GC-FID isoprene
115 concentrations at NK inferred that cycloalkanes provided a significant contribution to m/z 69
116 (Supplementary content C) (Erickson et al., 2014 ;Yuan et al, 2014). Although globally biomass
117 burning is the main source of acetonitrile (Holzinger et al., 2001), in urban areas emissions from
118 vehicle exhaust are prominent as diurnal profiles resembled a double rush hour pattern (Section 3.4)
119 with some increased acetonitrile emissions occurring at low temperatures possibly from solid fuel
120 burning (Section 3.3).

121 Mixing ratios for most of the compounds agreed with or were lower than observations from other
122 urban areas, but benzene and C_2 -benzenes concentrations were slightly higher at MRd compared
123 with previous observations in UK cities (Langford et al., 2009, 2010b). The measurement proximity to
124 the source emissions must be considered; for example, Langford et al. (2010b) reported
125 concentration measurements from tall towers where the effects of dilution and photochemical loss
126 are greater.

127 During both measurement periods the beginnings and ends were marked by high pollution episodes
128 (16th -18th, 24th -28th Jan and 3rd -7th Feb).

129 3.1.1 Site comparison

130 The volume mixing ratios of all compounds were significantly different ($p < 0.001$) between NK and
131 MRd, except for acetone ($p = 0.26$). Acetone has a relatively long atmospheric lifetime (Table 1a) and
132 therefore mixing ratios are often homogenous over larger areas. Apart from methanol, which was
133 1.5 times higher at NK, the remaining compounds were up to 3 times higher at the MRd site with a
134 mean site ratio (MRd/NK) of 2.3. This difference is related to the proximity to sources and
135 differences of source strengths. Comparison of both time periods using the AHN data from MRd
136 showed that aromatic compounds were significantly higher ($p < 0.001$) during the first period
137 indicating that the differences between the sites were indeed due to the location. These compounds
138 are found in tailpipe emissions, which so close to a heavily trafficked road was the main source. In
139 general, NK represents an urban location away from major sources and broadly representative of
140 city-wide background concentrations, e.g. urban residential areas, whereas MRd, an urban kerbside
141 site next to a major arterial route, represents central urban areas such as surrounding the
142 congestion charge zone in London.

143 3.2 Comparisons with the Automatic Hydrocarbon Network and PTR-MS quantification 144 limitations

145 Benzene, toluene, C₂- and C₃-benzenes from PTR-MS measurements were compared with the same
146 compounds or sum of compounds with similar masses measured by GC-FID in the framework of the
147 Automatic Hydrocarbon Network (AHN). Due to isobaric interference within the PTR-MS
148 measurements the sum of available GC-FID measurements was used for compounds with a
149 protonated mass of m/z 107 and m/z 121. Direct comparisons of 1h mean (± 2.9 -5.9% SE) PTR-MS
150 and GC-FID measurements (Figure 3) are summarized in Table 2. The PTR-MS data for these
151 compounds corresponded to within a factor of 1.3 for m/z 79, 93 and 107, and a factor of 2.5 for m/z
152 121 ($p < 0.001$). Comparison of the time series showed that the PTR-MS measurements closely
153 followed the diurnal variations of the GC-FID measurements (Figure 3).

154 As the PTR-MS cannot distinguish between compounds with similar masses, isobaric interference
155 can occur, e.g. benzaldehyde can produce mass interferences for C₂-benzenes (Warneke et al.,
156 2003). The m/z 107 likely has four contributing species: ethyl benzene, (m+p)-xylene, o-xylene, and
157 some benzaldehyde. C₃- benzenes may include a wider range of compounds: propyl benzene, two
158 ethyl methyl benzenes and three trimethylbenzene isomers. The AHN measurements included all of
159 the above for m/z 107, but only three trimethylbenzene isomers at m/z 121.

160 Humidity dependencies on instrument sensitivities and background were thoroughly investigated in
161 the laboratory after the campaign. Calibrations showed no significant variations of sensitivity with
162 humidity. Corrections were applied to compounds showing humidity effects on instrument
163 background, but not all effects could be recreated and accounted for, such as humidity effects on
164 inlet impurities affecting aromatics (Supplementary content B).

165 Fragmentation can become a concern at higher E/N ratios (de Gouw and Warneke, 2007; Maleknia
166 et al., 2007; Warneke et al., 2003). An E/N ratio of 125 Td was used in this study as this represents a
167 compromise between reagent ion clustering and fragmentation suppression (Hewitt et al., 2003).
168 Some fragmentation can still occur, as several studies using a coupled GC-PTR-MS with a range of
169 E/N ratios have identified various fragment ions. Benzaldehyde, ethyl benzene and xylene isomers
170 with m/z 107 may produce fragments of about 30-40% at m/z 79 with higher E/N ratios (Maleknia et
171 al., 2007), as well as propyl benzene isomers and smaller contributions of fragments of butyl
172 benzene (Warneke et al., 2003). As only *o*-xylene was present in the calibration standard, fragments
173 from other compounds at that mass cannot be accounted for and are likely to have contributed to
174 the increased PTR-MS signal. It is estimated that with an electrical field strength of 125 Td around
175 15% C_2 -benzenes may have contributed to m/z 79. Interference from fragments at m/z 93 could
176 include a range of biogenic terpenes and their isomers (Maleknia et al., 2007).

177 Previous studies have shown that there is good correlation between PTR-MS and GC-FID, however
178 the quantitative agreement can be poor with differences of up to a factor of 2 (de Gouw and
179 Warneke, 2007; Kato et al., 2004). The value for m/z 121 is somewhat higher than cited in the
180 literature, which may be due to humidity effects on inlet impurities which could not be accounted
181 for after the campaign, as well as isobaric interference from compounds and fragments not
182 measured by the AHN. All four m/z showed very good correlations (Figure 4) with r 0.90-0.91
183 ($p < 0.001$) in agreement with literature values (Kuster et al., 2004; Langford et al., 2010b).

184 **3.2.1 Correlations with carbon monoxide**

185 Carbon monoxide (CO) concentrations were used for correlations and ratios with VOCs to determine
186 whether the VOC sources were from fuel combustion (Table 3), as CO is a suitable marker for
187 anthropogenic combustion emissions.

188 High correlations for acetonitrile against CO indicate that fuel burning was likely the primary source
189 at NK. Correlations with CO were higher for PTR-MS than GC-FID (r 0.65 – 0.75, $p < 0.001$ for PTR-MS;
190 r 0.58-0.68, $p < 0.001$ for GC-FID). Possibly the higher temporal resolutions and the longer sampling
191 time of the PTR-MS allowed the detection of short-term variations in emission patterns.

192 3.3 VOC correlations and ratios

193 Correlations between the different VOCs yielded coefficients (r) ranging between -0.23 and 0.97 at
194 NK and -0.20 to 0.87 at MRd ($p < 0.001$). The poorer correlations involved methanol (r -0.23 - 0.35).
195 Methanol has a variety of different sources, which in this case had little commonality with the other
196 compounds. Strong linear correlations (r 0.67 - 0.97 at NK, 0.48 - 0.87 at MRd) indicate that the
197 other compounds shared some or almost all sources, however, bimodal distributions can relate to
198 multiple separate sources. In winter, vehicle exhaust and, to a small extent, evaporative emissions
199 account for a majority of the sources. The r -values at MRd were lower than at NK showing more
200 scatter (Figure 5). This may reflect a sequential sampling artefact due to the instrument continuously
201 cycling through the different m/z , combined with highly variable concentrations at this site.
202 Alternatively, it may represent true variability in the nearby emission source; within traffic
203 emissions, diverse types of vehicles, fuels, and driving patterns result in different traffic related VOC
204 ratios (Figure 5, A and B), which can be detected by online methods as the compounds reach the
205 inlet with little mixing (Chan et al., 1991; Chan et al., 2002).

206 Biomass burning for heating may explain a secondary source contribution to acetonitrile at MRd, as
207 it mostly occurs with cold temperatures and is not shared with benzene, hence is not related to
208 traffic emissions (Figure 5 D).

209 Using temperature as a third variable can illustrate temperature dependencies of source
210 contributions. Cycloalkanes/isoprene and benzene show a good correlation ($r = 0.77$ and 0.80) as
211 they are present in tailpipe emissions (Park et al., 2011) with a seasonally low biogenic component
212 (Figure 5, E and F). The main source of most C_2 - and C_3 -benzenes are motor vehicle emissions (Heeb
213 et al., 2000) which was reflected in the high correlations (0.72 to 0.97 , $p < 0.001$). These aromatics
214 have a shorter atmospheric lifetime making them important factors in urban photochemical smog
215 production (Table 1a).

216 Benzene-to-toluene (b/t) ratios can indicate the photochemical age of the pollution carried by air
217 masses (Warneke et al., 2001 and references therein). Due to seasonally low OH concentrations,
218 only changes in b/t ratios over longer periods were considered to be representative of air mass
219 transport.

220 The median (IQR) b/t ratios were around 0.6 (0.43-0.80) at both sites and agreed with previous
221 values (Chan et al., 2002; Heeb et al., 2000; Langford et al., 2009), as well as with those from the
222 AHN at MRd with a median of 0.6 (0.48-0.76) ($r = 0.90$, $p < 0.001$). These b/t ratios are consistent with
223 the air mass footprints derived from the UK Met Office's Numerical Atmospheric-dispersion
224 Modelling Environment (NAME) (Jones et al., 2007) using Unified Model (UM) Met data (Figure 6).

225 This model simulates the origin of the air masses affecting the ClearfLo sites within the previous 24h
226 (Bohnenstengel et al., in review). Shifts between high and low pollution episodes often are
227 correlated with changes in wind direction and intensity. For the low pollution periods (19th-23rd Jan
228 and 31st Jan-2nd Feb) strong westerlies brought air masses with regional influences and high b/t
229 ratios of 0.91 (0.64-1.31). The high pollution episodes (24th -25th Jan and 4th Feb) showed low wind
230 speeds resulting in shorter travel distances of the air masses and stronger local London influences
231 (up to 87%, campaign average 37%) and corresponding low b/t ratios of 0.48 (0.39-0.58).

232 **3.4 Diurnal averages**

233 Meteorological conditions can mask emission patterns, therefore diurnal averages are used to aid in
234 their identification (Figure 7). Concentrations can depend on the mixing height in the boundary
235 layer, however LIDAR measurements showed little diurnal variation in the seasonally shallow mixing
236 height (500-1000m) (Bohnenstengel et al., in review). All compounds, bar methanol, showed a
237 double rush hour peak during weekdays (07:00-10:00 and 17:00-20:00 GMT) and lower
238 concentrations with less variability on weekends (Figure 7, E - H), suggesting vehicle exhaust as a
239 major source. At MRd, rush hour peaks were less pronounced due to the continuously high daytime
240 traffic density (68002 vehicles per day; Department for Transport, 2012), which causes the road to
241 saturate for prolonged periods during the day.

242 The early morning minima (04:00 – 06:00 GMT) can be attributed to reduced human activity which
243 sharply increases during the morning rush hour peak (07:00-10:00 GMT) (Figure 7, F – H). Methanol
244 and acetone have numerous sources and longer atmospheric lifetimes resulting in no clear diurnal
245 pattern (Figure 7, A and B).

246 **3.5 Analyses of wind direction dependence**

247 **3.5.1 Synoptic polar plots**

248 Using wind speed and direction measurements from the BT tower (190 m a.g.l.), polar plots were
249 constructed for compound mixing ratios (Figure 8) using a generalized additive model (GAM) (Hastie
250 and Tibshirani, 1990; Wood, 2006) to interpolate between averaged data points in the R package
251 openair (Carslaw, 2012; Carslaw and Ropkins, 2012). At NK high concentrations for most compounds
252 were associated with low wind speeds (i.e. $<5 \text{ m s}^{-1}$) indicating local emission sources. Methanol
253 showed high concentrations with WSW wind directions and speeds $>5 \text{ m s}^{-1}$ possibly representing
254 pollution transported to the site from a biodiesel production facility located 1km SW of the site.
255 Biodiesel production from waste cooking oil by transesterification often involves evaporating
256 methanol.

257 At MRd methanol showed high concentrations with S and N winds $>10 \text{ m s}^{-1}$, whereas benzene is
258 representative of the other compounds with patches of increased concentrations at speeds of 5-10
259 m s^{-1} . The WSW and ENE patches coincide with the directional layout of Marylebone Rd, while the
260 SSW source may originate from traffic in the Marble Arch/Hyde Park Corner area, which boasted the
261 highest annual mean traffic count of 100574 motor vehicles per day in all of Westminster, London
262 (DfT, 2012).

263 **3.5.2 Synoptic wind direction dependencies and comparison with NAEI**

264 To quantify wind direction dependencies (Section 3.5.1) and compare measured VOC mixing ratios at
265 MRd with the National Atmospheric Emissions Inventory (NAEI) for estimated emissions, general
266 linear models were used for each compound concentration against the four wind direction
267 categories. There was no significant difference in wind speed with direction. Correlations of VOC
268 concentrations with wind speed showed weak negative relationships ($r = -0.38$ to -0.14 , $p < 0.05$)
269 indicating that a dilution effect depending on wind speed from above-canyon air mass mixing may
270 play a small role in street canyon concentrations.

271 All species showed significant differences in mixing ratios with wind direction (F- statistic 6.73 - 41.8,
272 $p < 0.001$ for measured compounds; $F = 4.48$, $p < 0.01$ for estimated benzene) and agreed with the
273 polar plots. Differential source density within the four sectors and fetch variability over the city are
274 likely reasons.

275 Estimated emissions and observed concentrations for benzene agreed that low emission source
276 densities to the N resulted in low observed mixing ratios. The largest estimated emissions were to
277 the E, whereas measurements indicated the S. Regent's Park to the N and Hyde Park to the S have
278 large areas of low emissions reducing the estimates in these sectors. Emission estimates also ignore
279 background values from greater fetch across London. High localized emission sources seen in the
280 polar plots (Figure 8) could be responsible for higher measured VOC concentrations to the W and S,
281 which partially agrees with the high estimated emissions from the nearest westerly grid cell.
282 Estimated emissions from the NAEI are integrated over 1 km^2 grid resolution, but localized sub-grid
283 scale effects may be masked by the grid averaging area. It must be emphasized that the volume
284 mixing ratios were measured at ground-level within the street canyon, whereas the wind data are
285 representative of synoptic winds above the street canyons.

286 **4 Conclusion**

287 High VOC concentrations during the winter in urban locations are mostly from traffic emissions. This
288 was reflected at both sites in diurnal profiles, VOC/VOC and VOC/CO correlations and ratios, wind
289 sector dependence analyses and polar plots. Measurements at the NK background site indicated

290 significantly lower mixing ratios than at the MRd kerbside site, even though AHN data showed that
291 kerbside concentrations were higher during the first measurement period, suggesting site
292 differences due to the location with different source strengths and proximity.

293 Comparison of PTR-MS and GC-FID data from MRd for aromatics showed good correlation and
294 qualitative agreement. However, PTR-MS data were significantly higher possibly due to some
295 isobaric interference from additional compounds and fragments, and possibly systematic errors
296 introduced during instrument background corrections. Short term variations in the ratio of traffic
297 related compounds from differences in traffic density, driving style, vehicle and fuel types were
298 observed by PTR-MS at MRd site and higher correlations with CO for PTR-MS than the GC-FID
299 measurements were likely due to the fast response and longer sampling times of the PTR-MS. The
300 AHN can only report hourly arithmetic means due to the methods employed, possibly leading to a
301 reporting bias and a loss of information on short term variability.

302 Elevated concentrations were mostly observed when synoptic-scale wind speeds were low at NK as
303 dispersion of localised emissions was reduced. However, some non-local emission sources were
304 detected using polar plots and possible sources were identified. There were significant differences in
305 VOC concentrations with wind direction. When compared with estimated benzene emissions by the
306 NAEI, estimates were less representative when VOC concentrations were high, as they are unable to
307 capture the influence of city background emissions and reduced local sub-grid emission source
308 contributions.

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317 and University of York) for the meteorological and CO data at NK.

318 **References**

- 319 Atkinson, R. (2000). Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*, 34(12-14),
320 2063–2101, doi:10.1016/S1352-2310(99)00460-4.
- 321 Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A., Meinardi, S., Simpson, I. J., Blake, D. R.
322 & Rowland, F. S. (2008). Measurements of nonmethane hydrocarbons in 28 United States cities.
323 *Atmospheric Environment*, 42(1), 170–182, doi:10.1016/j.atmosenv.2007.09.007,.
- 324 Bohnenstengel, S.I., Belcher, S.E., Allan, J.D., Allen, G., Bacak, A., Bannan, T.J., Barlow, J.F., Beddows,
325 D. C. S., Bloss, W. J., Booth, A. M., Chemel, C., Coceal, O., Di Marco, C.F., Faloon, K. H., Fleming, Z.,
326 Furger, M., Geitl, J. K., Graves, R. R., Green, D. C., Grimmond, C. S. B., Halios, C., Hamilton, J. F.,
327 Harrison, R. M., Heal, M. R., Heard, D. E., Helfter, C., Herndon, S. C., Holmes, R. E., Hopkins, J. R.,
328 Jones, A. M., Kelly, F. J., Kotthaus, S., Langford, B., Lee, J. D., Leigh, R. J., Lewis, A. C., Lidster, R. T.,
329 Lopez-Hilfiker, F. D., McQuaid, J. B., Mohr, C., Monks, P. S., Nemitz, E., Ng, N. L., Percival, C. J.,
330 Prévôt, A. S. H., Ricketts, H. M. A., Sokhi, R., Stone, D., Thornton, J. A., Tremper, A. H., Valach, A. C.,
331 Visser, S., Whalley, L. K., Williams, L. R., Xu, L., Young, D. E. & Zotter, P. (submitted 2013).
332 Meteorology, air quality, and health in London: The ClearLo project. *Bulletin of the American*
333 *Meteorological Society*.
- 334 Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J. C., & Guillermo, R. (2001). An
335 investigation into the traffic-related fraction of isoprene at an urban location, *Atmospheric*
336 *Environment*, 35(22), 3749-3760, doi:10.1016/S1352-2310(01)00170-4.
- 337 Broadway, G. & Tipler, A. (2008). *Gas Chromatography: Ozone Precursor Analysis Using a Thermal*
338 *Desorption- GC System (White paper)*, 1–13.
- 339 Cady-Pereira, K. E., Shephard, M. W., Millet, D. B., Luo, M., Wells, K. C., Xiao, Y., Payne, V. H. &
340 Worden, J. (2012). Methanol from TES global observations: retrieval algorithm and seasonal and
341 spatial variability. *Atmospheric Chemistry and Physics*, 12(17), 8189–8203, doi:10.5194/acp-12-8189-
342 2012.
- 343 Carslaw, D.C. & Ropkins, K. (2012). openair — an R package for air quality data analysis.
344 *Environmental Modelling & Software*, 27-28, 52-61.
- 345 Carslaw, D. (2012). *The openair manual — open-source tools for analysing air pollution data. Manual*
346 *for version 0.5-16*. King's College London.
- 347 Chan, C., Ozkaynak, H., Spengler, J. D., & Sheldon, L. (1991). Driver Exposure to Volatile Organic
348 Compounds , CO , Ozone , and NO , under Different Driving Conditions. *Environmental Science &*
349 *Technology*, (5), 964–972.
- 350 Chan, C. Y., Chan, L. Y., Wang, X. M., Liu, Y. M., Lee, S. C., Zou, S. C., Sheng, G. Y. & Fu, J. M. (2002).
351 Volatile organic compounds in roadside microenvironments of metropolitan Hong Kong,
352 *Atmospheric Environment* 36, 2039–2047.
- 353 de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W.C., Roberts, J. M.,
354 Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M.,
355 Bertman, S. B., & Bates, T. S. (2005). Budget of organic carbon in a polluted atmosphere: Results
356 from the New England Air Quality Study in 2002. *Journal of Geophysical Research*, 110, D16305.

- 357 de Gouw, J. & Warneke, C. (2007). Measurements of volatile organic compounds in the Earth's
358 atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry Reviews*, 26,
359 223– 257, doi:10.1002/mas.
- 360 Department for Transport, www.dft.gov.uk/traffic-counts/, accessed on 22/11/2013.
- 361 Derwent, R. G. (1995). *Sources, Distributions, and Fates of VOCs in the Atmosphere*, (23).
- 362 Erickson, M. H., Gueneron, M. & Jobson, B. T. (2014). Measuring long chain alkanes in diesel engine
363 exhaust by thermal desorption PTR-MS, *Atmospheric Measurement Techniques*, 7(1), 225-239,
364 doi:10.5194/amt-7-225-2014.
- 365 Hastie, T. J. & Tibshirani, R. (1990). *Generalized additive models*. Chapman and Hall, London.
- 366 Heeb, N. V, Forss, A., Bach, C., Reimann, S., Herzog, A., & Jäckle, H. W. (2000). A comparison of
367 benzene, toluene and C₂-benzenes mixing ratios in automotive exhaust and in the suburban
368 atmosphere during the introduction of catalytic converter technology to the Swiss Car Fleet.
369 *Atmospheric Environment*, 34, 3103–3116.
- 370 Hewitt, C. N., Hayward, S., & Tani, A. (2003). The application of proton transfer reaction-mass
371 spectrometry (PTR-MS) to the monitoring and analysis of volatile organic compounds in the
372 atmosphere. *Journal of Environmental Monitoring*, 5(1), 1–7. doi:10.1039/b204712h
- 373 Hewitt, C. N. (1999). *Reactive Hydrocarbons in the Atmosphere*. Elsevier, New York.
- 374 Holzinger, R., Jordan, A., & Hansel, A. (2001). Automobile Emissions of Acetonitrile : Assessment of
375 its Contribution to the Global Source, *Journal of Atmospheric Chemistry*, 38, 187–193.
- 376 Jobson, B. T., Volkamer, R. A., Velasco, E., Allwine, G., Westberg, H., Lamb, B. K., Alexander, M. L.,
377 Berkowitz, C. M. & Molina, L. T. (2010). Comparison of aromatic hydrocarbon measurements made
378 by PTR-MS, DOAS and GC-FID during the MCMA 2003 Field Experiment. *Atmospheric Chemistry and*
379 *Physics*, 10(4), 1989–2005, doi:10.5194/acp-10-1989-2010.
- 380 Jones, A.R., Thomson, D.J., Hort, M. & Devenish, B. (2007). The U.K. Met Office's next-generation
381 atmospheric dispersion model, NAME III. In B. C. A.-L., *Air Pollution Modeling and its Application*
382 *XVII: Proceedings of the 27th NATO/CCMS International Technical Meeting on Air Pollution*
383 *Modelling and its Application* (pp. 580-589). Springer.
- 384 Kansal, A. (2009). Sources and reactivity of NMHCs and VOCs in the atmosphere: a review. *Journal of*
385 *Hazardous Materials*, 166(1), 17–26. doi:10.1016/j.jhazmat.2008.11.048
- 386 Kato, S., Miyakawa, Y., Kaneko, T. & Kajii, Y. (2004). Urban air measurements using PTR-MS in Tokyo
387 area and comparison with GC-FID measurements, *International Journal of Mass Spectrometry*, 235
388 (2), 103-110, doi:10.1016/j.ijms.2004.03.013
- 389 Kim, Y. M., Harrad, S., & Harrison, R. M. (2001). Concentrations and sources of VOCs in urban
390 domestic and public microenvironments. *Environmental Science & Technology*, 35(6), 997–1004.
- 391 Kuster, W. C., Jobson, B. T., Karl, T., Riemer, D., Apel, E., & Goldan, P. D. (2004). Intercomparison of
392 Volatile Organic Carbon Measurement Techniques and Data at La Porte during the TexAQS2000 Air
393 Quality Study, *Environmental Science & Technology*, 38(1), 221–228.

- 394 Langford, B., Davison, B., Nemitz, E., & Hewitt, C. N. (2009). Mixing ratios and eddy covariance flux
395 measurements of volatile organic compounds from an urban canopy (Manchester, UK). *Atmospheric*
396 *Chemistry and Physics*, 9, 1971–1987.
- 397 Langford, B., Misztal, P. K., Nemitz, E., Davison, B., Helfter, C., Pugh, T. A. M., MacKenzie, A. R., Lim,
398 S. F. & Hewitt, C. N. (2010a). Fluxes and concentrations of volatile organic compounds from a South-
399 East Asian tropical rainforest. *Atmospheric Chemistry and Physics*, 10(17), 8391–8412,
400 doi:10.5194/acp-10-8391-2010
- 401 Langford, B., Nemitz, E., House, E., Phillips, G. J., Famulari, D., Davison, B., Hopkins, J. R., Lewis, A. C.
402 & Hewitt, C. N. (2010b). Fluxes and concentrations of volatile organic compounds above central
403 London, UK. *Atmospheric Chemistry and Physics*, 10, 627–645.
- 404 Lindinger, W., Hansel, A., & Jordan, A. (1998). On-line monitoring of VOCs at pptv levels by means of
405 PTR-MS. Medical applications, food control and environmental research. *International Journal of*
406 *Mass Spectrometry and Ion Processes*, 173(7), 191–241, doi:10.1016/0015-1882(95)90197-3.
- 407 Maleknia, S. D., Bell, T. L., & Adams, M. A. (2007). PTR-MS analysis of reference and plant-emitted
408 volatile organic compounds. *International Journal of Mass Spectrometry*, 262(3), 203–210,
409 doi:10.1016/j.ijms.2006.11.010.
- 410 Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R., & Arey, J. (1999). Formation of acetone from
411 the OH radical- and O₃-initiated reactions of a series of monoterpenes. *Journal of Geophysical*
412 *Research*, 104, 13869–13879.
- 413 Park, C., Schade, G. W., & Boedeker, I. (2011). Characteristics of the flux of isoprene and its oxidation
414 products in an urban area. *Journal of Geophysical Research: Atmospheres* (1984–2012), 116(D21).
- 415 Spaněl, P. & Smith, D. (2000). Influence of water vapour on selected ion flow tube mass
416 spectrometric analyses of trace gases in humid air and breath. *Rapid communications in mass*
417 *spectrometry : RCM*, 14(20), 1898–906, doi:10.1002/1097-0231(20001030)14:20<1898::AID-
418 RCM110>3.0.CO;2-G.
- 419 UK Met Office, <http://www.metoffice.gov.uk/>, accessed 10/2/2012.
- 420 Warneke, C., de Gouw, J. A., Kuster, W. C., Goldan, P. D., & Fall, R. (2003). Validation of atmospheric
421 VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic
422 pre-separation method. *Environmental Science & Technology*, 37(11), 2494–501.
- 423 Warneke, C., Karl, T., Judmaier, H., Hansel, A., Jordan, A., Lindinger, W., & Crutzen, P. J. (1999).
424 Acetone, methanol, and other partially oxidized volatile organic emissions from dead plant matter by
425 abiological processes: Significance for atmospheric HO_x chemistry. *Global Biogeochemical Cycles*, 13,
426 9–17.
- 427 Warneke, C., van der Veen, C., de Gouw, J. A., & Kok, A. (2001). Measurements of benzene and
428 toluene in ambient air using proton-transfer-reaction mass spectrometry : calibration , humidity
429 dependence , and field intercomparison, *International Journal of Mass Spectrometry*, 207, 167–182.
- 430 Wood, S. (2006). *Generalized Additive Models: An introduction with R*. Chapman & Hall/CRC.
- 431 Yardley, R., Dornie, J., & Dumitrean, P. (2012). UK Hydrocarbon Network Annual Report for 2011, (1).

432 Yuan, B., Warneke, C., Shao, M. & de Gouw, J. (2014). Interpretation of volatile organic compound
433 measurements by proton-transfer-reaction mass spectrometry over the Deepwater Horizon oil spill,
434 International Journal of Mass Spectrometry, 358, 43-48.

435

ACCEPTED MANUSCRIPT

436 **Figure 1.** *Top:* 5 min means of ambient air temperature ($^{\circ}\text{C}$) and relative humidity (%) during the
437 campaign 16th Jan – 7th Feb 2012. *Bottom:* Frequency plots of mesoscale wind direction (%) with
438 subcategories of wind speed (m s^{-1}) using 30 min mean data from the WXT520 (Vaisala Ltd) at 190m
439 on the BT tower at NK (16th – 25th Jan 2012) (*left*) and MRd (25th Jan – 7th Feb 2012) (*right*).

440 **Figure 2.** 5min mean (grey) and 25 min means (black) with detection limits (dashed line) for all
441 measured VOCs (ppb) at **(a)** North Kensington and **(b)** Marylebone Rd (16th Jan – 7th Feb 2012). *M/z*
442 are 33 (methanol), 42 (acetonitrile), 45 (acetaldehyde), 59 (acetone), 69 (cycloalkanes/isoprene), 79
443 (benzene), 93 (toluene), 107 (C_2 -benzenes) and 121 (C_3 -benzenes).

444 **Figure 3.** 1h means for benzene, toluene, C_2 - and C_3 -benzenes mixing ratios (ppb) measured by the
445 PTR-MS (solid line) and GC-FID (dashed line) at Marylebone Road (25th Jan – 7th Feb 2012).

446 **Figure 4.** Scatter plots of 1h mean VOC concentrations (ppb) (benzene, toluene, C_2 - and C_3 -benzenes)
447 of PTR-MS against GC-FID measurements at Marylebone Road (25th Jan – 7th Feb 2012) with reduced
448 major axis (RMA) linear regressions, $\pm 99^{\text{th}}$ confidence intervals, 1:1 line (dotted) with r-values.

449 **Figure 5.** Scatter plots of representative VOC correlations measured at North Kensington (left) and
450 Marylebone Rd (right) (16th Jan – 7th Feb 2012) using 5 min means (ppbv) with ambient air
451 temperature ($^{\circ}\text{C}$) at time of sampling (colour bar).

452 **Figure 6.** 24 hour back trajectories from the Met Office NAME dispersion model at North Kensington
453 (16th Jan-7th Feb 2012). Daily release for 3 hours from midday (20 m height) tracking the surface
454 layer only (0-100m) for the 24 hours prior. Reproduced with permission from Zoë Fleming (NCAS,
455 University of Leicester).

456 **Figure 7.** Diurnal plots of 25min averages (ppb) for representative VOCs at North Kensington and
457 Marylebone Road (16th Jan – 7th Feb 2012) with the 95% confidence interval (shaded areas), all days
458 (solid line), weekdays (dashed line) and weekends (dotted line).

459 **Figure 8.** Representative selection of polar plots of synoptic wind speed (m s^{-1}) against wind
460 direction ($^{\circ}$) from the BT tower (190m) with VOC mixing ratios (ppb) as a third variable (colour bar)
461 for methanol (*m/z* 33), acetonitrile (*m/z* 42) and benzene (*m/z* 79) at North Kensington (16th -25th Jan
462 2012) (*top*) and Marylebone Rd (25th Jan – 7th Feb 2012) (*bottom*).

463

464 **Table 1a. Summary of 5 min averages of VOC mixing ratios (ppb) at North Kensington, London (16th - 25th Jan 2012).**

Mixing ratios (ppb)	Methanol m/z 33	Aceto-nitrile m/z 42	Acetal-dehyde m/z 45	Acetone m/z 59	Cycloalkanes/ Isoprene m/z 69	Benzene m/z 79	Toluene* m/z 93	C ₂ -benzenes m/z 107	C ₃ -benzenes m/z 121
<i>Lifetime (OH^a)</i>	12 d	1.5 yr	8.8 h	53 d	1.4 h	9.4 d	1.9 d	5.9 h ^b	4.3 h ^c
N	2219	2202	2211	2213	2199	2227	2226	2225	2226
LoD	0.37	0.04	0.18	0.06	0.005	0.04	0.01	0.08	0.03
<i>Min.</i>	2.86	<LoD	<LoD	0.37	<LoD	<LoD	0.03	<LoD	0.04
1st quartile	5.06	0.05	0.29	0.95	0.08	0.14	0.21	0.23	0.24
<i>Median</i>	5.77	0.06	0.46	1.16	0.14	0.24	0.42	0.44	0.37
Geom. mean	6.17	0.07	0.50	1.25	0.13	0.24	0.42	0.45	0.40
<i>Arithm. mean</i>	6.40	0.08	0.62	1.34	0.17	0.31	0.60	0.63	0.50
3rd quartile	8.00	0.07	0.75	1.51	0.21	0.39	0.74	0.79	0.59
<i>Max.</i>	10.4	0.10	3.67	6.79	0.98	2.13	4.92	4.89	3.65
<i>SD</i>	1.84	0.05	0.51	0.67	0.13	0.26	0.61	0.62	0.42
<i>Skew</i>	0.39	2.09	2.08	3.02	1.90	2.19	2.53	2.62	2.61
Kurtosis	-0.89	6.03	5.25	13.5	4.85	6.96	8.71	9.45	9.36

465 ^a Atmospheric lifetimes with regard to OH for a 12-h daytime average OH radical concentration of 2.0×10^6
 466 molecule cm^{-3} (Atkinson, 2000).

467 ^b example using m-xylene.

468 ^c example using 1,2,4-trimethylbenzene.

469

470 **Table 1b. Summary of 5min averages of VOC mixing ratios (ppb) at Marylebone Rd, London (25th Jan - 7th Feb 2012).**

<i>Mixing ratios (ppb)</i>	<i>Methanol m/z 33</i>	<i>Aceto-nitrile m/z 42</i>	<i>Acetal-dehyde m/z 45</i>	<i>Acetone m/z 59</i>	<i>Cycloalkanes/ Isoprene m/z 69</i>	<i>Benzene m/z 79</i>	<i>Toluene m/z 93</i>	<i>C₂-benzenes m/z 107</i>	<i>C₃-benzenes m/z 121</i>
<i>N</i>	2712	2718	2716	2705	2720	2715	2713	2708	2715
<i>LoD</i>	0.37	0.04	0.18	0.06	0.005	0.04	0.01	0.08	0.03
<i>Min.</i>	1.34	0.08	0.38	0.70	0.15	0.06	0.02	<LoD	0.05
<i>1st quartile</i>	3.47	0.16	0.92	0.95	0.31	0.38	0.49	0.81	0.50
<i>Median</i>	5.00	0.19	1.34	1.15	0.39	0.56	0.80	1.21	0.86
<i>Geom. mean</i>	4.48	0.19	1.39	1.20	0.41	0.55	0.85	1.21	0.85
<i>Arithm. mean</i>	4.67	0.20	1.61	1.25	0.44	0.63	1.18	1.45	1.11
<i>3rd quartile</i>	5.61	0.24	2.07	1.47	0.53	0.81	1.50	1.87	1.52
<i>Max.</i>	7.39	0.56	6.18	3.78	1.18	3.57	10.0	7.60	4.76
<i>SD</i>	1.27	0.07	0.92	0.38	0.17	0.35	1.13	0.9	0.79
<i>Skew</i>	-0.47	1.33	1.29	1.21	1.05	1.68	2.8	1.62	1.21
<i>Kurtosis</i>	-0.72	2.28	1.53	2.04	0.65	5.36	11.6	0.02	1.20

471

472

473 Table 2 Summary of 1h averages of compounds (ppb) measured by both PTR-MS and GC-FID at Marylebone Rd, London
 474 (25th Jan – 7th Feb 2012).

Mixing ratios (ppb)	PTR-MS				GC-FID			
	Benzene m/z 79	Toluene m/z 93	C ₂ - benzenes m/z 107	C ₃ - benzenes m/z 121	Benzene m/z 79	Toluene m/z 93	C ₂ - benzenes m/z 107	C ₃ - benzenes m/z 121
<i>N</i>	274	274	274	256	302	302	302	302
LoD	0.04	0.01	0.08	0.03	0.01	0.01	0.01	0.01
Min.	0.17	0.13	0.29	0.13	0.14	0.07	0.03	0.01
<i>1st quartile</i>	0.39	0.52	0.87	0.46	0.30	0.38	0.57	0.13
Median	0.57	0.82	1.23	0.91	0.42	0.61	0.83	0.24
<i>Geom. mean</i>	0.58	0.95	1.30	0.81	0.41	0.66	0.86	0.24
Arithm. mean	0.63	1.17	1.44	1.07	0.47	0.87	1.01	0.33
<i>3rd quartile</i>	0.82	1.53	1.89	1.51	0.58	1.09	1.32	0.46
Max.	2.26	6.42	5.12	3.71	1.42	5.17	4.51	1.45
<i>SD</i>	0.32	1.01	0.81	0.74	0.23	0.83	0.63	0.29
Skew	1.30	2.06	1.38	0.93	1.53	2.33	1.39	1.27
<i>Kurtosis</i>	2.65	5.21	2.53	0.39	2.98	6.36	2.13	1.16

475

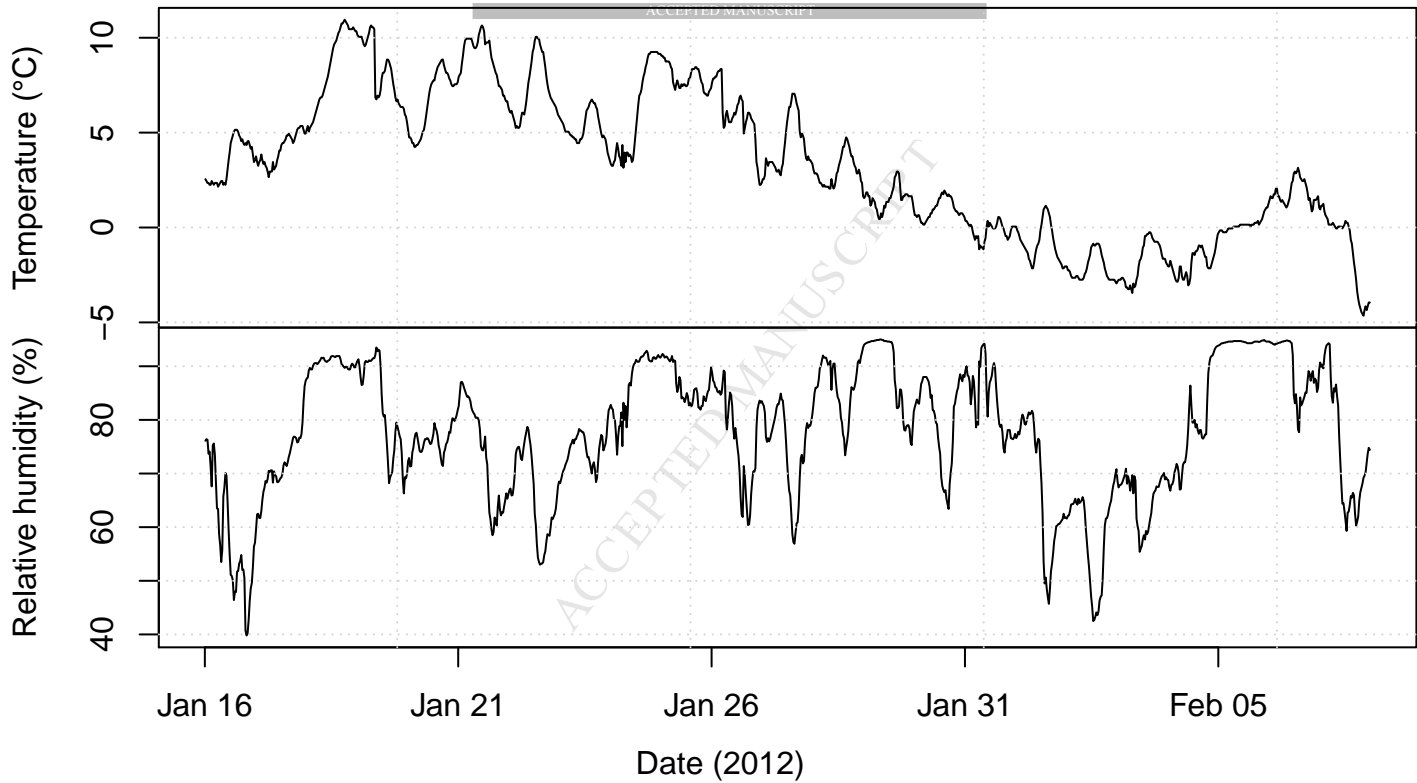
476

477 Table 3. Mean VOC/CO ratios for volume mixing ratios (ppbv/ppbv) at NK and MRd, London (16th Jan - 7th Feb 2012).

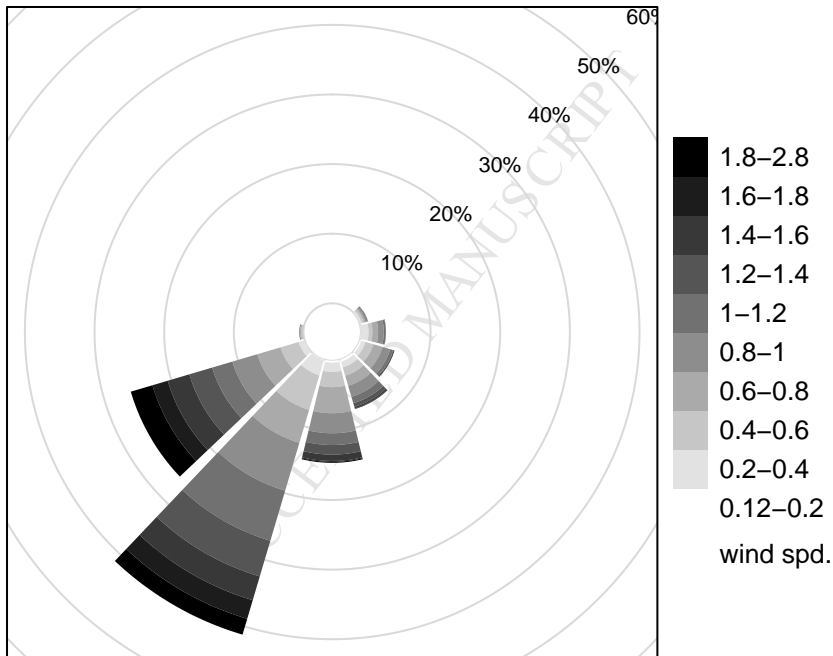
<i>Compound</i>	<i>ClearfLo</i>					
	<i>NK^a</i>		<i>MRd</i>			
	<i>PTR-MS</i>		<i>PTR-MS^b</i>		<i>GC-FID^c</i>	
	[VOC]/[CO]	<i>r</i>	[VOC]/[CO]	<i>r</i>	[VOC]/[CO]	<i>r</i>
<i>Methanol</i>	2.13E-02	0.28	1.20E-02	0.27		
<i>Acetonitrile</i>	2.70E-04	0.87	5.21E-04	0.55		
<i>Acetaldehyde</i>	2.14E-03	0.93	4.14E-03	0.84		
<i>Acetone</i>	4.53E-03	0.62	3.18E-03	0.74		
<i>Cycloalkanes/ Isoprene</i>	5.74E-04	0.80	1.13E-03	0.82		
<i>Benzene</i>	1.08E-03	0.96	1.59E-03	0.75	1.58E-03	0.68
<i>Toluene</i>	2.07E-03	0.93	3.09E-03	0.72	3.33E-03	0.65
<i>C2-benzenes</i>	2.16E-03	0.89	3.69E-03	0.66	4.70E-03	0.58
<i>C3-benzenes</i>	1.72E-03	0.86	2.60E-03	0.65	1.61E-03	0.68

478 ^aN = 226, ^bN = 256-274, ^cN = 302

479

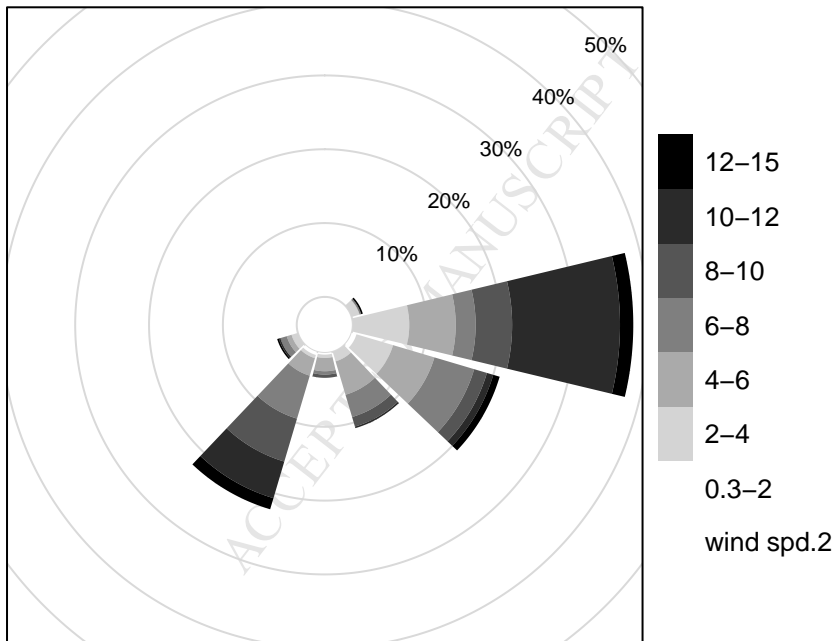


North Kensington wind frequency

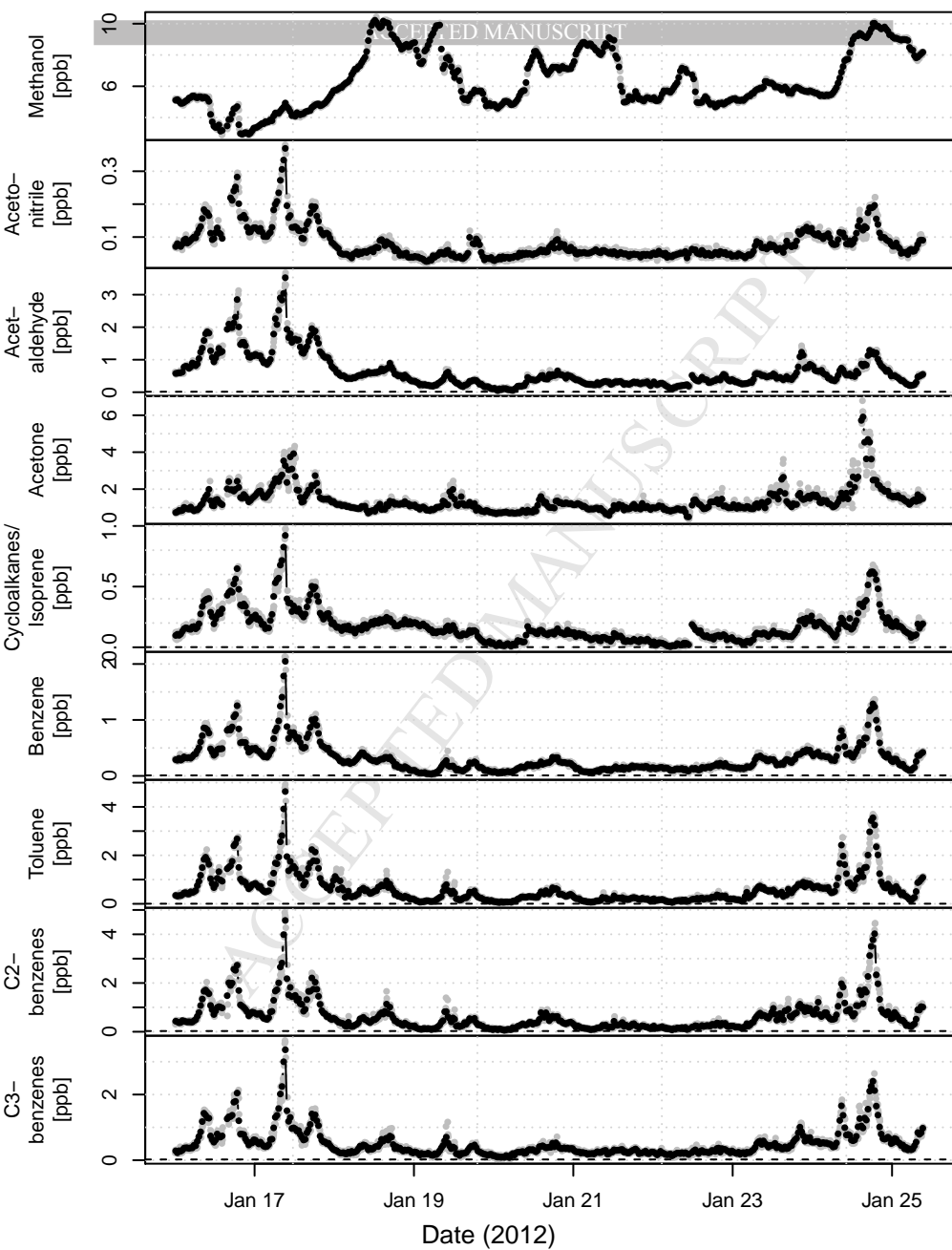


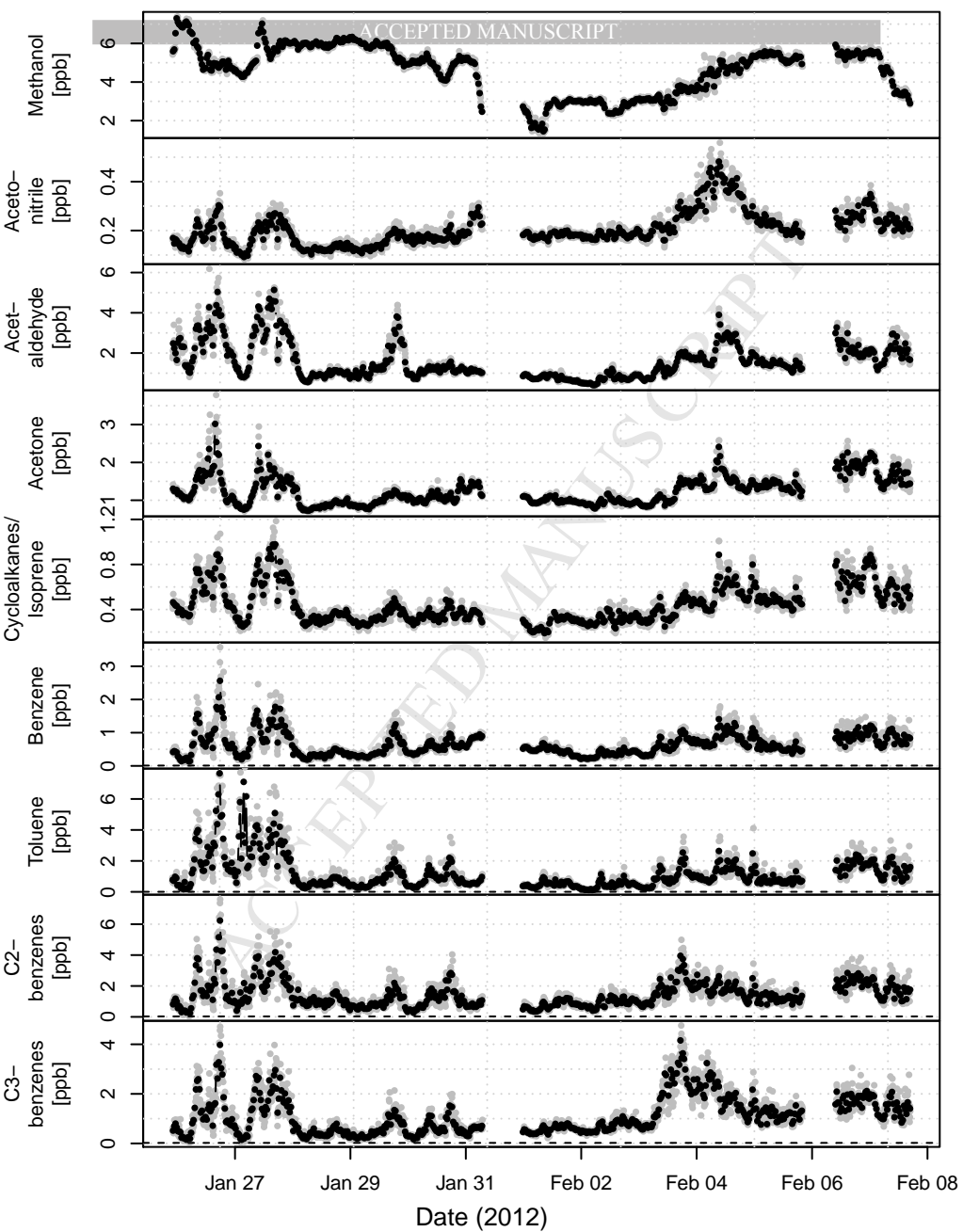
Frequency of counts by wind direction (%)

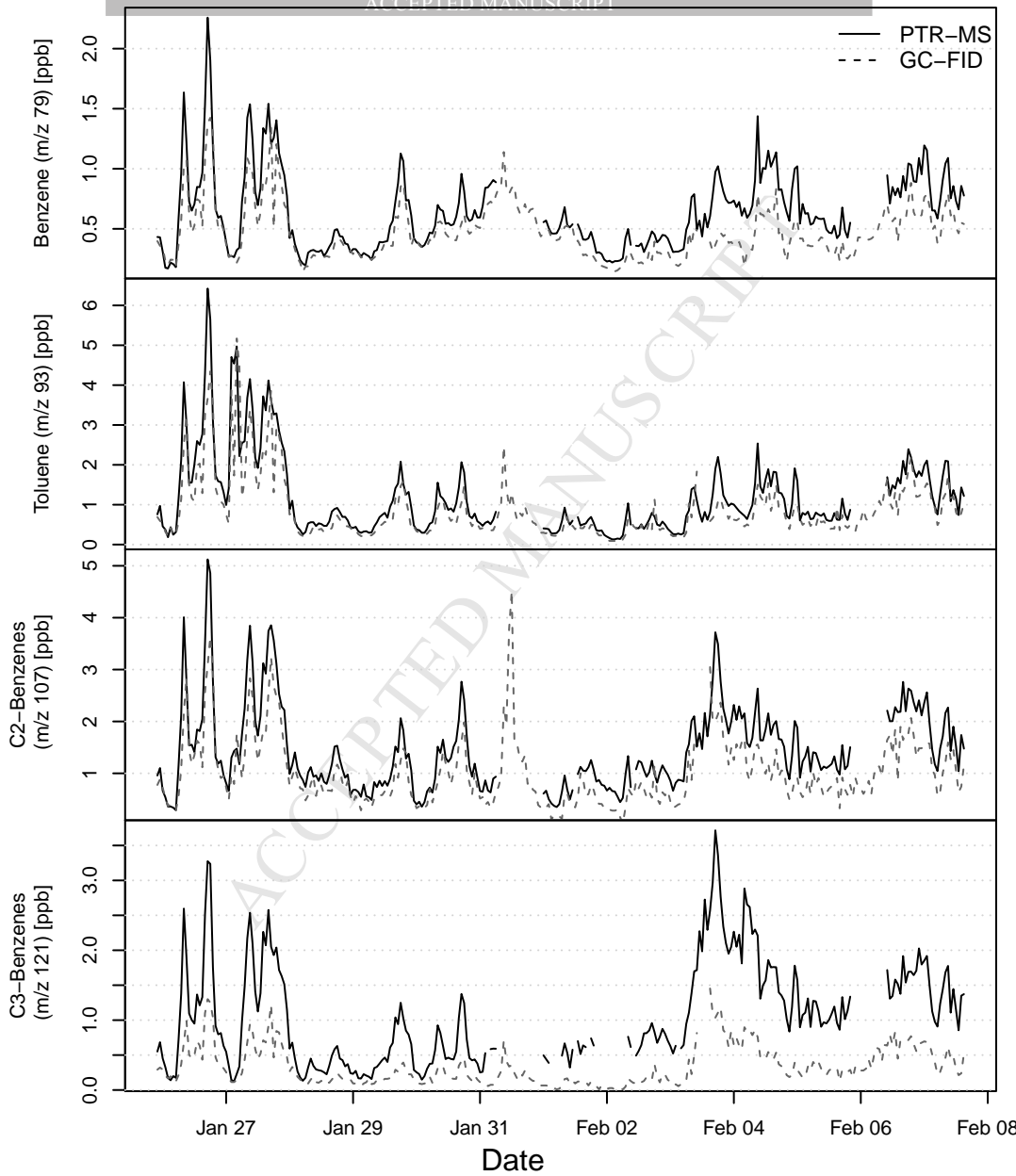
Marylebone Rd wind frequency

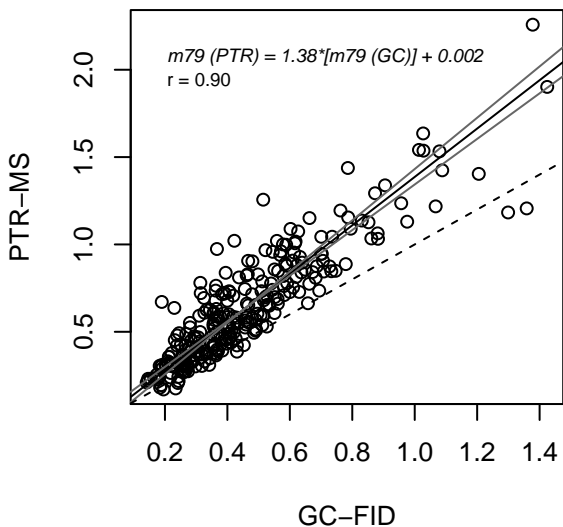
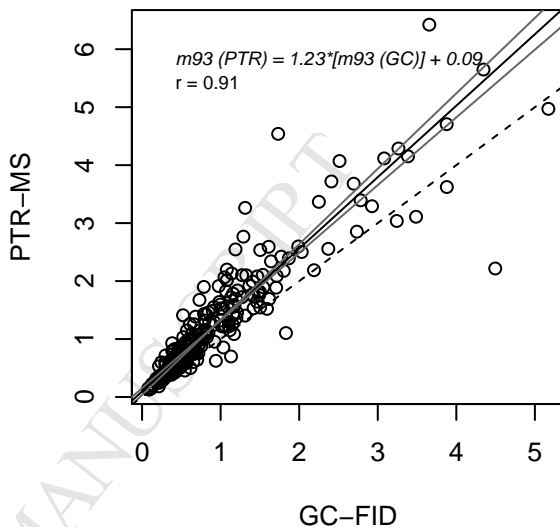
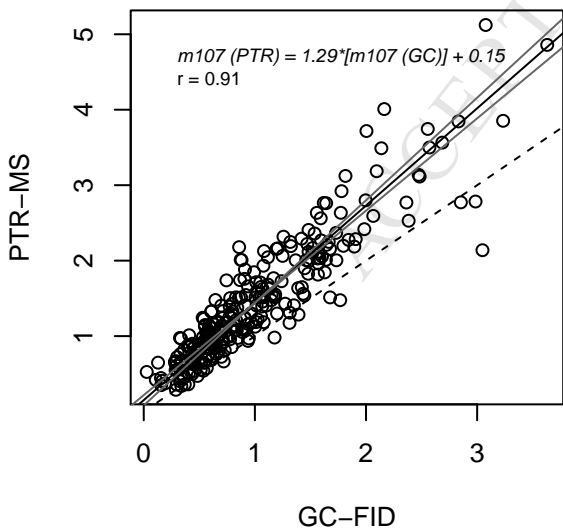
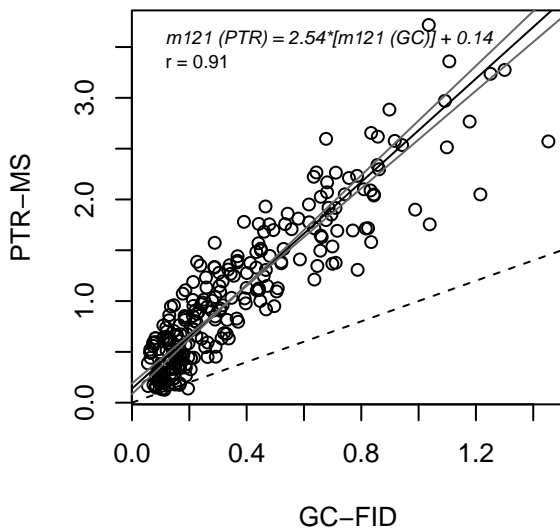


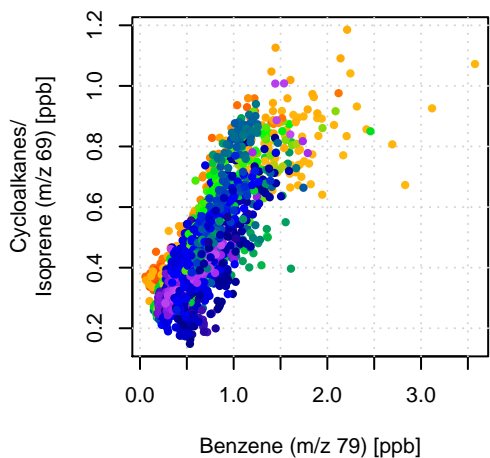
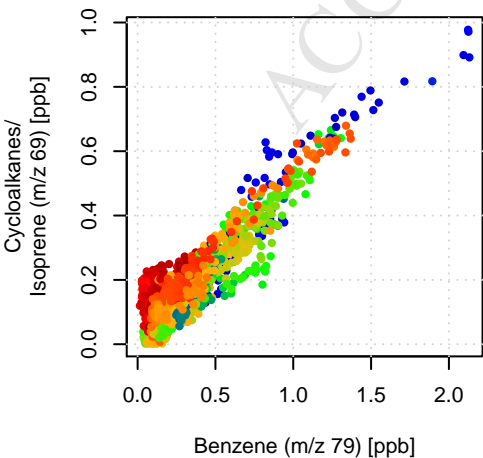
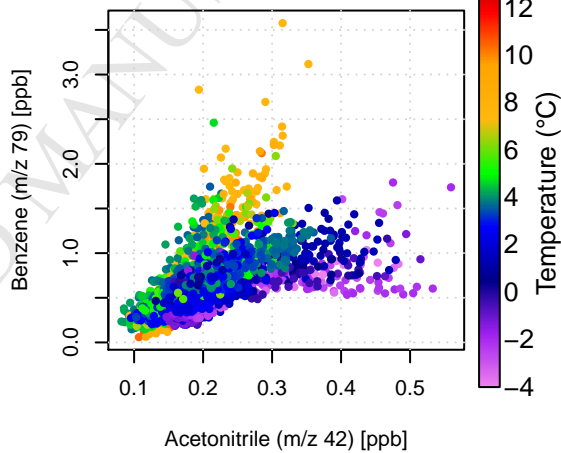
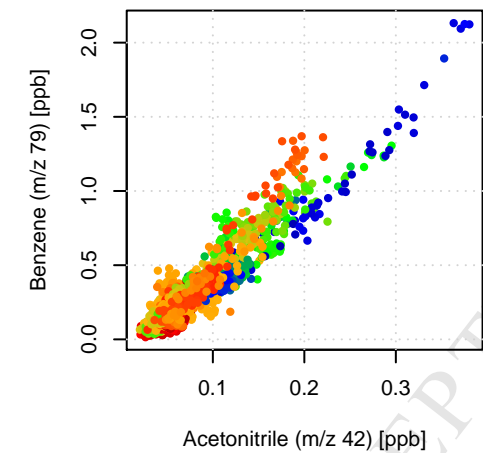
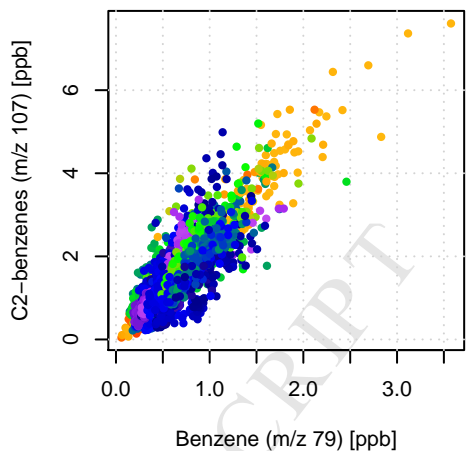
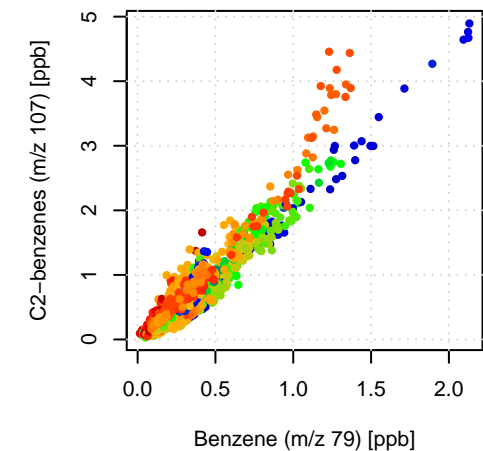
Frequency of counts by wind direction (%)







Benzene (m/z 79) [ppb]**Toluene (m/z 93) [ppb]****C2-Benzenes (m/z 107) [ppb]****C3-Benzenes (m/z 121) [ppb]**

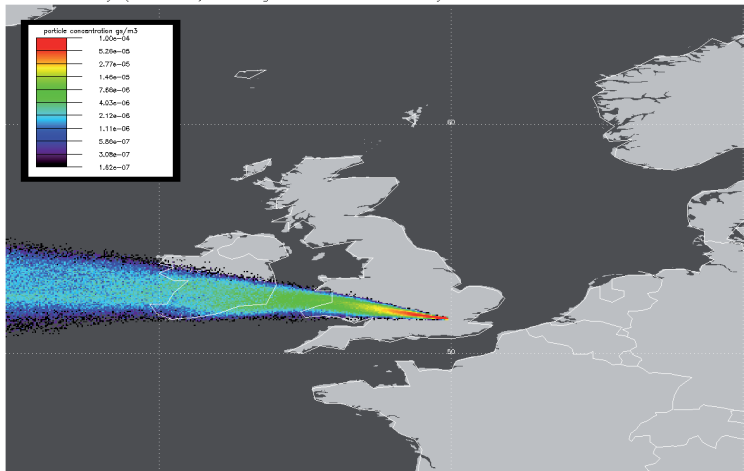


2012/01/21

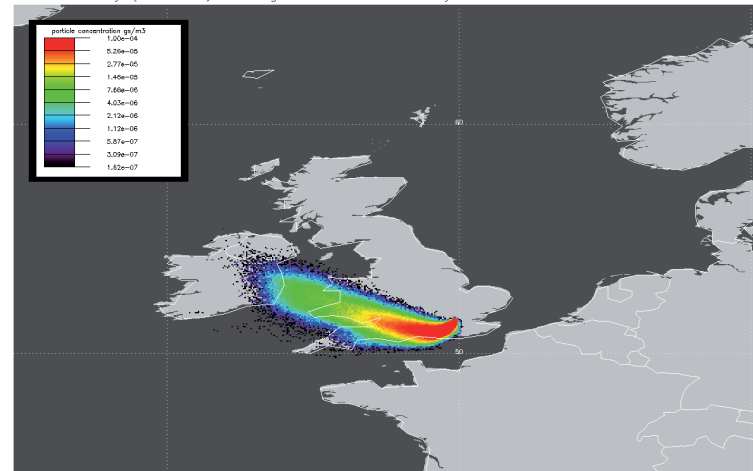
ACCEPTED MANUSCRIPT

2012/01/24

1 day (0–100m) arriving at BT tower 3 Hourly release from: 201201211200

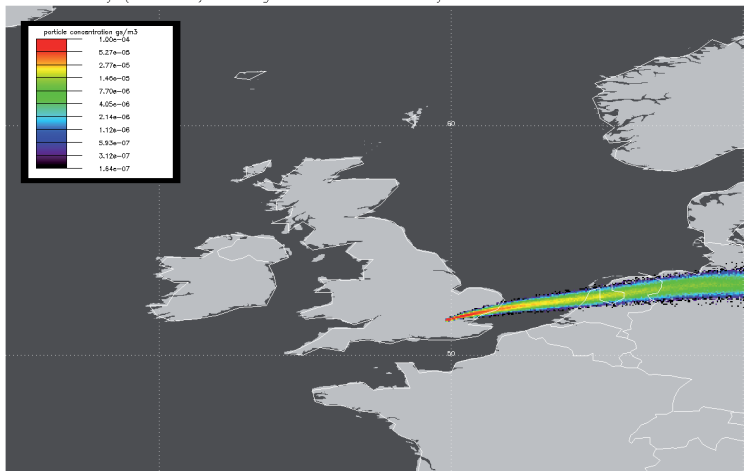


1 day (0–100m) arriving at BT tower 3 Hourly release from: 201201240900



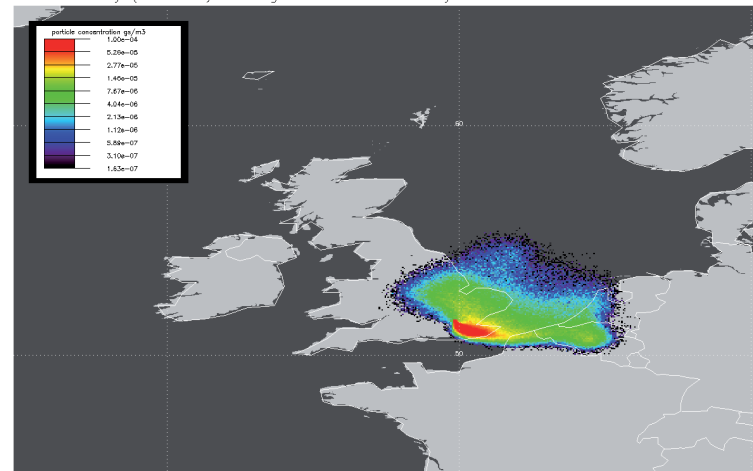
2012/02/01

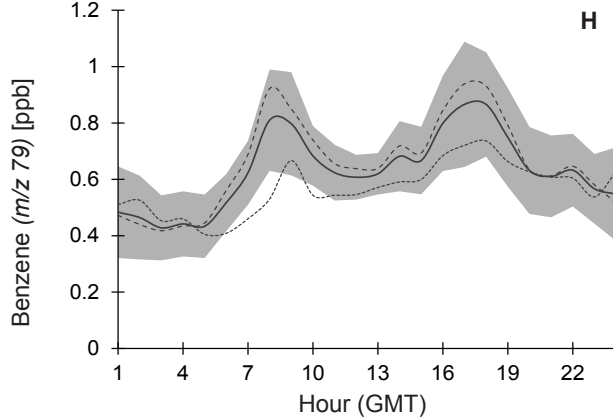
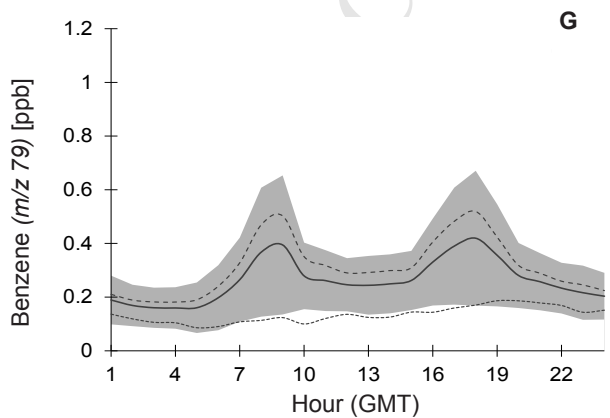
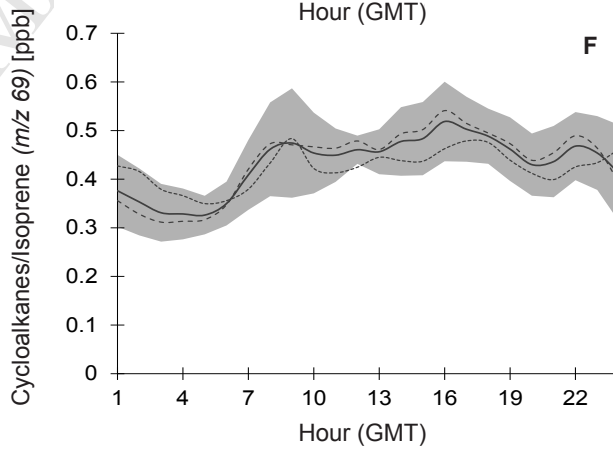
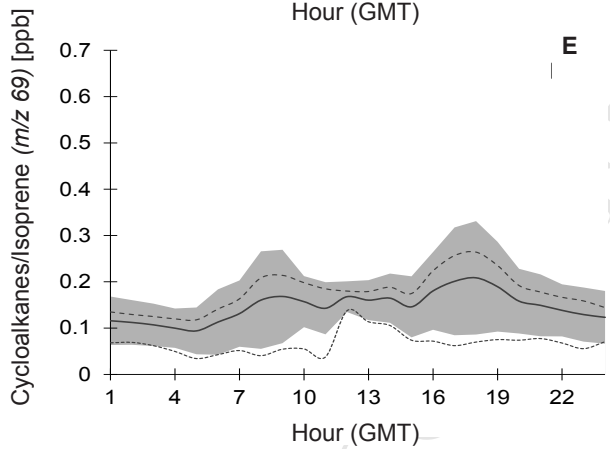
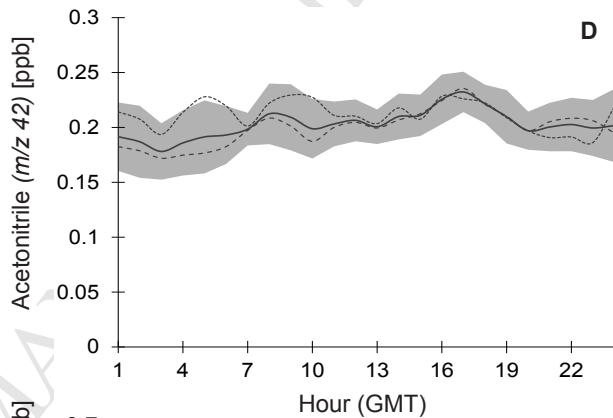
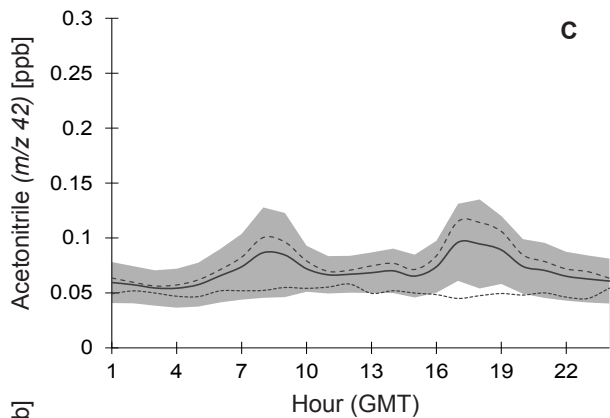
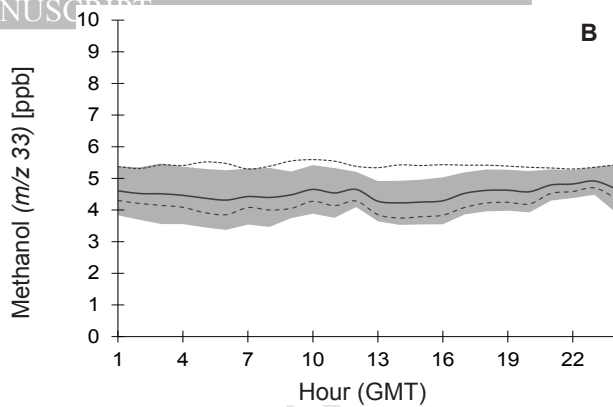
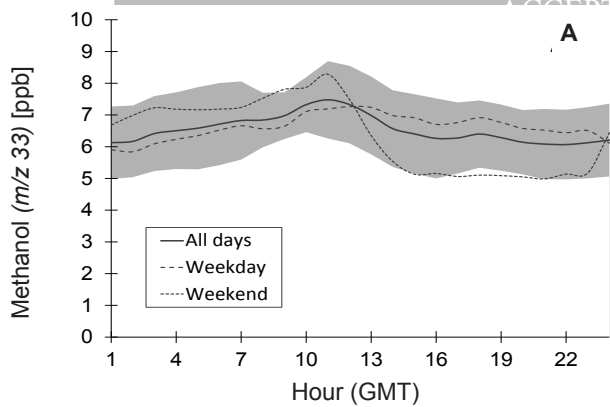
1 day (0–100m) arriving at BT tower 3 Hourly release from: 201202011200



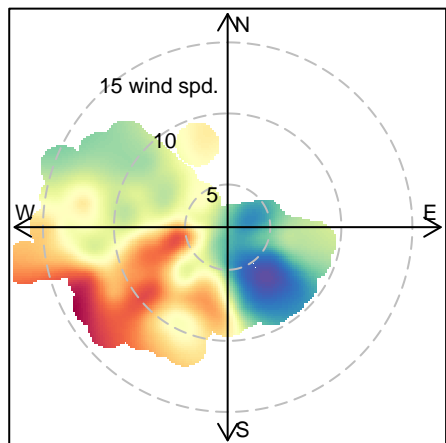
2012/02/04

1 day (0–100m) arriving at BT tower 3 Hourly release from: 201202041200

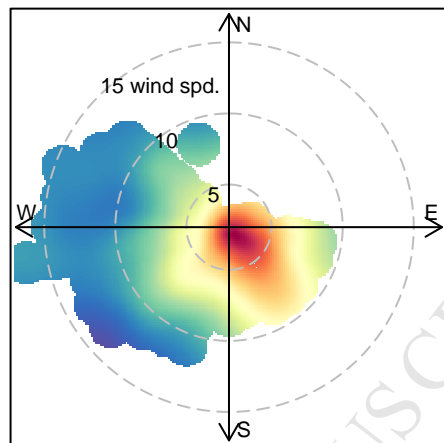




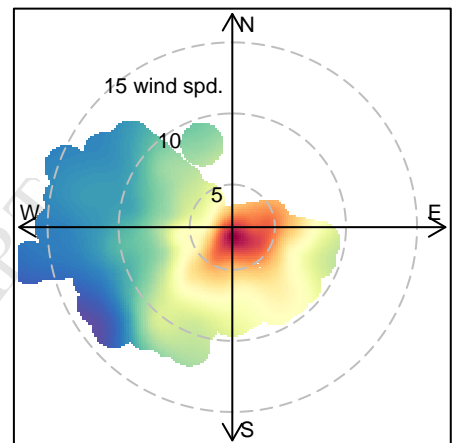
Methanol (m/z 33)



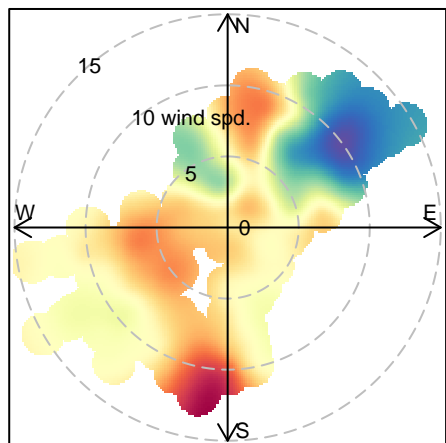
Acetonitrile (m/z 42)



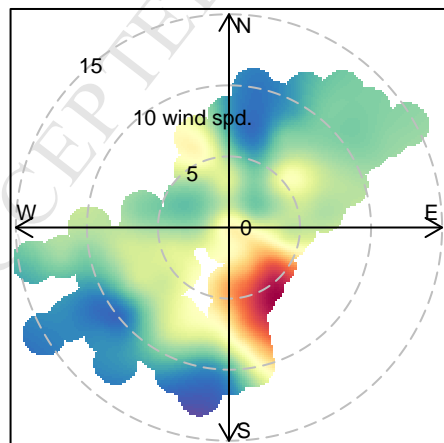
Benzene (m/z 79)



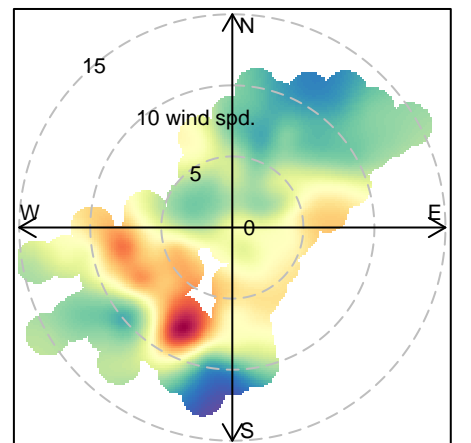
Methanol (m/z 33)



Acetonitrile (m/z 42)



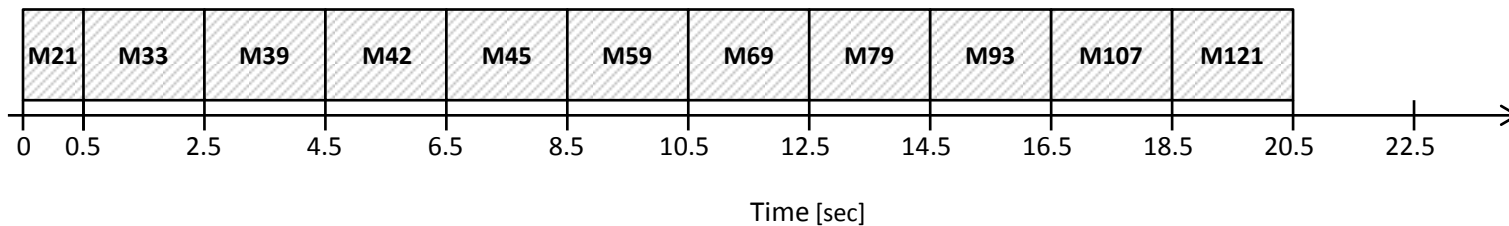
Benzene (m/z 79)



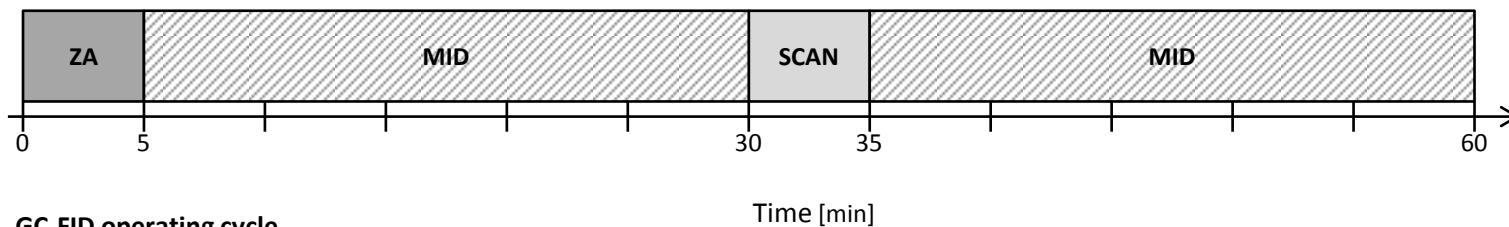
Highlights

- Volatile organic compound concentrations were measured in central London.
- Measurements were compared with the automatic hydrocarbon network.
- Vehicle emissions were the main source at both urban background and kerbside sites.
- Some effects of temperature on compound correlations were observed.
- Excellent qualitative agreement was seen between the measurement instruments.

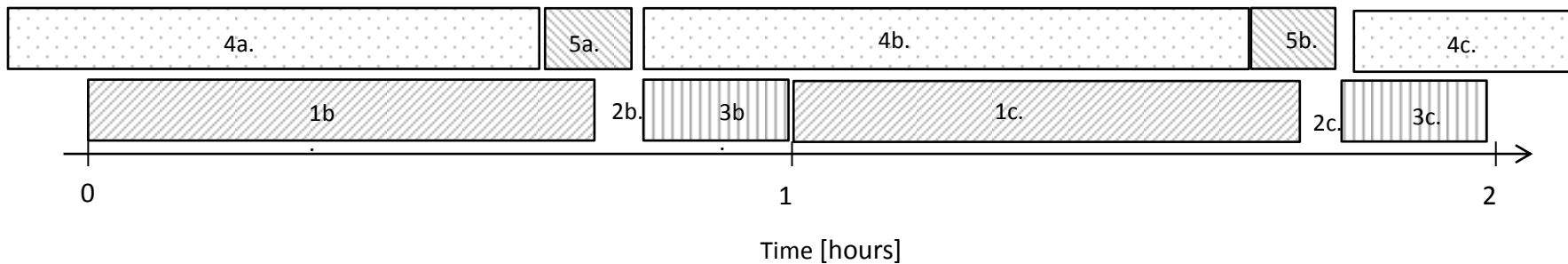
PTR-MS: MID measurement cycle

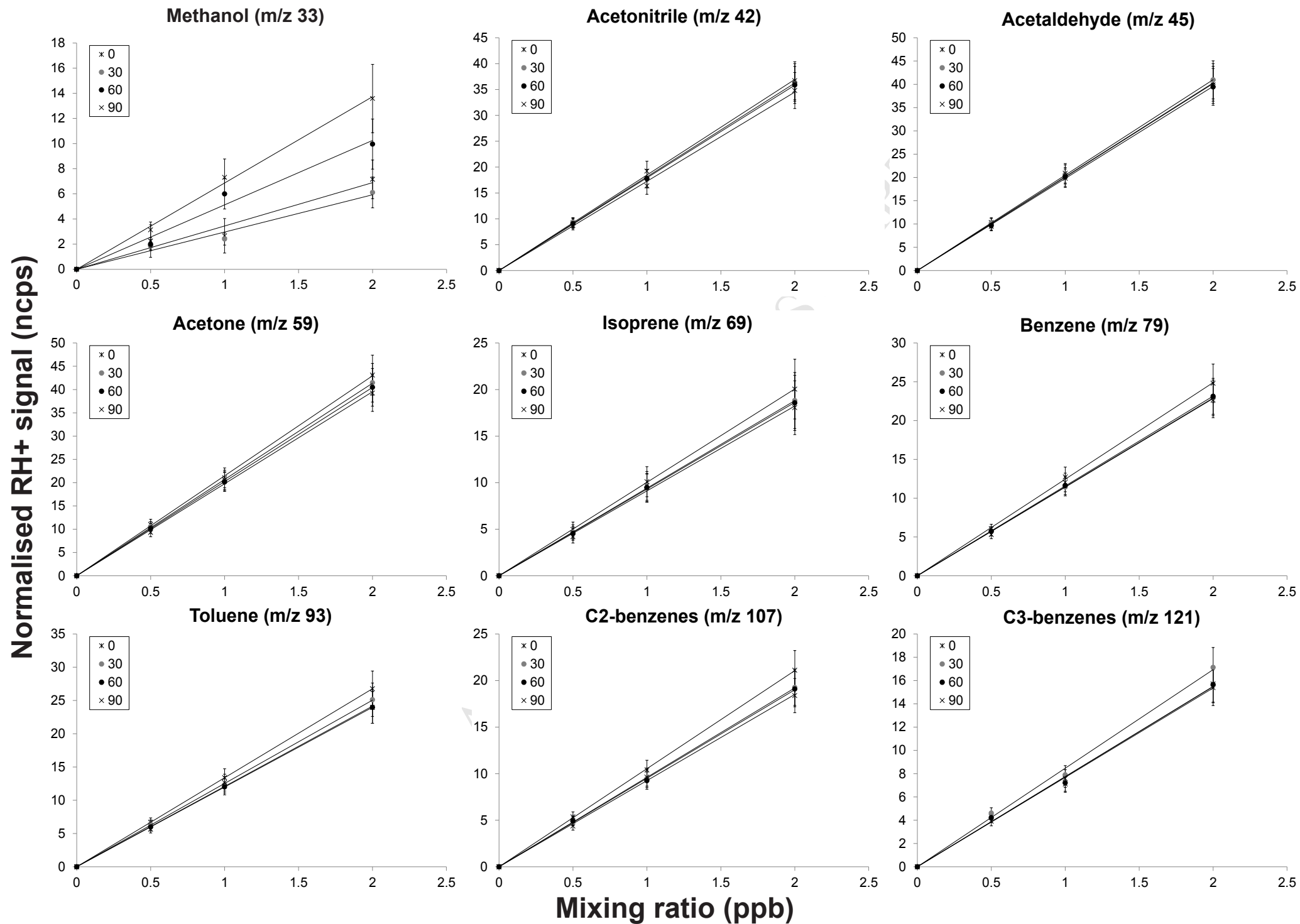


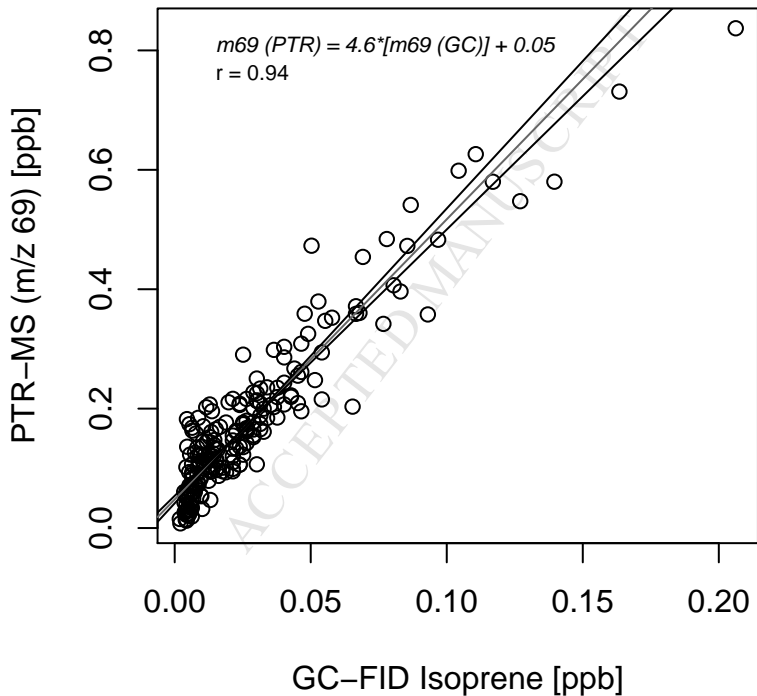
PTR-MS: 1h operating cycle



GC-FID operating cycle







1 **Supplementary content**

2 **A. Details on measurement sites, instrument parameters and duty cycles for both** 3 **PTR-MS and GC-FID**

4 Extensive comparisons of the measurement sites and the mean meteorological
5 measurements during the two measurement periods are summarised in Table A1.

6 **A1. PTR-MS**

7 A high-sensitivity proton transfer reaction- mass spectrometer (PTR-MS) fitted with three
8 Varian turbo-molecular pumps and a 9.5 cm long drift tube was used for online
9 measurements VOC mixing ratios. During each deployment of the PTR-MS, drift tube
10 pressure, temperature and voltage were kept constant at 2.06 mbar, 48 °C and 550 V
11 respectively to maintain an E/N ratio of 125 Td. Air was subsampled from the main line with
12 an inlet flow rate of 0.25-0.3 l min⁻¹. The primary ion count (m/z 19) ranged between 6 - 14 x
13 10⁶ cps with a mean of 11 x 10⁶ cps. The H₃O⁺.H₂O⁺ water cluster ions ranged between 6.5 x
14 10⁴ – 2.6 x 10⁵ cps with a mean of 1.4 x 10⁵ cps which represented on average 1.7% of the
15 primary ion signal, while the O₂⁺ signal (m/z 32) was <2% of the primary ion signal. The 1 h
16 measurement protocol consisted of 5 min zero air measurements using a zero air generator
17 (Parker Balston, UK), then 25 min MID mode, followed by 5 min mass scans and another 25
18 min in MID mode (Figure A1). During the MID mode, 11 selected masses were measured
19 with a dwell time of 2 s per mass and 0.5 s for the primary ion, resulting in a 20.5 s cycle
20 time, whereas SCAN modes cycled through the mass range m/z 21 – 206 with a dwell time
21 of 0.5 s each.

22 **A2. GC-FID**

23 The GC-FID method used by the AHN has recently been linked to the QA/QC procedures of
24 the EU Infrastructure Project ACTRIS (www.actris.net). The method includes a TurboMatrix
25 thermal desorption (TD) unit with an online sampling accessory to gather samples directly
26 from ambient air. The TD extracts the compounds onto an adsorbent trap, which is cooled to
27 -30°C. The analytes are then thermally desorbed and transported through a heated transfer
28 line by a carrier gas to the GC. The GC contains two columns and compounds are separated
29 by volatility into two fractions. The flame ionization detector (FID) monitors the
30 chromatography on two columns. After a 40 min sampling period the sample is injected into
31 the GC and the trap automatically begins collecting the next sample after 20 min ensuring
32 hourly sample acquisition.

33 Inter-comparisons with the VOC standards used by the AHN were not possible, therefore
34 uncertainties associated with the AHN standards cannot be discounted and may have

35 contributed to the offsets between the two methods. Especially in areas of high pollution,
36 datasets from automated monitoring systems using GC-FID can also be susceptible to high
37 variability, as was shown in Fortin et al., 2005, which would introduce additional uncertainty.

38 The GC-FID data were converted to ppbv using ambient pressure and temperature
39 measurements which may also have introduced some uncertainty in the AHN data.

40 **B. Calibrations and instrument background determination of the PTR-MS**

41 The multi-component VOC gas standard (Ionimed Analytik GmbH, Austria, 1ppm +/- 5%
42 uncertainty for all compounds) contained all VOCs selected for quantification by PTR-MS
43 except m/z 121. After the campaign it was independently validated against another multi-
44 component VOC standard (Apel Riemer Environmental Inc., CO, USA) containing the same
45 compounds with the addition of a 1,2,4-trimethylbenzene. Uncertainties for all compounds
46 were quantified in the Ionimed standard to be <10%, apart from methanol which was 15%.

47 The standard was diluted with air from the zero air generator. Normalized sensitivities were
48 between 1.4 (m/z 121) and 11.9 (m/z 45) ncps ppbv⁻¹. The original instrument used for the
49 measurements had been substantially upgraded, therefore a very similar instrument with
50 similar specifications and performance indicators was used to investigate relative changes in
51 background and sensitivity against humidity. These were thoroughly investigated in the
52 laboratory using a range of relative humidities and all variations in sensitivity were within the
53 overall calibration uncertainty (20% for methanol and <15% for all other compounds, see
54 Figure B1). Sensitivities were comparable between instruments, although those of the
55 original instrument started to decrease towards the higher masses. However, overall
56 sensitivities correlated well ($r = 0.94$, $p < 0.001$) and since the same instrument parameters
57 and conditions as during the campaign were maintained, it is assumed that instrument
58 responses are comparable.

59 PTR-MS sensitivities of benzene and toluene in particular have been shown to depend on
60 changes in relative humidity, i.e. when the fraction of $H_3O^+(H_2O)$ ions in the reactor change
61 (Warneke et al., 2001). For these two compounds the reaction with $H_3O^+(H_2O)$ ions is
62 energetically not permitted and does not occur (Spaněl and Smith, 2000). However, PTR-MS
63 sensitivities have a less pronounced humidity dependency at higher E/N ratios because the
64 reagent ions are dominated by H_3O^+ (de Gouw and Warneke, 2007). Although the absence
65 of the reaction with m/z 37 for these two compounds was taken into account when
66 normalising the signals, some humidity effects on background counts may have contributed
67 to the offset, as humidity effects were determined post-calibration and had to be extrapolated
68 resulting in large uncertainties.

69 A custom built zero air generator consisting of a platinum catalyst and charcoal heated to
70 200 °C was used to determine instrument background values. During the campaign dry air
71 was used, however this was insufficient in accounting for variations due to humidity.
72 Therefore, humidity effects were determined by humidifying the zero air over a range of
73 relative humidities in the laboratory after the campaign. The instrument background for the
74 campaign average relative humidity (72% with IQR 64-83%) was subtracted for compounds
75 showing moderate humidity dependency. For compounds with stronger humidity effects a
76 running correction based on the m/z 37/ m/z 19 ion ratio, which is a proxy for humidity, was
77 applied. These corrections produced a minimal difference due to the low variability of m/z 37
78 counts during the campaign (0.8-2.6% with a mean of 1.7% of primary ion signal). Impurities
79 in the inlet system during the campaign may have caused additional humidity dependency
80 for aromatic species. These could not be accurately recreated when investigating humidity
81 effects in the laboratory, hence this may have resulted in the remaining background offset for
82 m/z 79, 93, 107 and 121. The largest offset was seen in m/z 121, which may be due to a
83 number of factors (discussed in section 3.2 in more detail) including the fact that the
84 instrument was only calibrated against one trimethyl benzene, as standards for many of the
85 other contributing compounds were unavailable to calibrate separately. Correlations of the
86 compound against relative humidity showed low coefficients (r between 0.08 and 0.3,
87 $p > 0.05$), which suggests most humidity effects were sufficiently accounted for, although a
88 large uncertainty associated with the quantitative measurements remains, especially for the
89 higher m/z .

90 Isobaric interferences from O_2^+ ion on m/z 33 due to the $^{16}O^{17}O^+$ isotope were accounted
91 for, as this reacts with the water cluster in the drift tube causing a decrease in the instrument
92 background signal with higher humidities. During the campaign, however, the O_2^+ counts
93 were always <2% of the primary ion count. Additionally, interference of a CCl_4 isotope at m/z
94 121 was subtracted. Since the Montreal Protocol the addition of this compound in fire
95 extinguishers, cleaning agents, and precursors for refrigerants is prohibited and it is
96 uniformly distributed throughout the atmosphere at around 0.1 ppb. This provides a constant
97 contribution to m/z 121 in PTR-MS which can be subtracted.

98 **C. Comparison of m/z 69 with isoprene concentrations measured by GC-FID**

99 Globally isoprene is the dominant component of m/z 69, however due to the season and the
100 urban location, the biogenic contribution was absent. Comparison of the PTR-MS data for
101 m/z 69 against isoprene concentration measurements from a GC-FID at NK (courtesy of J.
102 Hopkins and R. Holmes) showed that the isoprene signal of m/z 69 was around 22% after
103 correcting for the instrument background signal (Figure C1). However, correlations with the

104 isoprene concentrations were high ($r = 0.94$, $p < 0.001$). The remaining offset could be from
105 isobaric interference from other compounds such as cyclic alkanes, which share emission
106 sources with anthropogenic isoprene, in which case they represent a considerable
107 contribution to m/z 69 (Yuan et al., 2014). Alternatively, it may be possible that, as seen in
108 the aromatic compounds, the large uncertainties associated with the calibration (15% total
109 uncertainty) or the background corrections of the PTR-MS resulted in the offset.

110 **References**

- 111 de Gouw, J. & Warneke, C. (2007). Measurements of volatile organic compounds in the
112 Earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrometry*
113 *Reviews*, 26, 223–257, doi:10.1002/mas.
- 114 Fortin, T. J., Howard, B. J., Parrish, D. D., Goldan, P.D., Kuster, W. C., Atlas, E. L. & Harley,
115 R. A. (2005). Temporal changes in US benzene emissions inferred from atmospheric
116 measurements, *Environmental Science & Technology*, 39(6), 1403-1408,
117 doi:10.1021/es049316n
- 118 Oke, T. R. (2006). Towards better scientific communication in urban climate. *Theoretical &*
119 *Applied Climatology*, 84, 179–190.
- 120 Spaněl, P. & Smith, D. (2000). Influence of water vapour on selected ion flow tube mass
121 spectrometric analyses of trace gases in humid air and breath. *Rapid communications in*
122 *mass spectrometry : RCM*, 14(20), 1898–906, doi:10.1002/1097-
123 0231(20001030)14:20<1898::AID-RCM110>3.0.CO;2-G.
- 124 Warneke, C., van der Veen, C., de Gouw, J. A., & Kok, A. (2001). Measurements of benzene
125 and toluene in ambient air using proton-transfer-reaction mass spectrometry : calibration ,
126 humidity dependence , and field intercomparison, *International Journal of Mass*
127 *Spectrometry*, 207, 167–182.
- 128 Yardley, R., Dernie, J., & Dumitrean, P. (2012). UK Hydrocarbon Network Annual Report for
129 2011, (1).
- 130 Yuan, B., Warneke, C., Shao, M. & de Gouw, J. (2014). Interpretation of volatile organic
131 compound measurements by proton-transfer-reaction mass spectrometry over the
132 Deepwater Horizon oil spill, *International Journal of Mass Spectrometry*, 358, 43-48.

133 **Table A1. Summary of site descriptions for measurements sites at North Kensington and Marylebone Rd,**
 134 **London and campaign average meteorology.**

	North Kensington	Marylebone Road
Time period	16 - 25 January 2012	25 January - 7 February 2012
Site category^a	Urban background (class A)	Urban kerbside (class A)
Area	Sion Manning School courtyard	Automatic Hydrocarbon Network ^c cabin
Coordinates (altitude)	51°31'15.18"N; 0°12'48.85"W (25m.s.l.)	51°31'21.14"N; 0°09'16.59"W (35m.s.l.)
Surroundings	Residential, <10m buildings to N and W, main road 95m E and A40 Westway 500m S (70 000- 100 000 vehicles per day)	Commercial, A501 Marylebone Rd (70 000 vehicles per day) 1.5m N, intersection Luxborough Street, Regent's Park (green area of 166 ha) 200 m N
Oke 2006 (UCZ^b) category	3	2
Inlet height (m)	4.7	2.5
Tube length (m)	7	4
Mean temperature (°C)	7.8 ±2.9 ^{d1}	3.0 ±2.8 ^{d2}
Mean RH (%)	71.8 ±12.2 ^{d1}	68.4 ±12.0 ^{d2}
Precipitation (mm)	3 ^{d1}	11 ^{d2}
Mean wind speed (m s⁻¹)	1 (at 4.7m) ^{d1}	6.4 (at 191m) ^{d2}
Mean wind direction (°)	205 (SSW) ^{d1}	62 (ENE) ^{d2}

135 ^aSite classification: Category A indicates sites highly representative of emissions for intended areas.

136 ^bUrban Climate Zone classifications by Oke, 2006.

137 ^cPermanent measurement site run by the Department for Environment, Food and Rural Affairs (DEFRA)

138 ^{d1}Data from WXT520 weather sensor (Vaisala Ltd, Finland) at NK

139 ^{d2}Data from WXT520 weather sensor at BT tower near MRd

140

141 **Figure captions**

142 **Figure A1. Top)** Representation of the PTR-MS measurement cycle used at both North
143 Kensington and Marylebone Rd sites. The multiple ion detection (MID) cycle lasted 20.5 sec
144 and was repeated during 25 min. **Bottom)** Approximation of the measurement cycle used by
145 the Automatic Hydrocarbon Network GC-FID at the Marylebone Rd measurement site.
146 Multiple sample analyses are indicated by *a* (previous hour), *b* (hour 1.) and *c* (hour 2.).
147 Each cycle consists of the following stages: 1. Sample acquisition (40 min), 2. analytes are
148 injected into GC columns, 3. trap cooling in preparation for the next sample acquisition (15
149 min), 4. GC analysis (50 min), and 5. GC cooling in preparation for the next sample analysis
150 (Yardley et al., 2012).

151 **Figure B1.** Post-campaign calibrations over a range of relative humidities (0, 30, 60, 90% +/-
152 5%) for all nine selected compounds (methanol [m/z 33], acetonitrile [m/z 42], acetaldehyde
153 [m/z 45], acetone [m/z 59], isoprene [m/z 69], benzene [m/z 79], toluene [m/z 93], o-xylene
154 [m/z 107], and 1,2,4-trimethylbenzene [m/z 121]) .

155 **Figure C1.** Comparison of 1 h averages of m/z 69 (ppb) measured by PTR-MS against
156 isoprene concentrations measured by GC-FID (ppb) at North Kensington during 16th – 25th
157 Jan 2012 showing the linear regression with correlation coefficient (r). We gratefully
158 acknowledge James Hopkins and Rachel Holmes (University of York) for making the data
159 available for analysis.

160