Atmospheric mixing ratios of methyl ethyl ketone (2-butanone) in tropical, boreal, temperate and marine environments

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Abstract

Methyl ethyl ketone (MEK) enters the atmosphere following direct emission from vegetation and anthropogenic activities, as well as being produced by the gas-phase oxidation of volatile organic compounds (VOCs) such as *n*-butane. This study presents the first overview of ambient MEK measurements at six different locations, characteristic of forested, urban and marine environments. In order to understand better the occurrence and behaviour of MEK in the atmosphere, we analyse diel cycles of MEK mixing ratios, vertical profiles, ecosystem flux data, and HYSPLIT back trajectories, and compare with co-measured VOCs. MEK measurements were primarily conducted with proton transfer reaction – mass spectrometer (PTR-MS) instruments. Results from the sites under biogenic influence demonstrate that vegetation is an important source of MEK. The diel cycle of MEK follows that of ambient temperature and the forest structure plays an important role in air mixing. At such sites, a high correlation of MEK with acetone was observed (e.g. $r^2 = 0.96$ for the SMEAR-Estonia site in a remote hemi-boreal forest in Tartumaa, Estonia, and $r^2 = 0.89$ at

40 the ATTO pristine tropical rainforest site in central Amazonia). Under polluted conditions, we ob-

41 served strongly enhanced MEK mixing ratios. Overall, the MEK mixing ratios and flux data pre-

42 sented here indicate that both biogenic and anthropogenic sources contribute to its occurrence in

43 the global atmosphere.

44

45 **Keywords:** Methyl ethyl ketone, plant emission, anthropogenic sources, air quality, rainforest, bo-

46 real forests.

47

1. Introduction

49 Methyl ethyl ketone (C_4H_8O; MEK, also known as 2-butanone, butanone, methyl acetone,

50 butan-2-one, methylpropanone, ethylmethylketone and methylacetone) is an oxygenated volatile

51 organic compound (OVOC). Its occurrence in the atmosphere has been reported over a wide range

52 of environments (Cecinato et al., 2002; Hellén et al., 2004; Ho et al., 2002; Kim et al., 2015;

53 McKinney et al., 2011; Singh et al., 2004) with typical mixing ratios of 0.03 - 4 ppb (Ciccioli and

54 Mannozzi, 2007; Kim et al., 2015). Although often being measured alongside other volatile organic

55 compounds (VOCs), atmospheric MEK has received little attention to date. The photochemistry of

56 acetone may serve as an example of how ketones affect the composition and chemistry of the at-

57 mosphere by delivering free radicals to the upper troposphere (Colomb et al., 2006; Finlayson-Pitts

58 and Pitts, 2000; McKeen et al., 1997), and thus increasing the ozone formation potential and alter-

59 ing the oxides of nitrogen (NO_x) regime (Ciccioli and Mannozzi, 2007; Folkins et al., 1998; Prather

60 and Jacob, 1997). This understanding may be transferred to MEK, as this molecule is structurally

61 similar to acetone with a comparable absorption spectrum (Martinez et al., 1992). Several studies

62 report that the mixing ratio of MEK in the free troposphere is roughly one quarter of that of acetone

63 (Moore et al., 2012; Singh et al., 2004). However, MEK is about an order of magnitude more

64 reactive than acetone with respect to the hydroxyl radical (OH) (Atkinson, 2000), which makes it

65 a compound of interest in ongoing discussions about the inability to fully account for the reactivity

66 of OH (Nölscher et al., 2016).

67 There are several known but poorly characterized sources of MEK to the atmosphere. Ter-

68 restrial vegetation (Bracho-Nunez et al., 2013; Brilli et al., 2014; Davison et al., 2008; De Gouw

69 et al., 1999; Isidorov et al., 1985; Jardine et al., 2010; Kirstine et al., 1998; König et al., 1995;

70 McKinney et al., 2011; Ruuskanen et al., 2011; Song and Ryu, 2013; Steeghs et al., 2004; Wilkins,

71 1996; Yáñez-Serrano et al., 2015), fungi (Wheatley et al., 1997) and bacteria (Song and Ryu, 2013;

72 Wilkins, 1996) are known to emit MEK. It is also emitted directly by several anthropogenic

73 sources, including man-made biomass burning (Andreae and Merlet, 2001), solvent evaporation

74 (Kim et al., 2015; Legreid et al., 2007) and vehicle exhaust (Bon et al., 2011; Brito et al., 2015; Liu

75 et al., 2015; Verschueren, 1983). In addition, MEK can be formed via the atmospheric oxidation

76 of other compounds (de Gouw et al., 2003; Jenkin et al., 1997; Neier and Strehlke, 2002;

77 Sommariva et al., 2011).

78   Looking in more detail at biogenic sources, MEK emissions have been observed from dif-

79 ferent types of vegetation, including forest canopies (Brilli et al., 2014; Jordan et al., 2009b; Yáñez-

80 Serrano et al., 2015), pasture (Davison et al., 2008; De Gouw et al., 1999; Kirstine et al., 1998) and

81 clover (De Gouw et al., 1999; Kirstine et al., 1998). The MEK production and release mechanisms

82 are manifold, but poorly understood. Studies show higher MEK emissions after cutting and drying

83 of leaves than under no-stress conditions (Davison et al., 2008; De Gouw et al., 1999). Due to the

84 water solubility of MEK in leaves and on surfaces (Sander, 2015), Jardine et al. (2010) suggested

85 MEK emissions to be dependent on evaporation from storage pools in leaves. It has been suggested

86 that MEK takes part in tri-trophic signalling following herbivore attack (Jardine et al., 2010; Song

87 and Ryu, 2013). The roots of plants have also been found to release MEK in root-aphid interactions

88 (Steeghs et al., 2004). Decaying plant tissue may also act as a source of MEK to the atmosphere

89 (Warneke et al., 1999). Furthermore, some studies indicate the importance of MEK emissions by

90 microbes, such as *Brevibacterum linens, Bacillus spp* and thermophilic gram-positive actinomy-

91 cetes bacteria (Song and Ryu, 2013; Wilkins, 1996), and fungi such as *Trichoderma spp* (Wheatley

92 et al., 1997).

93   MEK does not only enter the atmosphere via direct emissions, but also results from the

94 atmospheric photooxidation of VOCs such as *n*-butane, 2-butanol, 3-methyl pentane and 2-methyl-

95 1-butene (de Gouw et al., 2003; Jenkin et al., 1997; Neier and Strehlke, 2002; Sommariva et al.,

96 2011). Although butane in the atmosphere comes predominantly from anthropogenic sources

97 (Kesselmeier and Staudt, 1999), some studies have reported emission of *n*-butane from vegetation

98 (Donoso et al., 1996; Greenberg and Zimmerman, 1984; Hellén et al., 2006; König et al., 1995;

99   Zimmerman et al., 1988). The MEK yield from *n*-butane oxidation is ~ 80% (Singh et al., 2004).

100   It is important to note that no mechanistic pathways have been found for atmospheric MEK pro-

101   duction from the dominant biogenic VOCs isoprene, α- and β-pinene and methyl butenol oxidation

102   (Rollins et al., 2009; Singh et al., 2004).

103   In the atmosphere MEK reacts mainly with OH (k_{OH}=1.15x10^{-12} cm^3 s^{-1}) (Chew and

104   Atkinson, 1996), while reactions with O_3 and NO_3 are very slow during the day and hence negligi-

105   ble (Atkinson and Arey, 2003). MEK has a lifetime of 5.4 days at an OH concentration of 1.6×10^6

106   radicals cm^{-3}, whereas isoprene and acetone have lifetimes of 8.2 h and 38 days, respectively, under

107   the same conditions (Grant et al., 2008). The atmospheric degradation of MEK leads to acetalde-

108   hyde and formaldehyde formation. In the presence of NO_x, MEK can lead to peroxyacetyl nitrate

109   (PAN) and ozone formation (Grosjean et al., 2002; Pinho et al., 2005). In the upper troposphere,

110   MEK photolyzes and regenerates OH (Atkinson, 2000; Baeza Romero et al., 2005; De Gouw et

111   al., 1999) as does acetone, potentially increasing ozone formation.

112   Anthropogenic biomass burning leads to significant MEK emissions, of about 2 Tg a^{-1} glob-

113   ally (Andreae and Merlet, 2001 and unpublished updates; Schauer et al., 2001). Furthermore, about

114   9 Tg a^{-1} of other C4 compounds are emitted by biomass burning, which may act as MEK precursors.

115   Another strong source of MEK is biofuel and charcoal combustion, with emissions of ~830 mg kg^{-1}

116   of dry biomass (compared to an emission rate of ~260 mg kg^{-1} of dry mass for biomass burning

117   of savannah and grassland vegetation types, Andreae and Merlet, 2001). Despite the fact that bio-

118   mass burning emission rates have been fairly well characterized, vehicular emissions, food cook-

119   ing, industrial activities, cigarette smoke and other anthropogenic sources have not been character-

120   ized. Even though MEK is present in urban atmospheres, there are no observations of MEK emis-

121   sions from vehicles. Most of the urban MEK is released to the atmosphere via evaporation from

122   chemical plants and industrial and household applications, as it is widely used as a solvent (e.g. in

123   glues and as paint thinner). It has a low toxicity, and is not carcinogenic (National Center for

124   Biotechnology, 2015). As its manufacturing has been increasing in the last 10 years, global atmos-

125   pheric mixing ratios have probably increased as well.

126   Here we report recent findings on MEK from six different sites, including biogenic and

127   anthropogenic dominated environments, in order to understand MEK sources in different environ-

128   ments. Our large dataset allows a closer view of this important, almost ubiquitous species in Earth's

129   atmosphere.

130   **2. Sites and Methodology**

131   The field sites compared in our study cover areas from pristine to remote anthropogenically

132   influenced tropical forests, as well as boreal and Mediterranean regions. Measurements were per-

133   formed by proton transfer reaction – mass spectrometry (PTR-MS) and partly complemented by

134   gas chromatography - flame ionization detector (GC-FID) and gas chromatography - mass spec-

135   trometry (GC-MS) analytical techniques (Figure 1, Table 1).

136   Online MEK measurements were performed with quadrupole PTR-MSs (Ionicon Analytic

137   GmbH, Austria, Lindinger et al., 1998) at all sites, except for CYPHEX where a PTR-Time-of-

138   Flight-MS (PTR-ToF-MS, Ionicon Analytic GmbH, Austria, Jordan et al., 2009a) was used. The

139   PTR-MSs were operated at standard conditions (2.2 mbar drift pressure, 600 V drift voltage, 142

140   Td for ATTO and SMEAR-Estonia; 2.0 mbar drift pressure, 550 V drift voltage, 129 Td, for TT34;

141   2.2 mbar drift pressure, 600 V drift voltage, 135 Td for O_3HP; 2.2 mbar drift pressure, 560 V drift

142   voltage, 132 Td for T2 and 2.2 mbar drift pressure, 600 V drift voltage, 137 Td for CYPHEX).

143   Periodic background measurements and weekly humid calibrations were performed at all

144   sites. Gravimetrically prepared multicomponent standards were obtained from Apel & Riemer,

145   USA, for ATTO, TT34, T2 and CYPHEX, and from Ionicon Analytik GmbH, Austria, for O_3HP

146   and SMEAR-Estonia.

147   **2.1. The Amazon Tall Tower Observatory, ATTO: pristine tropical rainforest (Ama-**

148   **zon, Brazil)**

149   The Amazon Tall Tower Observatory (ATTO) site is located in central Amazonia, 150 km

150   NE of Manaus, Brazil (Figure 1) within a pristine primary tropical rainforest. The site is equipped

151   with a tall tower (325 m) and two 80 m towers. One of them (02°08'38.8" S, 58°59'59.5" W) is an

152   80-m walk-up tower, where the trace gas measurements take place. It is surrounded by a forest with

153   a canopy height of approximately 35 m and with at least 417 different tree species among 7293

154 screened trees of ≥ 10 cm diameter at breast height (DBH) in the twelve 1-ha inventoried plots

155 (Andreae et al., 2015). The climate of this site is typical for tropical rainforests with a drier season

156 (July-October) and a wet season (December-April, Nobre et al., 2009).

157 Measurements for this study took place 18 February - 15 March 2014. They were carried

158 out at seven different heights (0.05, 0.5, 4, 24, 53 and 79 m) with the PTR-MS switching sequen-

159 tially between each height in 2 minutes intervals. The inlet lines were made of PTFE, 9.5 mm OD,

160 insulated and heated to 50 ºC and had PTFE particle inlet filters. More information about the gra-

161 dient system and PTR-MS operation at ATTO can be found elsewhere (Nölscher et al., 2016;

162 Yáñez-Serrano et al., 2015). The limit of detection (LOD) and uncertainty of the PTR-MS were

163 0.05 ppb and 34% respectively.

164 Additionally, ambient samples for off-line measurements with GC-FID were taken on 11

165 March 2014 from 08:30 to 11:00 LT. They were collected at 24 m using a GSA SG-10-2 personal

166 sampler pump and adsorber tubes (Carbograph 1, Carbograph V 130 mg of Carbograph 1 (90 m^2

167 g^{-1}) followed by 130 mg of Carbograph 5 (560 m^2 g^{-1})). The size of the Carbograph particles was

168 in the range of 20–40 mesh. Carbograph 1 and 5 were provided by Lara s.r.l. (Rome, Italy). Samples

169 were collected for 20 min with a flow of 167 ml min^{-1} passing about 3.3 l of ambient air through

170 the adsorbent. Cartridges were transported to the laboratory for analysis by a Perkin Elmer Auto-

171 system XL GC-FID. These samples generally matched the results of the PTR-MS. For details on

172 sampling see Kesselmeier et al., (2002).

173 **2.2. TT34: remote tropical rainforest (Amazon, Brazil)**

174 The ZF2 site is located in the Reserva Biologica do Cuieiras in central Amazonia, 60 km

175 NNW of Manaus (2°35'39.4"S 60°12'33.4"W) within a remote primary tropical rainforest (Figure

176 1). The site is equipped with two towers, TT34 and the K34. The TT34 triangular tower is 40 m

177 high and embedded within the forest with a canopy height of approximately 30 m. The biodiversity

178 of this site is also high and the climate is very similar to that at the ATTO site. More information

179 about the site can be found elsewhere (Karl et al., 2009; Martin et al., 2010).

180 Measurements for this study were made from 1 September 2013 to 20 July 2014 at 41 m,

181 at a fast rate (0.5 Hz) for virtual disjunct eddy covariance (vDEC) flux derivations techniques (Karl

182 et al., 2002; Langford et al., 2009; Rinne et al., 2002). The high-resolution data was further aver-
183 aged to give 30-minute concentration and flux data. Wind vector data were obtained with a sonic
184 anemometer (Gill R3, USA) mounted at the top of the tower close to the PTR-MS inlet. The PTR-
185 MS inlet line was made of PFA (12.7 mm OD) (PFA-T8-062-100, Swagelok), and was insulated
186 and heated to 40 ℃ inside the air-conditioned cabin. The LOD and uncertainty averaged 30-minute
187 concentrations measurements were 0.18 ppb and 6 % respectively.

**2.3. Station for Measuring Ecosystem-Atmosphere Relations, SMEAR-Estonia: re-
mote hemi-boreal forest (Tartumaa, Estonia)**

190   The Station for Measuring Ecosystem-Atmosphere Relations (SMEAR-Estonia) site is lo-
191 cated in the Järvselja Experimental forest station in Tartumaa, SE Estonia (58°16'N 27°16'E),
192 within a remote hemi-boreal zone, far from major anthropogenic disturbances (Noe et al., 2011,
193 Figure 1). The site is equipped with a tower of 24 m height. The surrounding canopy is about 16-
194 20 m in height and the remote hemi-boreal forest consists of a mixture of tree species, with Norway
195 spruce *(Picea abies)* dominating. The climate is boreal with a growing season of 170-180 days.
196 More information about the site can be found elsewhere (e.g. Bourtsoukidis et al., 2014a; Noe et
197 al., 2011, 2016).

198   The measurements were made between 3 and 17 October 2012. Sampling was done using
199 a dynamic, automated glass enclosure with measurement cycles of 36 seconds. The inlet line (9.5
200 mm OD) was made of glass and was insulated and heated to 70℃. A dynamic exchange enclosure
201 was used to measure emission rates from a Norway spruce branch located in the upper canopy at
202 16 m. While the focus of this study was the quantification of emission rates of MEK from a Norway
203 spruce tree, ambient mixing ratios were derived as well using the box model described in
204 Bourtsoukidis et al., (2014b). The LOD and uncertainty of the PTR-MS were 0.04 ppb and 28%
205 respectively.

206   Furthermore, at SMEAR-Estonia, off-line measurements with a GC-MS were carried out
207 for periods of three days each in June and July 2012, with samples taken every 4 hours at two
208 heights (2 m and 20 m). Samples for GC-MS analysis were also taken from cuvettes enclosing
209 some common plant species at the site (Table 1). In addition, VOC emissions from soil litter were
210 monitored monthly. The air samples were drawn into multi-bed stainless steel cartridges (10.5 cm

211   length, 3 mm inner diameter, Supelco, Bellefonte, PA, USA) filled with Carbotrap C 20/40 mesh

212   (0.2 g), Carbopack C 40/60 mesh (0.1 g) and Carbotrap X 20-40 mesh (0.1 g) adsorbents (Supelco).

213   Even though the site usually experiences low ozone mixing ratios of 10 - 30 ppb (Noe et al., 2012),

214   a catalytic Cu(II) ozone scrubbing system (Sun et al., 2012) was applied. Three constant-flow air

215   sample pumps (1003-SKC, SKC Inc., Huston, TX, USA) and one multisample constant-flow air

216   sample pump (224-PCXR8, SKC Inc., Huston, TX, USA) allowed four samples to be collected at

217   the same time. Each sample took 30 min with a flow of 200 ml min^{-1} concentrating 6 l of ambient

218   air onto the adsorbent. More information can be found elsewhere (Noe et al., 2012).

2.4. Observatoire de Haute Provence, O₃HP: rural Mediterranean temperate forest (Provence, France)

219   **2.4. Observatoire de Haute Provence, O$_3$HP: rural Mediterranean temperate forest**

220   **(Provence, France)**

221   The oak observatory (O$_3$HP, https://o3hp.obs-hp.fr) at the "Observatoire de Haute Pro-

222   vence" (OHP, http://www.obs-hp.fr/welcome.shtml), is located within a rural Mediterranean tem-

223   perate forest in the French Mediterranean region, 60 km north of Marseille, the closest large city

224   (43°55'54.0" N 5°42'43.9" E, Figure 1). A 10 m mast was set up inside the oak forest with a canopy

225   height of approximately 5 m. The O$_3$HP site is dominated by *Quercus pubescens Willd* (75% of

226   trees) and *Acer monspessulanum L.* (25%) forming a sparse canopy, while *Cotinus coggygria Scop.*

227   and other grass species constitute the understorey canopy. The climate at the site is typical Medi-

228   terranean, with dry and hot summers and humid and cool winters. More information about the site

229   can be found elsewhere (Genard-Zielinski et al., 2015; Kalogridis et al., 2014).

230   The measurements took place during 29 May - 12 June 2014 as part of the CANOPEE

231   project (Biosphere-atmosphere exchange of organic compounds: impact of intra-canopy pro-

232   cesses). Ambient measurements were carried out at 2 m (inside the canopy) on consecutive days in

233   intervals of 5 minutes. The 9.5 mm OD Teflon inlet lines were insulated and heated above ambient

234   temperature and had no particle filter. The LOD and uncertainty of the PTR-MS were 0.11 ppb and

235   20% respectively. In addition, light non-methane hydrocarbons (from ethane to hexane) were meas-

236   ured with a GC-FID (Chromatotec, Saint-Antoine, France) in-line with the PTR-MS as described

237   in Zannoni et al. (2016).

238   **2.5. T2: mixed urban and rainforest influenced environment (Amazon, Brazil)**

239   The T2 site is part of a set of experimental sites within the GoAmazon project to study the

240   effect of the pollution plume from the city of Manaus on the otherwise pristine Amazonian atmos-

241   phere. The T2 site is located 8 km downwind, i.e. to the west, of Manaus (3°8'21.12" S, 60°7'53.52"

242   W, Figure 1). Given its location, near Manaus and across the Rio Negro, air mass transport to the

243   sampling site is strongly modulated by a river breeze, alternating between mostly biogenic condi-

244   tions, resulting from the surrounding forest, and the city emissions. The climate is tropical and

245   similar to that at the ATTO and ZF2 sites.

246   The measurements for this study took place between 15 February and 15 November 2014.

247   They were carried out at 12 m above the laboratory container with 30 minute cycles. The inlet line

248   was made of insulated Teflon (9.5 mm OD) without PFTE particle filter. The LOD and uncertainty

249   of the PTR-MS were 0.02 ppb and ~30% respectively.

250

251   **2.6. CYPHEX: mixed marine, rural environment influenced by aged air masses (Cy-**

252   **prus)**

253   The Cyprus Photochemistry Experiment (CYPHEX) campaign took place at a site located

254   in the NW inshore part of Cyprus, in the Paphos region (34º57'50.0" N, 32º22'37.0" E) (Figure 1).

255   The site experiences mixed marine and rural emissions influence. The climate is Mediterranean,

256   warm and dry, and shrubs and small trees dominate the sparse vegetation.

257   The measurements took place during July and August 2014 without a single rain event.

258   Instruments were installed inside containers and connected to a stack inlet that reached up 5 m

259   above the container roofs. Air was drawn through the 8 m stack inlet of 0.5 m with high flow rate

260    $(10 \, l \, min^{-1})$ to minimize wall losses. The subsampling inlet line was made of Teflon (13 mm OD),

261   was insulated and heated to 35 ºC, and had a PTFE inlet particle filter. The LOD and uncertainty

262   of the PTR-MS were 0.02 ppb and 11% respectively.

263   **3. Results**

264   **3.1. Sites dominated by biogenic emissions**

265   All the pristine or remote sites studied were characterized by relatively low mixing ratios

266   of nitrogen oxides (NO_x) (< 3 ppb of nitrogen dioxide (NO_2) for O₃HP (Kalogridis et al., 2014;

267   Zannoni et al., 2016), 0.2-0.8 ppb of NO_x for SMEAR-Estonia, and <1 ppb NO_x for the Amazon

268   rainforest (Kuhn et al., 2010)). The diel cycles of MEK at these sites followed a comparable pattern

269   (Figure 2), where MEK mixing ratios were highest in the middle of the day, following the maxima

270   of light and air temperature. The dominant source at these sites was considered to be biogenic.

271   Mixing ratios of MEK correlated well with ambient temperature (r^2=0.57 (ATTO), r^2=0.83

272   (SMEAR), r^2=0.47 (O_3HP)), while it was less well correlated with photosynthetically active radi-

273   ation (PAR) (r^2= 0.23 (ATTO), r^2=0.26 (SMEAR), r^2=0.67 (O_3HP)). This suggests that ambient

274   temperature predominantly influenced MEK emission rates from plants.

275   The vertical observations at ATTO revealed a strong diel variability of the magnitude and

276   vertical distribution of MEK mixing ratios throughout the forest canopy and in the atmosphere

277   above. Figure 3 shows an example of one day (7th of March 2014) hourly vertical profile of MEK

278   from 13:00-15:00 LT, from the ground to the atmosphere, suggesting that the canopy top is the

279   major source of MEK at the site on such days. Similar concentration gradients were found for 83%

280   (for the afternoon hours) and 45% (for the morning hours) of all days of measurements. In addition,

281   MEK mixing ratios decreased significantly beneath the canopy towards the forest floor, possibly

282   due to dry deposition or generally smaller vegetation emissions due to less light and temperature.

283   However, a possible production from the ozonolysis of alkanes or bidirectional plant exchange

284   cannot be ruled out. For a seasonal comparison, Yañez-Serrano et al., 2015 reported 0.43 ppb of

285   MEK for the dry season (September 2013) and 0.13 ppb of MEK for the wet season (February-

286   March 2013) at 38m. Curiously, at 24m, MEK mixing ratios for the wet season were 0.38 ppb, very

287   close to the measured values for this study. Possible differences in canopy structure temperature

288   and solar radiation among years may be the cause for this discrepancy.

289   At the TT34 rainforest site, ecosystem-scale fluxes were directly calculated from the PTR-

290   MS measurements using the method of virtual disjunct eddy covariance (vDEC) (Karl et al., 2001b;

291   Figure 4). The fluxes averaged over the entire 11-month measurement period (covering both parts

292   of dry and wet season) clearly demonstrate an emission of MEK by the rainforest during daytime

293   with the highest emissions around noon, and no emissions during nighttime. In terms of seasonal

294   variation, MEK mixing ratios were observed to be higher during the dry season (September-Octo-

295   ber 2013, ~0.6 ppb) and lower during the wet season (January-April, ~0.2 ppb) (data not shown).

296   Online ambient mixing ratios of MEK, as measured by the PTR-MS in the hemi-boreal

297   forest at the SMEAR-Estonia site during autumn 2012, were on average 0.15 ± 0.04 ppb (range

298   0.09 - 0.25 ppb). These mixing ratios are almost a factor of two lower than ATTO and O_3HP during

299   daytime hours. This difference among boreal forests, with growing season ending in October,

300   broad-leafed tropical (ATTO) and temperate (O_3HP) forests could be partly related to the temper-

301   ature dependence of MEK emissions apparently common among all biogenic sites.

302   The rural Mediterranean temperate forest site at O_3HP differs significantly from the tropical

303   rainforest (ATTO, TT34) or the hemi-boreal forest (SMEAR-Estonia, Figure 1). The trees at O_3HP

304   are predominantly *Quercus pubescens*, a high isoprene emitter (Keenan et al., 2009). At this site,

305   the exchange of air through the forest canopy is enhanced because the canopy is sparse. As shown

306   in Figure 2, ambient MEK mixing ratios measured inside the canopy (2 m) increased with temper-

307   ature in the morning. During the day, increased forest emissions of MEK seemed to balance the

308   rise of the boundary layer depth, resulting in a plateau until sunset. The fluctuation of MEK after

309   sunset may be understood as a result of a ceased source revealing the deposition as it can hardly be

310   explained by gas-phase chemistry or the reduced nocturnal boundary layer height.

311   During the CANOPEE campaign at the O_3HP site, additional GC-FID samples were taken

312   at 2 m, allowing measurements of several anthropogenic light hydrocarbons, including n-butane.

313   This sampling was performed in parallel to the PTR-MS measurements. All samples contained *n*-

314   butane, which typically has an anthropogenic origin with an average mixing ratio of 0.071±0.09

315   (much lower mixing ratios than MEK), indicating there is no significant source of *n*-butane nearby.

316   Hence, MEK at the O_3HP site could not be related to the atmospheric oxidation of *n*-butane. Fur-

317   thermore, the absence of a correlation with other anthropogenic tracers lets us conclude that MEK

318   at this site was predominantly of biogenic origin.

319   The measurements obtained by PTR-MS at the presented sites dominated by biogenic emis-

320   sions were occasionally confirmed by GC-FID and GC-MS, which are compound selective. At

321   ATTO the same range of MEK mixing ratios for the same hour of the day and height for the GC-

322   FID and the PTR-MS measurements was found, indicating that the PTR-MS signal was only or at

323   least dominated by MEK. To identify sources, canopy measurements at SMEAR-Estonia were

324   complemented by emission measurements using cuvettes with GC-MS identification. Common

325   hemi-boreal forest species, such as *Quercus robur, Tilia cordata, Sorbus aucuparia, Betula pu-*

326   *bescens* and *Picea abies*, were screened for VOC emissions. The highest emissions of MEK were

327   found from *Tilia cordata* and *Picea abies* (Table 2). The data are consistent with those reported by

328 (Bourtsoukidis et al., 2014b) who measured an emission rate of MEK of 2.6±2.2 ng $g_{(dw\ needle)}^{-1}$ s^{-1}

329 from *Picea abies* using PTR-MS. The GC-MS technique obtained a very similar value of 2.3 ng

330 $g_{(dw\ needle)}^{-1}$ s^{-1}. MEK emissions from *Picea abies* were relatively small compared to other VOCs

331 emitted by the same plant species such as total monoterpenes and acetone which reached 93.2 and

332 27.6 ng $g_{(dw\ needle)}^{-1}$ s^{-1}, respectively (Bourtsoukidis et al., 2014b). In addition to plant sources, the

333 emissions rates of MEK from leaf litter were quantified using a GC-MS. MEK litter emissions,

334 with a monthly average of 7 µg m^{-2} h^{-1}, were of comparable magnitude to the emissions rates of

335 MEK from the screened hemi-boreal forest tree species, including *Quercus robur* or *Sorbus aucu-*

336 *paria*, which emitted 8 - 9 µg m^{-2} h^{-1} of MEK (Table 2).

3.2. Anthropogenically influenced sites

338 Anthropogenically influenced sites are characterized by air masses that have passed over

339 polluted cities or industrialised regions. This air typically has elevated mixing ratios of NO_x, other

340 products of fossil fuel combustion such as aromatic compounds, carbon monoxide (CO), and higher

341 aerosol loading. Regional biomass burning plumes can also be a source of anthropogenic input to

342 air masses and are here considered as anthropogenic.

343 The T2 data set was sorted for polluted periods (air masses loaded with CO, black carbon,

344 high aerosol loading, aromatic compounds) and non-polluted periods. Periods with CO higher than

345 130 ppb during the tropical wet season and higher than 160 ppb during the dry season were con-

346 sidered polluted. As shown in Figure 5, MEK mixing ratios strongly increase with pollution. The

347 T2 site in Brazil is located on the bank of the Rio Negro and is affected by both, the tropical rain-

348 forest (biogenic) and the megacity of Manaus (anthropogenic). The location of the T2 site down-

349 wind of Manaus and upwind of the rainforest minimizes the biogenic influence. MEK mixing ratios

350 were generally lower for the clean conditions at T2 than mixing ratios found at ATTO or TT34

351 (Figure 2 and 5). Nevertheless, the mixing ratios of MEK during polluted conditions (0.7 ± 0.33

352 ppb during dry season at 13:00 LT) reached or even exceeded those at the other tropical rainforest

353 sites (0.32 ± 0.13 ppb at 13:00 LT for ATTO and 0.45 ± 0.28 ppb at TT34; Figure 2 and 5). Pre-

354 sumably, anthropogenically affected air as transported across the Rio Negro from the city of Ma-

355 naus (~2 million inhabitants; IBGE, 2014) generated a plume with a mixture of anthropogenic

356 MEK directly emitted in Manaus or MEK formed by oxidation of e.g. *n*-butane during transport.

357 The general trend observed in Figure 6 is an increase of MEK mixing ratios when easterly winds

358   came from Manaus (located to the East of T2). However, there were times when winds blew from
359   the North, and incident air masses passed through large rainforest areas, in which TT34 is included,
360   these air masses then crossed the river and arrived at the site). During these times, when air masses
361   were mostly dominated by biogenic emissions, MEK enhancement reached on average 0.2 ppb.

362   Mixing ratios of MEK at T2 were found to be significantly enhanced during polluted con-
363   ditions for both dry and wet season (Figure 7). The relative enhancement within polluted periods
364   at 13:00 LT ranged around a factor of 1.5 for the wet season and of 1.8 for the dry season. During
365   the dry season, the day-to-day variability was more intense, as reflected by the standard deviations
366   which increased by 360 % for the clean conditions and 410 % for the polluted conditions relative
367   to the wet season clean and polluted values, respectively. This may indicate a difference in the
368   sources and sinks regulating MEK mixing ratios among the different seasons. Examples of this
369   difference could be an increase of MEK due to biomass burning, more abundant during the dry
370   season, or changes in the deposition rates due to changes in rain frequency.

371   The CYPHEX campaign took place at Ineia, North-West Cyprus, at a location that has very
372   little significant vegetation nearby. The air masses that pass through the site are either from Western
373   Europe passing across France and Spain and then the Mediterranean Sea, or Eastern Europe (e.g.
374   Turkey, Greece). During the CYPHEX campaign, the hourly median MEK mixing ratios did not
375   show any distinct diel cycle or relations to temperature or net radiation (Figure 5) strongly suggest-
376   ing that no significant local sources were present. Furthermore, backward air mass trajectories, as
377   calculated by the HYSPLIT model (NOAA Air Resources Laboratory, USA, Stein et al., 2015)
378   (Figure 8), can be used to delineate times when Cyprus was affected by easterly and westerly flow.
379   These trajectories were started at 650 m height with the ensemble mode. The periods (east, west)
380   were chosen on the basis of the FLEXPART model. Further information can be found in Derstroff
381   et al., in preparation. On average, easterly air masses contained 0.13 ± 0.03 ppb whereas westerly
382   masses contained 0.08 ± 0.02 ppb. This difference can be due to differences in source strength, the
383   greater duration of boundary layer transport from the west and hence marine uptake, or to photo-
384   chemical loss during transport.

385   **3.3. Compilation of measurement data**

386   In order to investigate the origin and characteristics of MEK in the atmosphere, we calcu-
387   lated the correlation coefficient (r^2) between the mixing ratios of MEK and other co-measured VOC
388   species for each site (Table 3). This coefficient is the ratio of the variability of the MEK mixing
389   ratios over the variability of the other VOC mixing ratios available for each site. The   correlation
390   between MEK and other VOC helps to identify possible similarities such as common sources,
391   sinks, chemical mechanisms, or transport processes. However, this comparison does not neces-
392   sarily claim links between the various compounds. Acetone, acetaldehyde, monoterpenes, isoprene,
393   isoprene oxidation products and methanol are regarded as being mainly of biogenic origin espe-
394   cially in forested areas (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009). Neverthe-
395   less, acetone, acetaldehyde and methanol may have additional sources including direct and second-
396   ary anthropogenic emissions that cannot be neglected even at clean environments (Goldstein and
397   Schade, 2000; Yáñez-Serrano et al., 2015). Compounds such as benzene, toluene, xylene and ace-
398   tonitrile are considered as typical anthropogenic tracers (Andreae and Merlet, 2001; Finlayson-
399   Pitts et al., 1997).

400   In general, biogenic sites, namely ATTO, SMEAR-Estonia, and O$_3$HP, showed relatively
401   high correlations between MEK and almost all biogenic VOCs (r²>0.5). Exceptions are the r^2 of
402   isoprene, monoterpene and isoprene oxidation products for O$_3$HP. For instance, the highest corre-
403   lation coefficient (r^2) was found for MEK and acetone at the SMEAR site (r^2 =0.97). A high cor-
404   relation coefficient could indicate that the atmospheric processes governing acetone and MEK
405   abundance are likely very similar (Zhou and Mopper, 1993). In SMEAR-Estonia overall high cor-
406   relations were found between MEK and the oxygenated compounds, acetone, acetaldehyde and
407   methanol, as well as with monoterpenes and isoprene. At ATTO, correlations were only slightly
408   lower. The correlation coefficient (r^2) calculated for the O$_3$HP observations were generally lower
409   than for ATTO and SMEAR-Estonia, further influenced by the higher turbulent mixing due to
410   sparser vegetation, leading to fastest transport to the atmosphere. Nevertheless, the good correla-
411   tions of MEK with typical biogenically emitted compounds, such as isoprene, isoprene oxidation
412   products, monoterpenes, methanol and acetone, corroborated the biogenic origin of MEK emis-
413   sions at the biogenic sites.

414   At the anthropogenically influenced sites, T2 and CYPHEX, correlation coefficient (r^2) for
415 the biogenic compounds were generally lower, apart from the r^2 (0.64 and 0.45, respectively) be-
416 tween MEK and acetone. It is important to note that although T2 is a mixed anthropogenic and
417 biogenic site, the correlation coefficient (r^2) for MEK and acetone was high, but very low for the
418 rest of the biogenic compounds. For the anthropogenic compounds, T2 had an r^2 of 0.27 for MEK
419 and acetonitrile and MEK and xylene. Furthermore, the data from the Cyprus site showed poor
420 correlation of MEK with any biogenic compound, but a correlation coefficient of $r^2 = 0.58$ for
421 MEK and toluene, an anthropogenic tracer.

422 **4. Discussion**

423 **4.1. PTR-MS measurements**
424
425   Most of the measurements in this study were performed with a quadrupole PTR-MS, a
426 technique that monitors selected VOC ions, online and with fast time response. A disadvantage is
427 the separation by masses with a mass resolution of only 1 amu. For some masses, several com-
428 pounds and/or compound-fragments may be detected as one signal. The quadrupole PTR-MS sig-
429 nal at *m/z* 73 is attributed to MEK, but may have contributing signals of water clusters (de Gouw
430 et al., 2007), butanal (Inomata et al., 2010; McKinney et al., 2011; Slowik et al., 2010; Warneke et
431 al., 2007), acrylic acid (de Gouw et al., 2003), 2-methyl propanal (Baraldi et al., 1999; Jardine et
432 al., 2010), and methyl glyoxal (Holzinger et al., 2007; Jordan et al., 2009b). We have tried to take
433 into account possible interferences by using different analytical techniques and supplementary in-
434 formation. At the SMEAR-Estonia site, the accompanying GC-MS observations validated the sig-
435 nal for MEK. Additionally, the GC-FID samples taken at ATTO corroborated the signal for MEK
436 at this site. Nevertheless, we try to give a short overview below about the interferences of other
437 trace gases with the PTR-MS identification of MEK.

438   Methyl glyoxal is a likely contributor to the observed signal at the PTR-MS protonated
439 mass *m/z* 73, especially in areas where there are high levels of isoprene. It is formed following the
440 oxidation of methyl vinyl ketone and methacrolein, which are both isoprene oxidation products
441 (Calvert and Madronich, 1987; Lee et al., 2006). Supported by GC-FID measurements and rela-
442 tively low isoprene levels during the wet season (Yáñez-Serrano et al., 2015), we can assume that
443 the contribution of methyl glyoxal to this mass was insignificant at the rainforest sites (ATTO and

444   TT34). Despite the high isoprene emissions at O_3HP, the correlation between MEK and the iso-
445   prene oxidation products was low (r^2 =0.41), suggesting that methyl glyoxal did not significantly
446   contribute to the signal at *m/z* 73. During the CYPHEX campaign the PTR-ToF-MS could unam-
447   biguously distinguish between MEK and methyl glyoxal (at 73.0648 amu and 73.0284 amu respec-
448   tively).

449   Even though a contribution of butanal to *m/z* 73 of up to 65% (Lindinger et al., 1998) and
450   20% (Williams et al., 2001) has been reported previously, most butanal fragments on *m/z* 57 (Ion-
451   icon Analytic GmbH). Acrylic acid, a marine compound (Liu et al., 2016) that may interfere at *m/z*
452   73, was probably not of relevance at sites under biogenic influence. However, in the case of an-
453   thropogenically influenced sites, such as T2, interferences may have been of relevance. Karl et al.
454   (2007) and Ciccioli et al., (2014) measured tropical biomass burning emissions and found that *m/z*
455   73 is comprised of 74% MEK and 23% 2-methyl propanal (73.1057 amu). Even though none of
456   the sites presented in this study was severely influenced by biomass burning, we cannot completely
457   rule out a possible direct emission of 2-methyl propanal by plants, which is of lower magnitude
458   than from biomass burning (Hafner et al., 2013; Jardine et al., 2010; Karl et al., 2005a). Due to the
459   standard operation conditions of the PTR-MS under our measurement conditions, we neglected
460   water clusters as they are regarded to be insignificant (McKinney et al., 2011; Yáñez-Serrano et
461   al., 2015). Summarizing these issues, we note that several studies have concluded *m/z* 73 to origi-
462   nate from MEK only (Bourtsoukidis et al., 2014b; Crutzen et al., 2000; De Gouw et al., 1999, 2000;
463   Holzinger et al., 2000; Karl et al., 2001b, 2005a; Kim et al., 2015; Millet et al., 2015; Steeghs et
464   al., 2004). Based on these considerations and the similarity of magnitudes measured by the PTR-
465   MS as compared with the GC results, we assume *m/z* 73 is representative of the atmospheric MEK
466   present.

467   **4.2. The biogenic MEK**

468   The data obtained at the biologically influenced sites demonstrated that MEK was emitted
469   by vegetation. This is clearly supported by the canopy-scale net flux observations of MEK at the
470   TT34 rainforest site (Figure 4) as well as the diel cycles of the mixing ratios at the other biogeni-
471   cally influenced sites (Figure 2). Furthermore, the leaf-level cuvette measurements at SMEAR-
472   Estonia also corroborated the MEK emission by vegetation. In addition, a contribution by other
473   biogenic sources such as dead and decaying plant matter was also observed at SMEAR-Estonia to

474 be of similar magnitude to boreal plant species emissions, and indicating a source from plant litter,

475 in accordance with the results from Warneke et al., (1999) that measured MEK emission from the

476 abiotic processes of plant decaying matter. This is not the case for the tropical sites where vertical

477 profiles show that canopy emissions dominate.

478   High correlation coefficients suggested strong relations between the emission processes for

479 MEK and other biogenic compounds (Table 3). A similar approach has been used previously by

480 Goldstein and Schade (2000) to unveil the sources of acetone. Similarly, Davison et al. (2008)

481 found a high correlation coefficient between MEK and acetone of $r^2=0.87$ and a relatively poor

482 correlation between MEK and monoterpenes ($r^2=0.54$). They surmised that good correlations indi-

483 cated a common origin for biogenically emitted compounds. Furthermore, a resemblance of the

484 pattern of acetone and MEK has been reported for the ATTO site before (Yáñez-Serrano et al.,

485 2015). In our study, we found high correlation coefficients (r^2) for MEK with acetone and MEK

486 with temperature, and lower r^2 for MEK and compounds such as isoprene and monoterpenes for

487 all the biogenic sites (Table 3). This could indicate that MEK forest emissions are more related to

488 processes resembling acetone emissions and temperature dependent processes, rather than light and

489 temperature dependent emission mechanisms, as for isoprene and monoterpenes (Jardine et al.,

490 2015; Kesselmeier and Staudt, 1999).

491   Plant physiological production pathways have been reported for MEK formation. MEK can

492 be formed, similarly to acetone, as a by-product of a cyanohydrin lyase reaction during cyanogen-

493 esis (Fall, 2003; Vetter, 2000). This chemical defence pathway was also identified in clover by

494 Kirstine et al. (1998) and de Gouw et al. (1999) as a result of mechanical stress, and can be of

495 special importance for tropical rainforests (Miller et al., 2006). On the other hand, in places such

496 as SMEAR-Estonia, dominating plant species are not cyanogenic, and other processes for MEK

497 formation are probably more dominant. In pine trees, acetone is produced from light-dependent

498 and –independent processes that can be associated with the decarboxylation of acetoacetate occur-

499 ring in microorganisms and animals (Fall, 2003), oxidation of fatty acids leading to ketone emis-

500 sions (Niinemets et al., 2014), from pyruvic acid leading to acetyl-CoA (Kesselmeier and Staudt,

501 1999), or produced from uncharacterized biochemical reactions (Fall, 2003). Such processes could

502 also be related to MEK emissions.

503   Even though extensive laboratory measurements are needed to identify the dominant plant
504   process or processes responsible for MEK emission, this study demonstrated the role that temper-
505   ature can exert on such emissions. Hence, forests around the world may act as very different sources
506   for atmospheric MEK. This can be seen for boreal forests (SMEAR-Estonia), with distinctly lower
507   temperatures, where MEK levels were significantly lower. However, other factors must be consid-
508   ered (Schade et al., 2011), such as Leaf Area Index (LAI) and plant species composition, as well
509   as the environmental factors, water availability and mechanical stress, the latter having already
510   been observed by de Gouw et al. (1999) to act as a driver for MEK emissions.

511   Due to its relatively long atmospheric lifetime (~5 days for the reaction with OH; Grant et
512   al., 2008), MEK is expected to accumulate in the atmosphere until removal. Hence, atmospheric
513   mixing ratios can reflect seasonality and changes in dominating sources, affected by radiation,
514   temperature and phenology, from more biogenic dominance during the wet season to transport
515   phenomena and oxidation processes of primarily emitted compounds from regional biomass burn-
516   ing, as it has been seen in 2013 at the ATTO site (Yáñez-Serrano et al., 2015). Moreover, a possible
517   production from certain terpenes through ozonolysis cannot be excluded (Holzinger et al., 2005).
518   Additionally, the canopy structure seems to be important for air mixing and transport, as seen for
519   the O_3HP site with an apparently faster mixing due to sparser vegetation and consequent dampen-
520   ing of the amplitude of the diel cycle. Furthermore, due to its oxygenated nature, partitioning to
521   and from aqueous surfaces is likely, including deposition and surface reactions. Its high water sol-
522   ubility might allow dissolution within leaf water (Sander, 2015) triggering bidirectional exchange
523   of MEK (Karl et al., 2005b; McKinney et al., 2011; Niinemets et al., 2014). Due to its high solu-
524   bility in water and its relatively long lifetime, MEK could potentially influence gas-aqueous reac-
525   tions on aerosol surfaces (Nozière, 2005). This has been shown indirectly by the production of
526   methyl glyoxal after its oxidation by OH, having implications for the formation of organics in the
527   aerosol aqueous phase (Rodigast et al., 2015).

528   **4.3. The anthropogenic MEK**

529   A clear difference could be observed between the anthropogenic and biogenic influenced
530   sites presented in this study. The T2 site represented a site with mixed influence by urban area and
531   tropical rainforest. Affected by anthropogenic and biogenic sources ambient mixing ratios of MEK
532   were higher than at the pristine ATTO rainforest site. Polluted episodes (from the Manaus plume)

with an increase of MEK could be distinguished for both, the wet and the dry season, suggesting a short range transport of air masses. On the other hand, when the wind is blowing from the North, MEK mixing ratios were also present, showing an influence from biogenic forest emissions (Figure 7), thus having a mix of biogenic and anthropogenic influence at the T2 site. A strong seasonality of MEK mixing ratios at T2 reflected biomass burning as a common occurrence in the Amazon region during the dry season (Artaxo et al., 2013). In addition to MEK, a higher contribution of butanal affecting m/z 73 (Inomata et al., 2010; Karl et al., 2007) might be possible, although MEK has been reported to have a much higher emission factor (range from 0.17 to 0.83) than butanal (range from 0.04 to 0.21) for biomass burning (Andreae and Merlet, 2001).

We regarded CYPHEX as an anthropogenically influenced site with weak or no apparent direct sources, but affected by anthropogenic air masses after long range transport over marine areas. Losses by transport over the sea and chemical decomposition led to the lowest averaged MEK mixing ratios of all compared sites. Correlation coefficients (r^2) of MEK with the biogenic tracers were relatively poor for T2 and CYPHEX. However, correlations were also poor for the anthropogenic tracers, although slightly better than at the biogenic sites. MEK showed highest correlation with acetone, indicating similar sources and fate in air mixing and chemistry processes. MEK transported over a long distances (10 days) is lost by photochemical aging or deposition as evidenced by the lowest values reported from CYPHEX. This is despite known secondary photochemical sources, i.e. n-butane oxidation (Katzenstein et al., 2003; Kwok et al., 1996). Interestingly, even under polluted conditions, MEK did not correlate with aromatic compounds, except during CYPHEX, although this correlation deteriorated in the more aged westerly air masses. This can only be understood as a result of a very complex mixture of anthropogenic sources of MEK which vary from direct emission by industry (Legreid et al., 2007), gasoline combustion (Verschueren, 1983), biomass burning (Andreae and Merlet, 2001) and vehicular emissions (Brito et al., 2015). Furthermore, chemical processing during transport may contribute, such as oxidation of n-butane, however, the longer transport times during CYPHEX from the west corresponded to lower values.

5. Remarks and conclusions

The comparison of MEK mixing ratios in different parts of the world is necessary in order to understand how this ubiquitous compound occurs and behaves in the atmosphere. Summarizing,

563 Table 4 aims to provide a numerical comparison of MEK mixing ratios reported around the globe.

564 While MEK mixing ratios in our study are relatively constant, MEK has been measured in many

565 different ecosystems ranging from 0.073 ppb to up to 4 ppb. Therefore, it is important to consider

566 the variability of this compound as MEK can lead to PAN and ozone formation in the atmosphere

567 (Pinho et al., 2005). Photochemical odd-hydrogen production in the upper troposphere (Atkinson,

568 2000; Baeza Romero et al., 2005; De Gouw et al., 1999) can further enhance the MEK ozone

569 forming potential (Folkins et al., 1998; Prather and Jacob, 1997).. Of the widely used atmospheric

570 chemistry models, only GEOS-Chem explicitly computes MEK but only with regard to anthropo-

571 genic origin. On the basis of the data presented here from forest sites, it is necessary for atmospheric

572 chemistry models to also include biogenic MEK emissions to better estimate its effects on the

573 environment. Sites under biogenic influence showed marked diel variability, matching biogenic

574 VOC emissions and temperature. Structural forest features seem to affect turbulent mixing and

575 diluting of trace gases like MEK, as in the case of O_3HP with patchy vegetation. MEK seemed to

576 be produced in plants in a similar fashion to acetone, likely released during mechanical stress.

577 Possible pathways for productions in plants are oxidation of fatty acids, cyanogenesis, production

578 from pyruvic acid leading to Acetyl-CoA, light-dependent and –independent processes that can be

579 associated with the decarboxylation of acetoacetate occurring in microorganisms and animals.

580 This study presents the first compilation and comparison of ambient measurements of MEK

581 at different sites. MEK patterns and mixing ratios differ around the globe depending on sources

582 and transport. Vegetation and litter have been identified as sources of MEK and magnitude of

583 sources varied among the tropical rainforest, the Mediterranean temperate forest and the hemi bo-

584 real forest following a likely temperature dependence. However, via different filtering methodolo-

585 gies (CO filtering and backward trajectories), the anthropogenic input from polluted regions, such

586 as the mixed urban and tropical rainforest and mixed marine environmentis, is often found to be

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918 **8. Tables**

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Table 1: Measurement sites, site environment, sampling dates, methods used and sampling heights.

Site	Characteristics	Canopy height	Time of Sampling	Technique	Type of measurement	Measurement heights
ATTO (Brazil)	Pristine tropical rainforest	35 m dense veg.	Feb/Mar 2014	PTR-MS GC-FID (samples for off-line analysis, collected volume=3.34 L)	Ambient	0.05, 0.5, 4, 24, 38, 53, 79 m 24 m
TT34 (Brazil)	Remote tropical rainforest	30 m dense veg.	Sep 2013 – Jul 2014	PTR-MS	Ambient, including canopy-scale fluxes	41 m
SMEAR (Estonia)	Remote hemi-boreal forest	16-20 m dense veg.	Jun, Jul, Oct 2012 Oct 2012	GC-MS (samples for off-line analysis, collected volume=6 L) PTR-MS	Ambient, plant, soil enclosure Ambient, plant enclosure	2, 20 m 16 m
O$_3$HP (France)	Rural temperate forest	5 m sparse veg.	May-Jun 2014	PTR-MS	Ambient	2 m
T2 (Brazil)	Mixed urban and rainforest influenced environment	Influence from veg. nearby	Feb-April 2014 July-Oct 2014	PTR-MS	Ambient	14 m
CYPHEX (Cyprus)	Mixed marine, rural environment influenced by aged air masses	None, on top of a hill	Jul-Aug 2014	PTR-TOF-MS	Ambient	8 m

Table 2: Emission rates of MEK for typical hemi-boreal plant species and soil litter measured by GC-MS technique at the SMEAR site.

Plant species and soil cuvettes	Mean μg m^{-2} h^{-1}	Standard deviation μg m^{-2} h^{-1}	Standard error μg m^{-2} h^{-1}	Median μg m^{-2} h^{-1}	Number of data points for statistics
Quercus robur	8.12	-	-	-	1
Tilia cordata	12.93	4.89	3.46	12.93	3
Sorbus aucuparia	9.08	-	-	-	1
Betula pubsecens	9.36	5.10	2.94	8.21	3
Picea abies	13.76	5.05	2.91	15.51	3
Leaf litter	7.00	3.37	2.11	6.58	24

Table 3: Correlation coefficients (r^2) of MEK with other co-measured VOC at the sites investigated. The correlations above 0.5 are colour coded with warmest colours for highest correlation coefficients. Correlation coefficients (r^2) for the TT34 site in Amazonia are missing due to lack of data.

				Biogenic tracers				Anthropogenic tracers			
r^2		Acetone	Acetaldehyde	Monoterpenes	Isoprene oxidation products	Methanol	Isoprene	Acetonitrile	Benzene	Toluene	Xylene
Biogenic sites	**TT34**	-	-	-	-	-	-	-	-	-	-
	SMEAR	0.97	0.89	0.72		0.90	0.84	-	-	-	-
	ATTO	0.89	0.62	0.75	0.75	0.51	0.77	0.49	0.07	0.27	0.04
	O₃PH	0.61	0.62	0.12	0.41	0.57	0.14	0.19	0.03	0.15	0.00
Anthropogenic sites	**T2**	0.64	0.21	-	0.41	0.27	0.06	0.27	0.11	0.07	0.27
	CYPHEX	0.45	0.42	0.07	0.10	0.25	0.08	0.00	0.58	0.09	-

Table 3: Literature compilation of MEK mixing ratios measurements in different ecosystems around the globe from a wide range of atmospheric environments.

Reference	MEK mixing ratio in ppb	Type of environment	Reported data	Height from surface	Time of measurement
Zhou and Mopper, 1993	0.03	Caribbean ocean	Cruise data, total average	10m	October 1988
Ho et al., 2002	0.14	Hong Kong urban centre	annual average	6m	April 2000-April 2001
Cecinatto et al., 2002	0.15	Algeria rural residential site	Daytime average	Not specified	January 2001
Cecinatto et al., 2002	0.23	Algeria rural residential site	Daytime average	Not specified	August 2001
Feng et al., 2004	2.11	China urban site	Evening time	Not specified	August–September 2002
Hellen et al., 2004	0.073	Finnish boreal forest site	Diel average	1 m	March-April 2003
Sighn et al., 2004	0.12	Tropospheric pacific ocean	Non specified	0-2km	February-April 2001
Legreid et al., 2007	0.2*	Swiss urban site	Annual average	8 m	Throughout 2005
Davison et al., 2007	0.8*	Swiss permanent grassland site	Daytime average	1.2 m	June 2005

Grant et al., 2008	~ 0.5	Senegalese rural site	Daytime average	6 m	September 2006
Jordan et al., 2009	0.13	USA mixed rural site	Interannual median from 2005-2008	12 m	From 2005 to 2008
Kim et al., 2015	~4	South Korea semi rural site	Diel average	15 m	June 2013
Yáñez-Serrano et al., 2015	0.43	Brazilian tropical rainforest site (ATTO)	Daytime average	38 m	September 2013
Yáñez-Serrano et al., 2015	0.13	Brazilian tropical rainforest site (ATTO)	Daytime average	38 m	February-March 2013
This study	0.39	Brazilian tropical rainforest site (ATTO)	Daytime average	38 m	February-March 2014
This study	0.39	Brazilian tropical rainforest site (TT34)	Daytime average	41 m	September 2013- July 2014
This study	0.19	Hemi boreal forest site (SMEAR-Estonia)	Daytime average	16 m	October 2012
This study	0.30	French Mediterranean forest (O$_3$HP)	Daytime average	2 m	May-June 2014
This study	0.13	Brazilian mixed Tropical rainforest site(T2)	Daytime average	14 m	February - October 2014
This study	0.11	Cyprian rural site (CYPHEX)	Daytime average	8 m	July -August 2014

*average from different seasons reported. **average of different conditions cutting, a day after cutting removing hay and a day after removing hay.

9. Figures
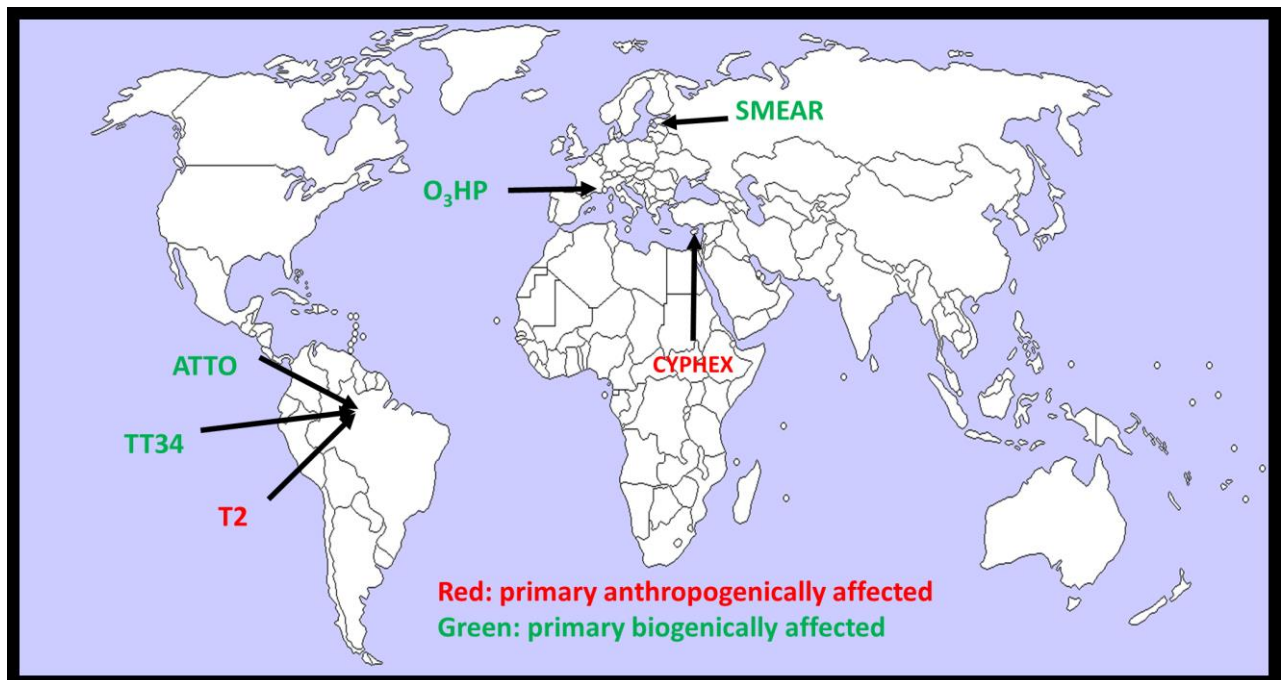
Figure 1: World map showing the location of the different sites. The names are colour coded depending on whether they have primarily biogenic influence (green) or a primarily anthropogenic influence (red). Wikimedia Foundation, 2016.
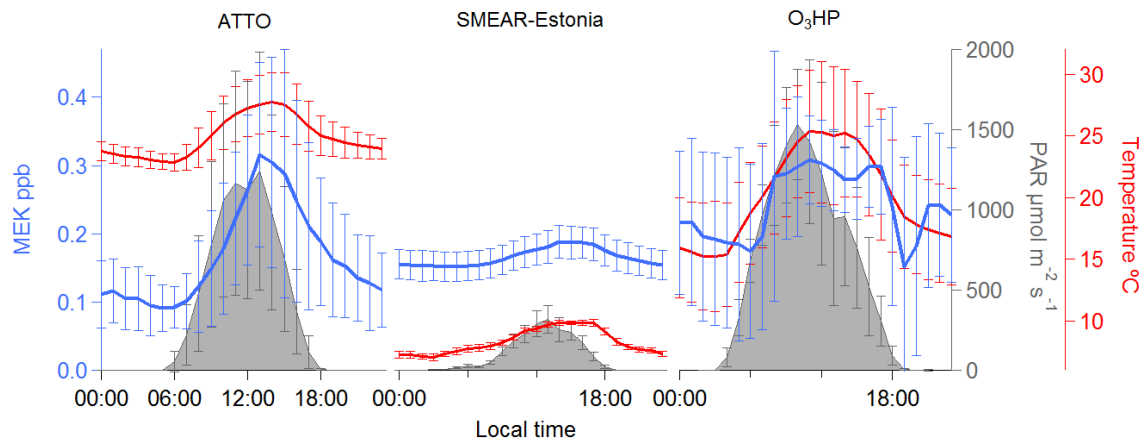
Figure 2: Hourly average diel cycles of MEK at the ATTO (left), SMEAR-Estonia (middle) and O₃HP (right) sites, for the period of measurements (wet season 2014 for ATTO at 38 m October 2014 for SMEAR-Estonia at 16 m, and May and June 2014 for O₃HP at 2 m). Hourly mean diel cycles of temperature and PAR are also shown in red and grey, respectively. Error bars represent the standard deviations.
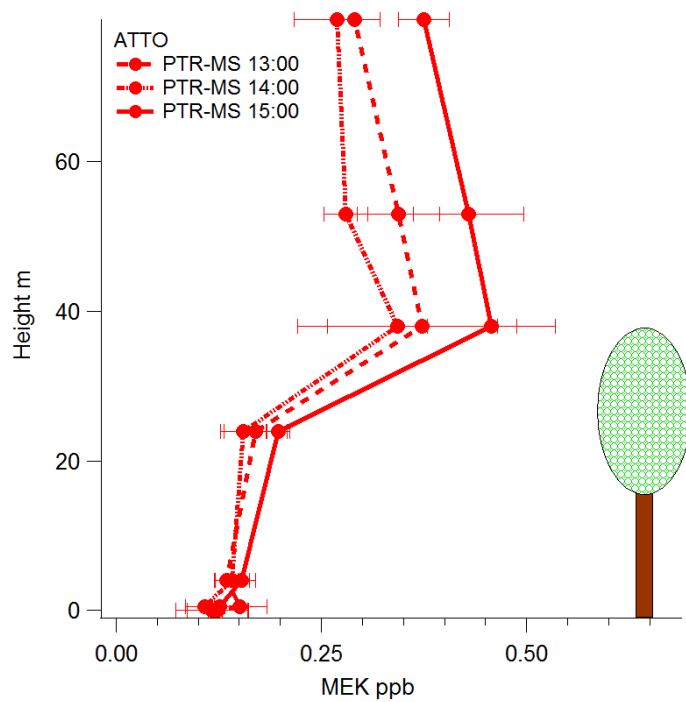
Figure 3: Hourly average vertical profiles of MEK mixing ratios at ATTO for the 7th of March 2014 for 13:00 LT (dashed lines), 14:00 LT (dotted and dashed lines) and 15:00 LT (thick lines). Error bars of vertical profiles are the standard deviations.
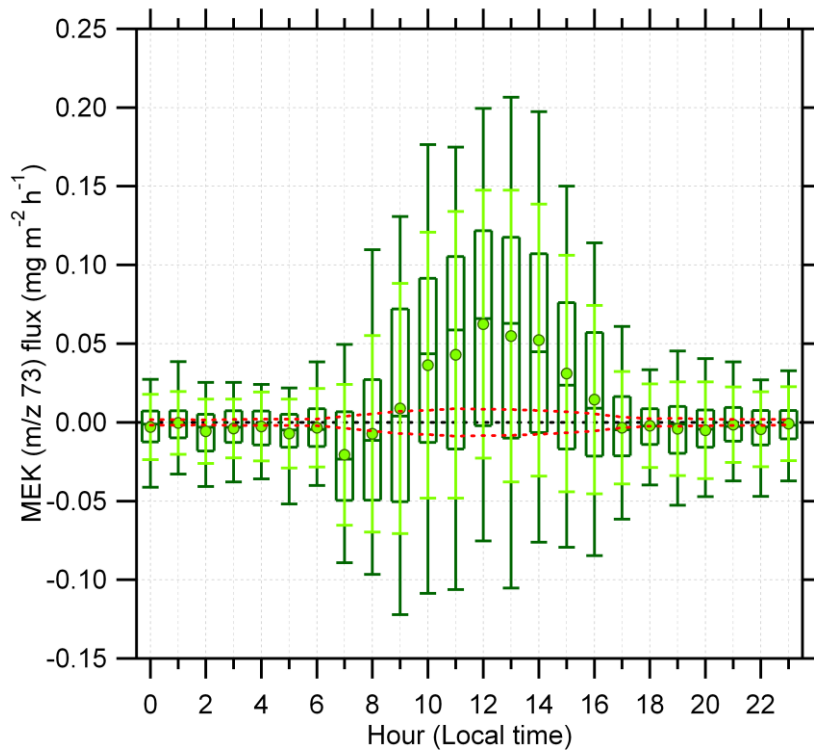
Figure 4: Hourly average MEK fluxes at the TT34 tower for the period Sept 2013 - July 2014. The light green circles represent means and associated error bars are one standard deviation. The central line of the box plots (dark green) indicates the median, bottom and top lines the 25th and 75th percentile respectively and whiskers are the 5th and 95th percentiles. Red dashed lines indicate the propagated limit of detection calculated according to the method outlined by (Langford et al., 2015).
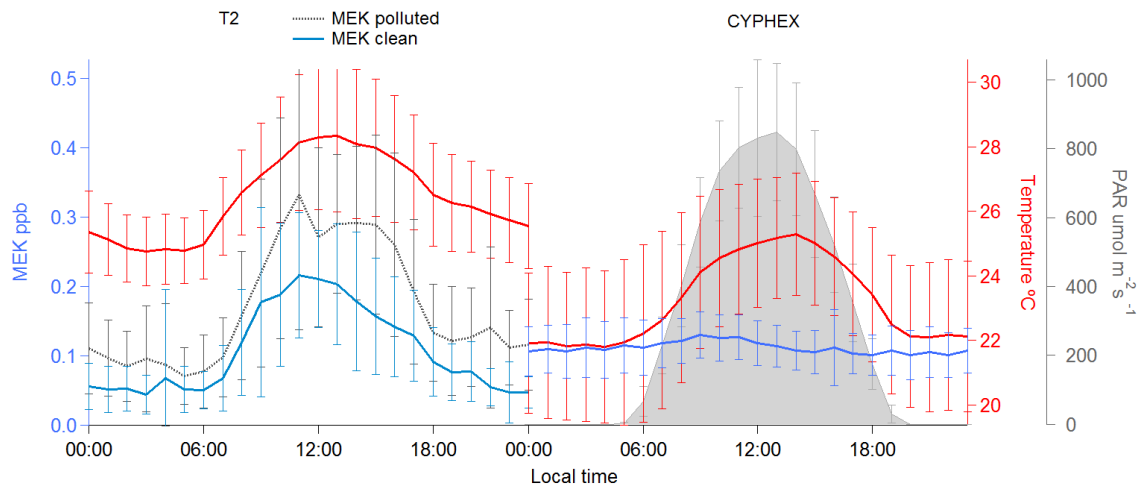
Figure 5: Hourly average diel cycles of MEK at the T2 (left) and CYPHEX (right) sites, for the period of measurements (wet season 2014 for T2 at 14 m, July and August 2014 for CYPHEX at 12 m). For T2 a separation between polluted (dotted black line) and clean (thick blue line) air masses was done. Hourly mean diel cycles of temperature and PAR are also shown in red and grey, respectively. Error bars represent the standard deviations.
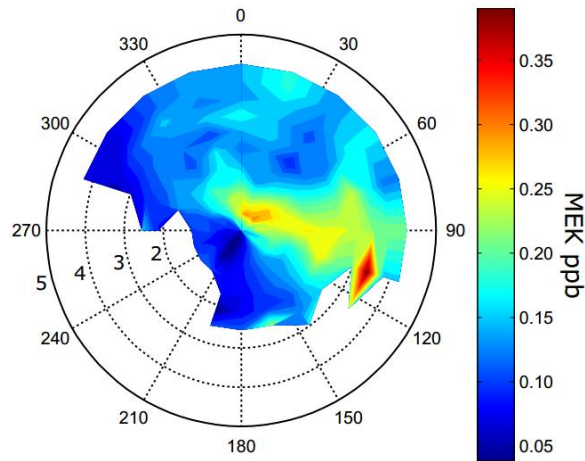
Figure 6: Polar surface plot for average MEK mixing ratios at a given wind direction (angle, 1-5 m s^{-1}) and wind speed (radius).
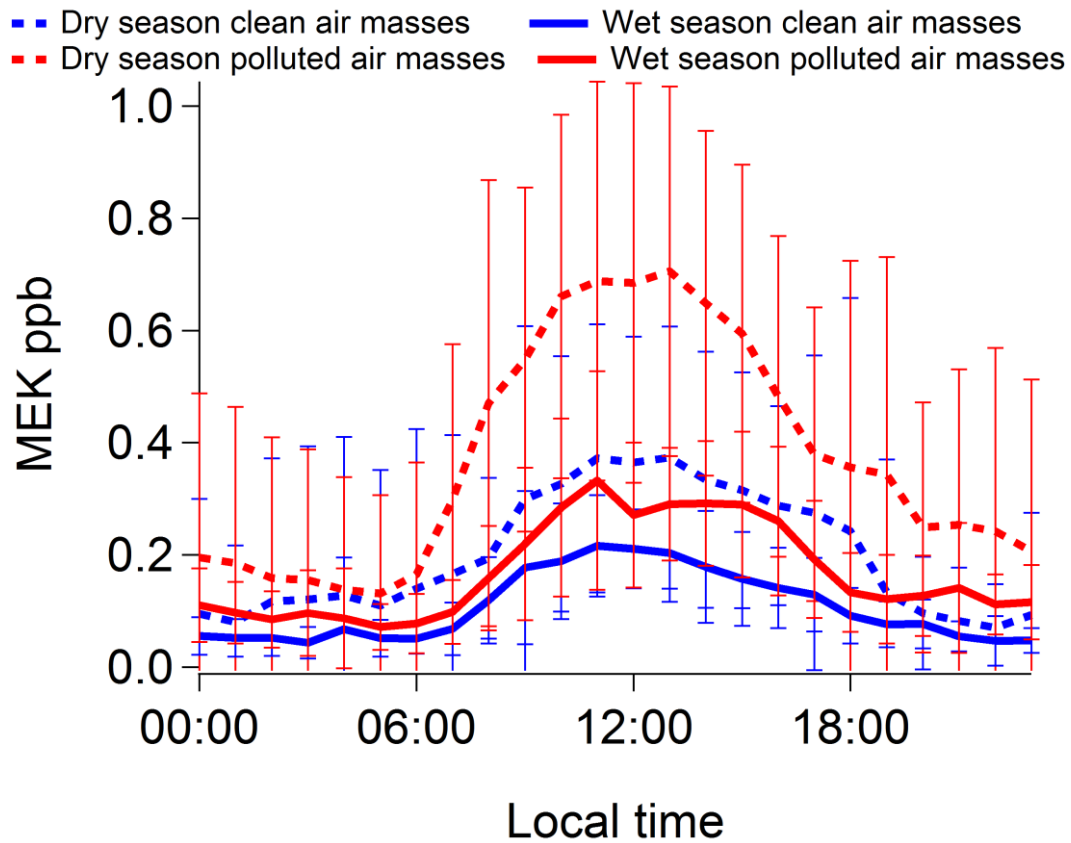
Figure 7: Hourly average concentrations of MEK in ppb for the clean conditions (blue) and the polluted conditions (red) at the T2 site. Dashed lines represent the dry season and thick lines represent the wet season. Error bars represent the standard deviation.
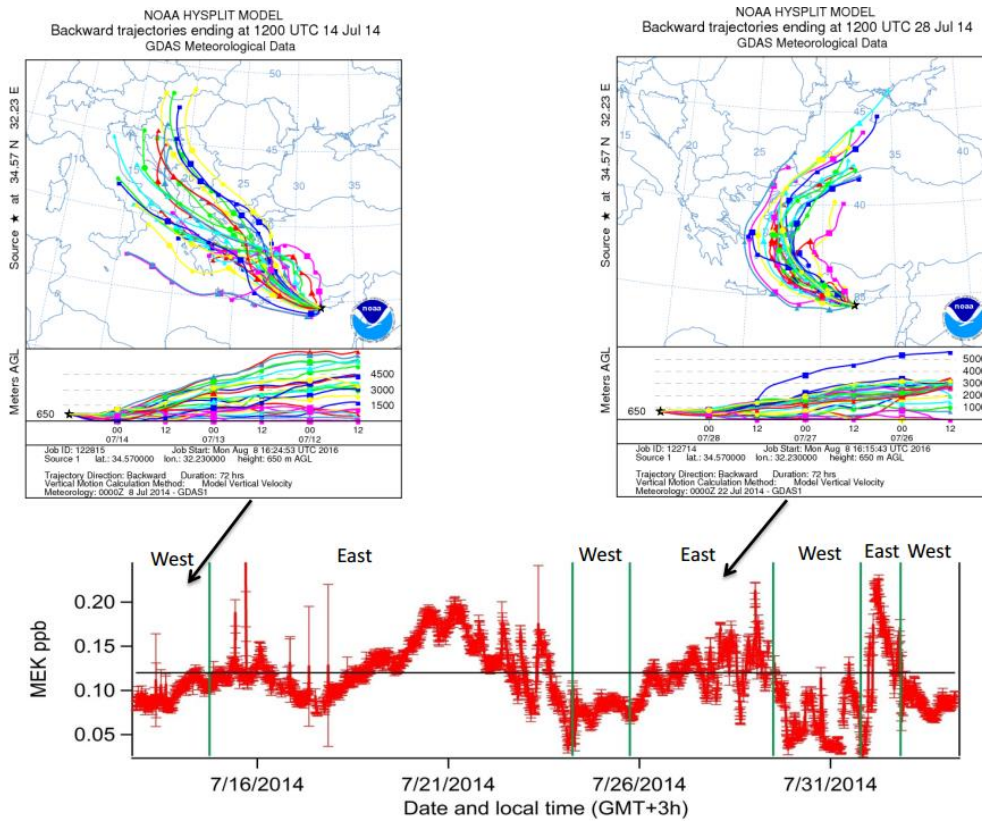
Figure 8: Timeline of MEK mixing ratios divided into periods when the air was coming from either Eastern or Western Europe. The HYSPLIT backward trajectories from 14 July and 28 August 2014 are shown based on the origin of the air masses. The black line represents the average of the whole campaign.