



1 **Atmospheric mixing ratios of methyl ethyl ketone (2-butanone) in tropical, bo-**  
2 **real, temperate and marine environments**

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26 **Abstract**

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



39 the ATTO pristine tropical rainforest site in central Amazonia). Under polluted conditions, we ob-  
40 served strongly enhanced MEK mixing ratios. Overall, the MEK mixing ratios and flux data pre-  
41 sented here indicate that both biogenic and anthropogenic sources contribute to its occurrence in  
42 the global atmosphere.

43

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

46

## 47 1. Introduction

48 Methyl ethyl ketone (C<sub>4</sub>H<sub>8</sub>O; MEK, also known as 2-butanone, butanone, methyl acetone,  
49 butan-2-one, methylpropanone, ethylmethylketone and methylacetone) is an oxygenated volatile  
50 organic compound (OVOC). Its occurrence in the atmosphere has been reported over a wide range  
51 of environments (Cecinato et al., 2002; Hellén et al., 2004; Ho et al., 2002; Kesselmeier et al.,  
52 1997; Kim et al., 2015; McKinney et al., 2011; Singh et al., 2004) with typical mixing ratios of  
53 0.03 - 4 ppb (Ciccioli and Mannozi, 2007; Kim et al., 2015). Although often being measured  
54 alongside other volatile organic compounds (VOCs), atmospheric MEK has received little attention  
55 to date. The photochemistry of acetone may serve as an example of how ketones affect the compo-  
56 sition and chemistry of the atmosphere by delivering free radicals to the upper troposphere (Colomb  
57 et al., 2006; Finlayson-Pitts and Pitts, 2000; McKeen et al., 1997) and thus increasing the ozone  
58 formation potential and altering the oxides of nitrogen (NO<sub>x</sub>) regime (Ciccioli and Mannozi, 2007;  
59 Folkins et al., 1998; Prather and Jacob, 1997). This understanding may be transferred to MEK, as  
60 this molecule is structurally similar to acetone with a comparable absorption spectrum (Martinez  
61 et al., 1992). Several studies report that the mixing ratio of MEK in the free troposphere is roughly  
62 one quarter of that of acetone (Moore et al., 2012; Singh et al., 2004). However, MEK is about an  
63 order of magnitude more reactive than acetone with respect to the hydroxyl radical (Atkinson,  
64 2000), which makes it a compound of interest in ongoing discussions about the inability to fully  
65 account for the reactivity of OH (Nölscher et al., 2016).

66 There are several known but poorly characterized sources of MEK to the atmosphere. Ter-  
67 restrial vegetation (Bracho-Nunez et al., 2013; Brilli et al., 2014; Davison et al., 2008; De Gouw



68 et al., 1999; Isidorov et al., 1985; Jardine et al., 2010; Kirstine et al., 1998; König et al., 1995;  
69 McKinney et al., 2011; Ruuskanen et al., 2011; Song and Ryu, 2013; Steeghs et al., 2004; Wilkins,  
70 1996; Yáñez-Serrano et al., 2015), fungi (Wheatley et al., 1997) and bacteria (Song and Ryu, 2013;  
71 Wilkins, 1996) are known to emit MEK. It is also emitted directly by several anthropogenic  
72 sources, including biomass burning (Andreae and Merlet, 2001), solvent evaporation (Le Calvé, et  
73 al., 1998; Kim et al., 2015; Legreid et al., 2007) and vehicle exhaust (Bon et al., 2011; Brito et al.,  
74 2015; Guha et al., 2015; Liu et al., 2015; Verschuere, 1983). In addition, MEK can be formed via  
75 the atmospheric oxidation of other compounds (de Gouw et al., 2003; Jenkin et al., 1997; Neier  
76 and Strehlke, 2002; Sommariva et al., 2011).

77 Looking in more detail at biogenic sources, MEK emissions have been observed from dif-  
78 ferent types of vegetation, including forest canopies (Brilli et al., 2014; Jordan et al., 2009; Yáñez-  
79 Serrano et al., 2015), pasture (Davison et al., 2008; De Gouw et al., 1999; Kirstine et al., 1998) and  
80 clover (De Gouw et al., 1999; Kirstine et al., 1998). The MEK production and release mechanisms  
81 are manifold, but poorly understood. Studies show higher MEK emissions after cutting and drying  
82 of leaves than under no-stress conditions (Davison et al., 2008; De Gouw et al., 1999). Due to the  
83 water solubility of MEK in leaves and on surfaces (Sander, 2015), Jardine et al. (2010) suggested  
84 MEK emissions to be dependent on evaporation from storage pools in leaves. It has been suggested  
85 that MEK takes part in tri-trophic signalling following herbivore attack (Jardine et al., 2010; Song  
86 and Ryu, 2013). The roots of plants have also been found to release MEK in root-aphid interactions  
87 (Steeghs et al., 2004). Decaying plant tissue may also act as a source of MEK to the atmosphere  
88 (Warneke et al., 1999). Furthermore, some studies indicate the importance of MEK emissions by  
89 microbes, such as *Brevibacterium linens*, *Bacillus spp* and thermophilic gram-positive actinomy-  
90 cetes bacteria (Song and Ryu, 2013; Wilkins, 1996), and fungi such as *Trichoderma spp* (Wheatley  
91 et al., 1997).

92 MEK does not only enter the atmosphere via direct emissions, but also results from the  
93 atmospheric photooxidation of VOCs such as *n*-butane, 2-butanol, cis-2-butene/pentene, 3-methyl  
94 pentane and 2-methyl-1-butene (de Gouw et al., 2003; Jenkin et al., 1997; Neier and Strehlke, 2002;  
95 Sommariva et al., 2011). Although butane in the atmosphere comes predominantly from anthropo-  
96 genic sources (Kesselmeier and Staudt, 1999), some studies have reported emission of *n*-butane  
97 from vegetation (Donoso et al., 1996; Greenberg and Zimmerman, 1984; Hellén et al., 2006; König



98 et al., 1995; Zimmerman et al., 1988). The MEK yield from *n*-butane oxidation is ~ 80% (Singh et  
99 al., 2004). It is important to note that no mechanistic pathways have been found for atmospheric  
100 MEK production from the dominant biogenic VOCs isoprene,  $\alpha$ - and  $\beta$ -pinene and methyl butenol  
101 oxidation (Rollins et al., 2009; Singh et al., 2004).

102 In the atmosphere MEK reacts mainly with OH ( $k_{OH}=1.15\times 10^{-12}\text{ cm}^3\text{ s}^{-1}$ ) (Chew and Atkin-  
103 son, 1996), while reactions with  $O_3$  and  $NO_3$  are very slow during the day and hence negligible  
104 (Atkinson and Arey, 2003). MEK has a lifetime of 5.4 days at an OH concentration of  $1.6\times 10^6$   
105 radicals  $\text{cm}^{-3}$ , whereas isoprene and acetone have lifetimes of 8.2 h and 38 days, respectively, under  
106 the same conditions (Grant et al., 2008). The atmospheric degradation of MEK leads to acetalde-  
107 hyde and formaldehyde formation. In the presence of  $NO_x$ , MEK can lead to peroxyacetyl nitrate  
108 (PAN) and ozone formation (Grosjean et al., 2002; Pinho et al., 2005). In the upper troposphere,  
109 MEK photolyzes and regenerates OH (Atkinson, 2000; Baeza Romero et al., 2005; De Gouw et  
110 al., 1999) as does acetone, potentially increasing ozone formation.

111 Anthropogenic biomass burning leads to significant MEK emissions, of about  $2\text{ Tg a}^{-1}$  glob-  
112 ally (Andreae and Merlet, 2001 and unpublished updates; Schauer et al., 2001). Furthermore, about  
113  $9\text{ Tg a}^{-1}$  of other C4 compounds are emitted by biomass burning, which may act as MEK precursors.  
114 Another strong source of MEK is biofuel and charcoal combustion, with emissions of  $\sim 830\text{ mg kg}^{-1}$   
115 of dry biomass (compared to an emission rate of  $\sim 260\text{ mg kg}^{-1}$  of dry mass for biomass burning  
116 of savannah and grassland vegetation types, Andreae and Merlet, 2001). Despite the fact that bio-  
117 mass burning emission rates have been fairly well characterized, vehicular emissions, food cook-  
118 ing, industrial activities, cigarette smoke and other anthropogenic sources have not been character-  
119 ized. Even though MEK is present in urban atmospheres, there are no observations of MEK emis-  
120 sions from vehicles. MEK is also emitted by chemical plants as it is widely used in industry as a  
121 solvent, and is toxic (Le Calvé, et al., 1998), but not carcinogenic (National Center for Biotechnol-  
122 ogy, 2015).

123 Here we report recent findings on MEK from six different sites, including biogenic and  
124 anthropogenic dominated environments, in order to understand MEK sources in different environ-  
125 ments. Our large dataset allows a closer view of this important, almost ubiquitous species in Earth's  
126 atmosphere.



## 127 2. Sites and Methodology

128 The field sites compared in our study cover areas from pristine to remote anthropogenically  
129 influenced tropical forests, as well as boreal and Mediterranean regions. Measurements were per-  
130 formed by proton transfer reaction – mass spectrometry (PTR-MS) and partly complemented by  
131 gas chromatography - flame ionization detector (GC-FID) and gas chromatography - mass spec-  
132 trometry (GC-MS) analytical techniques (Figure 1, Table 1).

133 Online MEK measurements were performed with quadrupole PTR-MSs (Ionicon Analytic  
134 GmbH, Austria, Lindinger et al., 1998) at all sites, except for CYPHEX where a PTR-Time-Of-  
135 Flight-MS (PTR-ToF-MS, Ionicon Analytic GmbH, Austria, Lindinger et al., 1998) was used. The  
136 PTR-MSs were operated at standard conditions (2.2 mbar drift pressure, 600 V drift voltage, 142  
137 Td for ATTO and SMEAR-Estonia; 2.0 mbar drift pressure, 550 V drift voltage, 129 Td, for TT34;  
138 2.2 mbar drift pressure, 600 V drift voltage, 135 Td for O<sub>3</sub>HP; 2.2 mbar drift pressure, 560 V drift  
139 voltage, 132 Td for T2 and 2.2 mbar drift pressure, 600 V drift voltage, 137 Td for CYPHEX).

140 Periodic background measurements and weekly humid calibrations were performed at all  
141 sites. Gravimetrically prepared multicomponent standard were obtained from Apel & Riemer,  
142 USA, for ATTO, TT34, T2 and CYPHEX, and from Ionicon Analytik GmbH, Austria, for O<sub>3</sub>HP  
143 and SMEAR-Estonia.

### 144 2.1. The Amazon Tall Tower Observatory, ATTO: pristine tropical rainforest (Ama- 145 zon, Brazil).

146 The Amazon Tall Tower Observatory (ATTO) site is located in central Amazonia, 150 km  
147 NE of Manaus, Brazil (Figure 1) within a pristine primary tropical rainforest. The site is equipped  
148 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 a  
149 80-m walk-up tower, where the trace gas measurements take place. It is surrounded by a forest with  
150 a canopy height of approximately 35 m and with at least 417 different tree species among 7293  
151 screened trees of  $\geq 10$  cm diameter at breast height (DBH) in the twelve 1-ha inventoried plots  
152 (Andreae et al., 2015). The climate of this site is typical for tropical rainforests with a drier season  
153 (July-October) and a wet season (December-April, Nobre et al., 2009).



154 Measurements for this study took place 18 February - 15 March 2014. They were carried  
155 out at seven different heights (0.05, 0.5, 4, 24, 53 and 79 m) for 2 minutes at each height. The inlet  
156 lines were made of PTFE, 9.5 mm OD, insulated and heated to 50 °C and had PTFE particle inlet  
157 filters. More information about the gradient system and PTR-MS operation at ATTO can be found  
158 elsewhere (Nölscher et al., 2016; Yáñez-Serrano et al., 2015).

159 Additionally, ambient samples for off-line measurements with GC-FID were taken on 11  
160 March 2014 from 08:30 to 11:00 LT. They were collected at 24 m using a GSA SG-10-2 personal  
161 sampler pump and adsorber tubes (Carbograph 1, Carbograph V 130 mg of Carbograph 1 (90 m<sup>2</sup>  
162 g<sup>-1</sup>) followed by 130 mg of Carbograph 5 (560 m<sup>2</sup> g<sup>-1</sup>). The size of the Carbograph particles was  
163 in the range of 20–40 mesh. Carbograph 1 and 5 were provided by Lara s.r.l. (Rome, Italy). Samples  
164 were collected for 20 min with a flow of 167 ml min<sup>-1</sup> passing about 3.3 l of ambient air through  
165 the adsorbent. Cartridges were transported to the laboratory for analysis by a Perkin Elmer Auto-  
166 system XL GC-FID. These samples generally matched the results of the PTR-MS. For details on  
167 sampling see Kesselmeier et al., (2002).

## 168 **2.2. TT34: remote tropical rainforest (Amazon, Brazil)**

169 The ZF2 site is located in the Reserva Biologica do Cuieiras in central Amazonia, 60 km  
170 NNW of Manaus (2°35'39.4"S 60°12'33.4"W) within a remote primary tropical rainforest (Figure  
171 1). The site is equipped with two towers, TT34 and the K34. The TT34 triangular tower is 40 m  
172 high and embedded within the forest with a canopy height of approximately 30 m. The biodiversity  
173 of this site is also high and the climate is very similar to that at the ATTO site. More information  
174 about the site can be found elsewhere (Karl et al., 2009; Martin et al., 2010).

175 Measurements for this study were made from 1 September 2013 to 20 July 2014 at 41 m,  
176 at a fast rate (0.5 Hz) for virtual disjunct eddy covariance (vDEC) flux derivations techniques (Karl  
177 et al., 2002; Langford et al., 2009; Rinne et al., 2002). Wind vector data were obtained with a sonic  
178 anemometer (Gill R3, USA) mounted at the top of the tower close to the PTR-MS inlet. The PTR-  
179 MS inlet line was made of PFA (12.7 mm OD) (PFA-T8-062-100, Swagelok), and was insulated  
180 and heated to 40 °C inside the air-conditioned cabin.

## 181 **2.3. Station for Measuring Ecosystem-Atmosphere Relations, SMEAR-Estonia: re-** 182 **remote hemi-boreal forest (Tartumaa, Estonia)**



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

190           The measurements were made between 3 and 17 October 2012. Sampling was done using  
191 a dynamic, automated glass enclosure with measurement cycles of 36 seconds. The inlet line (9.5  
192 mm) was made of glass and was insulated and heated to 70°C. A dynamic exchange enclosure was  
193 used to measure emission rates from a Norway spruce branch located in the upper canopy at 16 m.  
194 While the focus of this study was the quantification of emission rates from a Norway spruce tree,  
195 ambient mixing ratios were derived as well using the box model described in Bourtsoukidis et al.,  
196 (2014b).

197           Furthermore, at SMEAR-Estonia, off-line measurements with a GC-MS were carried out  
198 for periods of three days each in June and July 2012, with samples taken every 4 hours at two  
199 heights (2 m and 20 m). Samples for GC-MS analysis were also taken from cuvettes enclosing  
200 some common plant species at the site (Table 1). In addition, VOC emissions from soil litter were  
201 monitored monthly. The air samples were drawn into multi-bed stainless steel cartridges (10.5 cm  
202 length, 3 mm inner diameter, Supelco, Bellefonte, PA, USA) filled with Carbotrap C 20/40 mesh  
203 (0.2 g), Carbopack C 40/60 mesh (0.1 g) and Carbotrap X 20-40 mesh (0.1 g) adsorbents (Supelco).  
204 Even though the site usually experiences low ozone mixing ratios of 10 - 30 ppb (Noe et al., 2012),  
205 a catalytic Cu(II) ozone scrubbing system (Sun et al., 2012) was applied. Three constant-flow air  
206 sample pumps (1003-SKC, SKC Inc., Huston, TX, USA) and one multisample constant-flow air  
207 sample pump (224-PCXR8, SKC Inc., Huston, TX, USA) allowed four samples to be collected at  
208 the same time. Each sample took 30 min with a flow of 200 ml min<sup>-1</sup> concentrating 6 l of ambient  
209 air onto the adsorbent. More information can be found elsewhere (Noe et al., 2012).

210           **2.4. Observatoire de Haute Provence, O<sub>3</sub>HP: rural Mediterranean temperate forest**  
211 **(Provence, France)**



212 The oak observatory (O<sub>3</sub>HP, <https://o3hp.obs-hp.fr>) at the “Observatoire de Haute Pro-  
213 vence” (OHP, <http://www.obs-hp.fr/welcome.shtml>), is located within a rural Mediterranean tem-  
214 perate forest in the French Mediterranean region, 60 km north of Marseille, the closest large city  
215 (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  
216 height of approximately 5 m. The O<sub>3</sub>HP site is dominated by *Quercus pubescens* Willd (75% of  
217 trees) and *Acer monspessulanum* L. (25%) forming a sparse canopy, while *Cotinus coggygria* Scop.  
218 and other grass species constitute the understorey canopy. The climate at the site is typical Medi-  
219 terranean, with dry and hot summers and humid and cool winters. More information about the site  
220 can be found elsewhere (Genard-Zielinski et al., 2015; Kalogridis et al., 2014).

221 The measurements took place during 29 May - 12 June 2014 as part of the CANOPEE  
222 project (Biosphere-atmosphere exchange of organic compounds: impact of intra-canopy pro-  
223 cesses). Ambient measurements were carried out at 2 m (inside the canopy) on consecutive days in  
224 intervals of 5 minutes. The 9.5 mm Teflon inlet lines were insulated and heated above ambient  
225 temperature and had no particle filter. In addition, light non-methane hydrocarbons (from ethane  
226 to hexane) were measured with a GC-FID (Chromatotec, Saint-Antoine, France) in-line with the  
227 PTR-MS as described in Zannoni et al. (2016).

## 228 **2.5. T2: mixed urban and rainforest influenced environment (Amazon, Brazil)**

229 The T2 site is part of a set of experimental sites within the GoAmazon project to study the  
230 effect of the pollution plume from the city of Manaus on the otherwise pristine Amazonian atmos-  
231 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"  
232 W, Figure 1). Given its location, near Manaus and across the Rio Negro, air mass transport to the  
233 sampling site is strongly modulated by a river breeze, alternating between mostly biogenic condi-  
234 tions, resulting from the surrounding forest, and the city emissions. The climate is tropical and  
235 similar to that at the ATTO and ZF2 sites.

236 The measurements for this study took place between 15 February and 15 November 2014.  
237 They were carried out at 12 m above the laboratory container with 30 minute cycles. The inlet line  
238 was made of insulated Teflon (9.5 mm OD) without PFTE particle filter.

## 239 **2.6. CYPHEX: mixed marine, rural environment influenced by aged air masses (Cy-** 240 **prus)**





241 The Cyprus Photochemistry Experiment (CYPHEX) campaign took place at a site located  
242 in the NW inshore part of Cyprus, in the Paphos region (34°57'50.0" N, 32°22'37.0" E) (Figure 1).  
243 The site experiences mixed marine and rural emissions influence. The climate is Mediterranean,  
244 warm and dry, and shrubs and small trees dominate the sparse vegetation.

245 The measurements took place during July and August 2014 without a single rain event.  
246 Instruments were installed inside containers and connected to a stack inlet that reached up 5 m  
247 above the container roofs. Air was drawn through the 15 m stack inlet of 0.5 m with high flow rate  
248 ( $5 \text{ l min}^{-1}$ ) to minimize wall losses. The subsampling inlet line was made of Teflon (13 mm OD),  
249 was insulated and heated to 35 °C, and had a PTFE inlet particle filter.

### 250 3. Results

#### 251 3.1. Sites dominated by biogenic emissions

252 All the pristine or remote sites studied were characterized by relatively low mixing ratios  
253 of nitrogen oxides ( $\text{NO}_x$ ) ( $< 3$  ppb of nitrogen dioxide ( $\text{NO}_2$ ) for O<sub>3</sub>HP (Kalogridis et al., 2014;  
254 Zannoni et al., 2016), 0.2-0.8 ppb of  $\text{NO}_x$  for SMEAR-Estonia, and  $< 1$  ppb  $\text{NO}_x$  for the Amazon  
255 rainforest (Kuhn et al., 2010)). The diel cycles of MEK at these sites followed a comparable pattern  
256 (Figure 2), where MEK mixing ratios were highest in the middle of the day, following the maxima  
257 of light and air temperature. The dominant source at these sites was considered to be biogenic.  
258 Mixing ratios of MEK correlated well with ambient temperature ( $r^2=0.57$  (ATTO),  $r^2=0.83$   
259 (SMEAR),  $r^2=0.47$  (O<sub>3</sub>HP)), while it was less well correlated with photosynthetically active radi-  
260 ation (PAR) ( $r^2=0.23$  (ATTO),  $r^2=0.26$  (SMEAR),  $r^2=0.67$  (O<sub>3</sub>HP)). This suggests that ambient  
261 temperature predominantly influenced MEK emission rates from plants.

262 The vertical observations at ATTO revealed a strong diel variability of the magnitude and  
263 vertical distribution of MEK mixing ratios throughout the forest canopy and in the atmosphere  
264 above. Figure 3 shows an example of one day (7<sup>th</sup> of March 2014) hourly vertical profile of MEK  
265 from 13:00-15:00 LT, from the ground to the atmosphere, suggesting that the canopy top is the  
266 major source of MEK at the site on such days. Such figures were found for 83% (for the afternoon  
267 hours) and 45% (for the morning hours) of all days of measurements. In addition, MEK mixing  
268 ratios decreased significantly beneath the canopy towards the forest floor, possibly due to dry dep-  
269 osition or generally smaller emissions due to less light and temperature.



270 At the TT34 rainforest site, ecosystem-scale fluxes were directly calculated from the PTR-  
271 MS measurements using the method of virtual disjunct eddy covariance (vDEC) (Karl et al., 2001b;  
272 Figure 4). The fluxes averaged over the entire 11-month measurement period (covering both parts  
273 of dry and wet season) clearly demonstrate an emission of MEK by the rainforest during daytime  
274 with the highest emissions around noon, and no emissions during nighttime.

275 Online ambient mixing ratios of MEK, as measured by the PTR-MS in the hemi-boreal  
276 forest at the SMEAR-Estonia site during autumn 2012, were on average  $0.15 \pm 0.04$  ppb (range  
277 0.09 - 0.25 ppb). These mixing ratios are almost a factor of 2 lower than ATTO and O<sub>3</sub>HP during  
278 daytime hours. This difference among boreal forests and broad-leafed forests (of ATTO and O<sub>3</sub>HP)  
279 could be related to the temperature dependence of MEK emissions apparently common among all  
280 biogenic sites.

281 The rural Mediterranean temperate forest site at O<sub>3</sub>HP differs significantly from the tropical  
282 rainforest (ATTO, TT34) or the hemi-boreal forest (SMEAR-Estonia, Figure 1). The trees at O<sub>3</sub>HP  
283 are predominantly *Quercus pubescens*, a high isoprene emitter (Keenan et al., 2009). At this site,  
284 the exchange of air through the forest canopy is enhanced because the canopy is sparse. As shown  
285 in Figure 2, ambient MEK mixing ratios measured inside the canopy (2 m) increased with temper-  
286 ature in the morning. During the day, increased forest emissions of MEK seemed to balance the  
287 rise of the boundary layer depth, resulting in a plateau until sunset. The fluctuation of MEK after  
288 sunset may be understood as a result of a ceased source revealing the deposition as it can hardly be  
289 explained by gas-phase chemistry or the reduced nocturnal boundary layer height.

290 During the CANOPEE campaign at the O<sub>3</sub>HP site, additional GC-FID samples were taken  
291 at 2 m, allowing measurements of several anthropogenic light hydrocarbons, including *n*-butane.  
292 This sampling was performed in parallel to the PTR-MS measurements. All samples contained *n*-  
293 butane, which was of anthropogenic origin. The MEK signal of the PTR-MS did not show any  
294 covariance with the *n*-butane signal as measured by the GC-FID. Hence, MEK at the O<sub>3</sub>HP site  
295 could not be related to the atmospheric oxidation of *n*-butane. Furthermore, the absence of a cor-  
296 relation with other anthropogenic tracers let us conclude that MEK at this site was predominantly  
297 of biogenic origin.



298 The measurements obtained by PTR-MS at the presented sites dominated by biogenic emis-  
299 sions were occasionally confirmed by GC-FID and GC-MS, which are compound selective. At  
300 ATTO the same range of MEK mixing ratios for the same hour of the day and height for the GC-  
301 FID and the PTR-MS measurements was found, indicating that the PTR-MS signal was only or at  
302 least dominated by MEK. To identify sources, canopy measurements at SMEAR-Estonia were  
303 complemented by emission measurements using cuvettes with GC-MS identification. Common  
304 hemi-boreal forest species, such as *Quercus robur*, *Tilia cordata*, *Sorbus aucuparia*, *Betula pu-*  
305 *bescens* and *Picea abies*, were screened for VOC emissions. The highest emissions of MEK were  
306 found from *Tilia cordata* and *Picea abies* (Table 2). The data match those reported by  
307 (Bourtsoukidis et al., 2014a) who measured an emission rate of MEK of  $2.6 \pm 2.2 \text{ ng g}_{(\text{dw needle})}^{-1} \text{ s}^{-1}$   
308 from *Picea abies* using PTR-MS. The GC-MS technique obtained a very similar value of  $2.3 \text{ ng}$   
309  $\text{g}_{(\text{dw needle})}^{-1} \text{ s}^{-1}$ . MEK emissions from *Picea abies* were relatively small compared to other VOCs  
310 emitted by the same plant species such as total monoterpenes and acetone which reached 93.2 and  
311  $27.6 \text{ ng g}_{(\text{dw needle})}^{-1} \text{ s}^{-1}$ , respectively (Bourtsoukidis et al., 2014a). In addition to plant sources, the  
312 emissions of MEK from leaf litter were quantified with GC-MS. MEK litter emissions, with a  
313 monthly average of  $7 \mu\text{g m}^{-2} \text{ h}^{-1}$ , were of comparable magnitude to the emissions of MEK from the  
314 screened hemi-boreal forest tree species, including *Quercus robur* or *Sorbus aucuparia*, which  
315 emitted  $8 - 9 \mu\text{g m}^{-2} \text{ h}^{-1}$  of MEK (Table 2).

### 316 3.2. Anthropogenically influenced sites

317 Anthropogenically influenced sites are characterized by air masses that have passed over  
318 polluted cities or industrially used regions. This air typically has elevated mixing ratios of  $\text{NO}_x$ ,  
319 other products of fossil fuel combustion such as aromatic compounds, carbon monoxide (CO), and  
320 higher aerosol loading. Regional biomass burning plumes can also be a source of anthropogenic  
321 input to air masses and are here considered as anthropogenic.

322 The T2 data set was sorted for polluted periods (air masses loaded with CO, black carbon,  
323 high aerosol loading, aromatic compounds) and non-polluted periods. Periods with CO higher than  
324 130 ppb during the tropical wet season and higher than 160 ppb during the dry season were con-  
325 sidered polluted. As shown in Figure 5, MEK mixing ratios strongly increase with pollution. The  
326 T2 site in Brazil is located on the bank of the Rio Negro and is affected by both, the tropical rain-



327 forest (biogenic) and the megacity of Manaus (anthropogenic). The location of the T2 site down-  
328 wind of Manaus and upwind of the rainforest minimizes the biogenic influence. MEK mixing ratios  
329 were generally lower for the clean conditions at T2 than mixing ratios found at ATTO or TT34  
330 (Figure 2 and 5). Nevertheless, the mixing ratios of MEK during polluted conditions ( $0.7 \pm 0.33$   
331 ppb during dry season at 13:00 LT) reached or even exceeded those at the other tropical rainforest  
332 sites ( $0.32 \pm 0.13$  ppb at 13:00 LT for ATTO and  $0.45 \pm 0.28$  ppb at TT34; Figure 2 and 5). Pre-  
333 sumably, anthropogenically affected air as transported across the Rio Negro from the city of Ma-  
334 naus (~2 million inhabitants; IBGE, 2014) generated a plume with a mixture of anthropogenic  
335 MEK directly emitted in Manaus or MEK formed by oxidation of e.g. *n*-butane during transport.  
336 The general trend observed in Figure 6 is an increase of MEK mixing ratios when easterly winds  
337 came from Manaus (located to the East of T2). However, there were times when winds blew from  
338 the North, and incident air masses passed through large rainforest areas, in which TT34 is included,  
339 these air masses then crossed the river and arrived at the site). During these times, when air masses  
340 were mostly dominated by biogenic emissions, MEK enhancement reached on average 200 ppt.

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

350         The CYPHEX campaign took place at Ineia, North-West Cyprus, at a location that has very  
351 little significant vegetation nearby. The air masses that pass through the site are either from Western  
352 Europe passing across France and Spain and then the Mediterranean Sea, or Eastern Europe (e.g.  
353 Turkey, Greece). During the CYPHEX campaign, the hourly median MEK mixing ratios did not  
354 show any distinct diel cycle or relations to temperature or net radiation (Figure 5) strongly suggest-  
355 ing no significant local sources were present. Furthermore, backward air mass trajectories, as cal-  
356 culated by the HYSPLIT model (NASA, USA) (Figure 8), can be used to delineate times when



357 Cyprus was affected by easterly and westerly flow. On average, easterly air masses contained 0.13  
358  $\pm 0.03$  ppb whereas westerly masses contained  $0.08 \pm 0.02$  ppb. This difference can be due to  
359 differences in source strength, the greater duration of boundary layer transport from the west and  
360 hence marine uptake, or to photochemical loss during transport.

### 361 **3.3. Compilation of measurement data**

362 In order to investigate the origin and characteristics of MEK in the atmosphere, we calcu-  
363 lated the determination coefficient ( $r^2$ ) between the mixing ratios of MEK and other co-measured  
364 VOC species for each site (Table 3). This coefficient is the ratio of the variability of the MEK  
365 mixing ratios over the variability of the other VOC mixing ratios available for each site. Acetone,  
366 acetaldehyde, monoterpenes, isoprene, isoprene oxidation products and methanol (Kesselmeier and  
367 Staudt, 1999; Laothawornkitkul et al., 2009) are regarded as being of biogenic origin. Compounds  
368 such as benzene, toluene, xylene and acetonitrile are considered as typical anthropogenic tracers  
369 (Andreae and Merlet, 2001; Finlayson-Pitts et al., 1997).

370 The determination coefficients ( $r^2$ ) between MEK and other VOCs may indicate similarities  
371 of production and consumption pathways. In general, biogenic sites, namely ATTO, SMEAR-Es-  
372 tonia, and O<sub>3</sub>HP, showed relatively high correlations between MEK and almost all biogenic VOCs  
373 ( $r^2 > 0.5$ ). Exceptions are the  $r^2$  of isoprene, monoterpene and isoprene oxidation products for O<sub>3</sub>HP.

374 For instance, the highest determination coefficient was found for MEK and acetone at the  
375 SMEAR site ( $r^2 = 0.97$ ). In SMEAR-Estonia overall high correlations were found with the oxygen-  
376 ated compounds, acetone, acetaldehyde and methanol, as well as with monoterpenes and isoprene.  
377 At ATTO, correlations were only slightly lower. The determination coefficients calculated for the  
378 O<sub>3</sub>HP observations were generally lower than for ATTO and SMEAR-Estonia, further influenced  
379 by the higher turbulent mixing due to sparser vegetation, leading to a quick oxidation. Nevertheless,  
380 the good correlations of MEK with typical biogenically emitted compounds, such as isoprene, iso-  
381 prene oxidation products, monoterpenes, methanol and acetone, corroborated the biogenic origin  
382 of MEK emissions at the biogenic sites.

383 At the anthropogenically influenced sites, T2 and CYPHEX, determination coefficients for  
384 the biogenic compounds were generally lower, apart from the  $r^2$  (0.64 and 0.45, respectively) be-  
385 tween MEK and acetone. It is important to note that although T2 is a mixed anthropogenic and



386 biogenic site, the determination coefficient for MEK and acetone was high, but very low for the  
387 rest of the biogenic compounds. For the anthropogenic compounds, T2 had an  $r^2$  of 0.27 for MEK  
388 and acetonitrile and MEK and xylene. Furthermore, the data from the Cyprus site showed poor  
389 correlation of MEK with any biogenic compound, but a correlation coefficient of  $r^2 = 0.58$  for  
390 MEK and toluene, an anthropogenic tracer.

#### 391 4. Discussion

##### 392 4.1. PTR-MS measurements

393 Most of the measurements in this study were performed with a quadrupole PTR-MS, a  
394 technique that monitors selected VOC ions, online and with fast time response. A disadvantage is  
395 the separation by masses with a mass resolution of only 1 amu. For some masses, several com-  
396 pounds and/or compound-fragments may be detected as one signal. The quadrupole PTR-MS sig-  
397 nal at  $m/z$  73 is attributed to MEK, but may have contributing signals of water clusters (de Gouw  
398 et al., 2007), butanal (Inomata et al., 2010; McKinney et al., 2011; Slowik et al., 2010; Warneke et  
399 al., 2007), acrylic acid (de Gouw et al., 2003), 2-methyl propanal (Baraldi et al., 1999; Jardine et  
400 al., 2010), and methyl glyoxal (Holzinger et al., 2007; Jordan et al., 2009). We have tried to take  
401 into account possible interferences by using different analytical techniques and supplementary in-  
402 formation. At the SMEAR-Estonia site, the accompanying GC-MS observations validated the sig-  
403 nal for MEK. Additionally, the GC-FID samples taken at ATTO corroborated the signal for MEK  
404 at this site. Nevertheless, we try to give a short overview below about the interferences of other  
405 trace gases with the PTR-MS identification of MEK.  
406

407 Methyl glyoxal is a likely contributor to the observed signal at the PTR-MS protonated  
408 mass  $m/z$  73, especially in areas where there are high levels of isoprene. It is formed following the  
409 oxidation of methyl vinyl ketone and methacrolein, which are both isoprene oxidation products  
410 (Calvert and Madronich, 1987; Lee et al., 2006). Supported by GC-FID measurements and rela-  
411 tively low isoprene levels during the wet season (Yáñez-Serrano et al., 2015), we can assume that  
412 the contribution of methyl glyoxal to this mass was insignificant at the rainforest sites (ATTO and  
413 TT34). Furthermore, at  $O_3HP$  the correlation between MEK and the isoprene oxidation products  
414 was low ( $r^2 = 0.41$ ). Despite the high isoprene emissions it seems that these oxidation products and



415 methyl glyoxal did not significantly contribute to the signal at  $m/z$  73. During the CYPHEX cam-  
416 paign the PTR-ToF-MS could unambiguously distinguish between MEK and methyl glyoxal (at  
417 73.0648 amu and 73.0284 amu respectively).

418 Even though a contribution of butanal to  $m/z$  73 of up to 65% (Lindinger et al., 1998) and  
419 20% (Williams et al., 2001) has been reported previously, most butanal fragments on  $m/z$  57 (Ion-  
420 icon Analytic GmbH). Acrylic acid, a marine compound (Liu et al., 2016) that may interfere at  $m/z$   
421 73, was probably not of relevance at sites under biogenic influence. However, in the case of an-  
422 thropogenically influenced sites, such as T2, interferences may have been of relevance. Karl et al.  
423 (2007) and Ciccioli et al., (2014) measured tropical biomass burning emissions and found that  $m/z$   
424 73 is comprised of 74% MEK and 23% 2-methyl propanal (73.1057 amu). Even though none of  
425 the sites presented in this study was severely influenced by biomass burning, we cannot completely  
426 rule out a possible direct emission of 2-methyl propanal by plants, which is of lower magnitude  
427 than from biomass burning (Hafner et al., 2013; Jardine et al., 2010; Karl et al., 2005). Due to the  
428 standard operation conditions of the PTR-MS under our measurement conditions, we neglected  
429 water clusters as they are regarded to be insignificant (McKinney et al., 2011; Yáñez-Serrano et  
430 al., 2015). Summarizing these issues, we note that several studies have concluded  $m/z$  73 to origi-  
431 nate from MEK only (Bourtsoukidis et al., 2014a; Crutzen et al., 2000; De Gouw et al., 1999, 2000;  
432 Holzinger et al., 2000; Karl et al., 2001a, 2005; Kim et al., 2015; Millet et al., 2015; Steeghs et al.,  
433 2004). Based on these considerations and the similarity of magnitudes measured by the PTR-MS  
434 as compared with the GC results, we assume  $m/z$  73 is representative of the atmospheric MEK  
435 present.

#### 436 **4.2. The biogenic MEK**

437 The data obtained at the biologically influenced sites demonstrated that MEK was emitted  
438 by vegetation. This is clearly supported by the canopy-scale net flux observations of MEK at the  
439 TT34 rainforest site (Figure 4) as well as the diel cycles of the mixing ratios at the other biogeni-  
440 cally influenced sites (Figure 2). Furthermore, the cuvette-level measurements at SMEAR-Estonia  
441 also corroborated the MEK emission by vegetation. In addition, a contribution by other biogenic  
442 sources such as dead and decaying plant matter was also observed at SMEAR-Estonia to be of  
443 similar magnitude to boreal plant species emissions, and indicating a source from plant litter, in  
444 accordance with the results from Warneke et al., (1999) that measured MEK emission from the



445 abiotic processes of plant decaying matter. This is not the case for the tropical sites where vertical  
446 profiles show canopy emissions dominate.

447 High correlation coefficients suggested strong relations between the emission processes for  
448 MEK and other biogenic compounds (Table 3). A similar approach has been used previously by  
449 Goldstein and Schade (2000) to unveil the sources of acetone. Similarly, Davison et al. (2008)  
450 found a high correlation coefficient between MEK and acetone of  $r^2=0.87$  and a relatively poor  
451 correlation between MEK and monoterpenes ( $r^2=0.54$ ). They surmised that good correlations indi-  
452 cated a common origin for biogenically emitted compounds. Furthermore, a resemblance of the  
453 pattern of acetone and MEK has been reported for the ATTO site before (Yáñez-Serrano et al.,  
454 2015). In our study, we found high determination coefficients for MEK with acetone and MEK  
455 with temperature, and lower  $r^2$  for MEK and compounds such as isoprene and monoterpenes for  
456 all the biogenic sites (Table 3). This could indicate that MEK forest emissions are more related to  
457 processes resembling acetone emissions and temperature dependent processes, rather than light and  
458 temperature dependent emission mechanisms, as for isoprene and monoterpenes (Jardine et al.,  
459 2015; Kesselmeier and Staudt, 1999).

460 Plant physiological production pathways have been reported for MEK formation. MEK can  
461 be formed, similarly to acetone, as a by-product of a cyanohydrin lyase reaction during cyanogen-  
462 esis (Fall, 2003; Vetter, 2000). This chemical defence pathway was also identified in clover by  
463 Kirstine et al. (1998) and de Gouw et al. (1999) as a result of mechanical stress, and can be of  
464 special importance for tropical rainforests (Miller et al., 2006). On the other hand, in places such  
465 as SMEAR-Estonia, dominating plant species are not cyanogenic, and other processes for MEK  
466 formation are probably more dominant. In pine trees, acetone is produced from light-dependent  
467 and –independent processes that can be associated with the decarboxylation of acetoacetate occur-  
468 ring in microorganisms and animals (Fall, 2003), oxidation of fatty acids leading to ketone emis-  
469 sions (Niinemets et al., 2014), from pyruvic acid leading to acetyl-CoA (Kesselmeier and Staudt,  
470 1999), or produced from uncharacterized biochemical reactions (Fall, 2003). Such processes could  
471 also be related to MEK emissions.

472 Even though extensive laboratory measurements are needed to identify the dominant plant  
473 process or processes responsible for MEK emission, this study demonstrated the role that temper-  
474 ature can exert on such emissions. Hence, forests around the world may act as very different sources





475 for atmospheric MEK. This can be seen for boreal forests (SMEAR-Estonia), with distinctly lower  
476 temperatures, where MEK levels were significantly lower. However, other factors must be consid-  
477 ered, such as Leaf Area Index (LAI) and plant species composition, as well as the environmental  
478 factors, water availability and mechanical stress. Mechanical stress has already been observed by  
479 de Gouw et al. (1999) to act as a driver for MEK emissions. This is in close agreement with in-  
480 creased emissions of MEK as observed at the SMEAR site in Estonia during the installation of the  
481 branch enclosure, causing a disturbance of the branch during the installation of the dynamic cham-  
482 ber (Bourtsoukidis et al., 2014a).

483 Due to its relatively long atmospheric lifetime (~5 days for the reaction with OH; Grant et  
484 al., 2008), MEK is expected to accumulate in the atmosphere until removal. Hence, atmospheric  
485 mixing ratios can reflect seasonality and changes in dominating sources, affected by radiation,  
486 temperature and phenology, from more biogenic dominance during the wet season to transport  
487 phenomena and oxidation processes of primarily emitted compounds from regional biomass burn-  
488 ing, as it has been seen in 2013 at the ATTO site (Yáñez-Serrano et al., 2015). Additionally, the  
489 canopy structure seems to be important for air mixing and fast oxidation, as seen for the O<sub>3</sub>HP site  
490 with an apparently faster mixing due to sparser vegetation and consequent dampening of the am-  
491 plitude of the diel cycle. Furthermore, due to its oxygenated nature, partitioning to and from aque-  
492 ous surfaces is likely, including deposition and surface reactions. Its high water solubility might  
493 allow dissolution within leaf water (Sander, 2015) triggering bidirectional exchange of MEK  
494 (McKinney et al., 2011; Niinemets et al., 2014). Due to its high solubility in water and its relatively  
495 long lifetime, MEK could potentially influence gas-aqueous reactions on aerosol surfaces (Nozière,  
496 2005). This has been shown indirectly by the production of methyl glyoxal after its oxidation by  
497 OH, having implications for the formation of organics in the aerosol aqueous phase (Rodigast et  
498 al., 2015).

### 499 **4.3. The anthropogenic MEK**

500 A clear difference could be observed between the anthropogenic and biogenic influenced  
501 sites presented in this study. The T2 site represented a site with mixed influence by urban area and  
502 tropical rainforest. Affected by anthropogenic and biogenic sources ambient mixing ratios of MEK  
503 were higher than at the pristine ATTO rainforest site. Polluted episodes (from the Manaus plume)  
504 with an increase of MEK could be distinguished for both, the wet and the dry season, suggesting a



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

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

## 531 5. Remarks and conclusions

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



534 to PAN and ozone formation in the atmosphere (Pinho et al., 2005) and photochemical odd-hydro-  
535 gen production in the upper troposphere (Atkinson, 2000; Baeza Romero et al., 2005; De Gouw et  
536 al., 1999) which can further enhance the MEK ozone forming potential (Folkins et al., 1998;  
537 Prather and Jacob, 1997). Furthermore, as higher mixing ratios of MEK have been found under  
538 polluted conditions, human exposure to this toxic compound should be considered (Le Calvé, et al.,  
539 1998). Of the widely used atmospheric chemistry models, only GEOS-Chem explicitly computes  
540 MEK but only with regard to anthropogenic origin. On the basis of the data presented here from  
541 forest sites, it is necessary for atmospheric chemistry models to also include biogenic MEK emis-  
542 sions to better estimate its effects on the environment. Sites under biogenic influence showed  
543 marked diel variability, matching biogenic VOC emissions and temperature. Structural forest fea-  
544 tures seem to affect turbulent mixing and diluting of trace gases like MEK, as in the case of O<sub>3</sub>HP  
545 with patchy vegetation. MEK seemed to be produced in plants in a similar fashion to acetone, likely  
546 released during mechanical stress. Possible pathways for productions in plants are oxidation of  
547 fatty acids, cyanogenesis, production from pyruvic acid leading to Acetyl-CoA, light-dependent  
548 and –independent processes that can be associated with the decarboxylation of acetoacetate occur-  
549 ring in microorganisms and animals.

550 This study presents the first compilation and comparison of ambient measurements of MEK  
551 at different sites. MEK patterns and mixing ratios differ around the globe depending on sources  
552 and transport. Vegetation and litter have been identified as sources of MEK and magnitude of  
553 sources varied among the tropical rainforest, the Mediterranean temperate forest and the hemi bo-  
554 real forest following a likely temperature dependence. However, via different filtering methodolo-  
555 gies (CO filtering and backward trajectories), the anthropogenic input from polluted regions, such  
556 as the mixed urban & tropical rainforest and mixed marine environments, is often found to be the  
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876

877 **8. Tables**

878



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 <sub>3</sub> 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 $\mu\text{g m}^{-2} \text{h}^{-1}$	Standard deviation $\mu\text{g m}^{-2} \text{h}^{-1}$	Standard error $\mu\text{g m}^{-2} \text{h}^{-1}$	Median $\mu\text{g m}^{-2} \text{h}^{-1}$	Number of data points for statistics
<i>Quercus robur</i>	8.12	-	-	-	1
<i>Tilia cordata</i>	12.93	4.89	3.46	12.93	3
<i>Sorbus aucuparia</i>	9.08	-	-	-	1
<i>Betula pubescens</i>	9.36	5.10	2.94	8.21	3
<i>Picea abies</i>	13.76	5.05	2.91	15.51	3
Leaf litter	7.00	3.37	2.11	6.58	24

 Table 3: Determination coefficient ( $r^2$ ) of MEK and other co-measured VOC at the sites investigated. Green indicates sites with biogenic influence and red sites with anthropogenic influence. In the second column, the mean noon mixing ratios are expressed in ppb. The correlations above 0.5 are colour coded with warmest colours for highest determination coefficients. Determination coefficients for the TT34 site in Amazonia are missing due to lack of data.

$r^2$		Biogenic tracers					Anthropogenic tracers				
		Acetone	Acetaldehyde	Monoterpenes	Isoprene oxidation products	Methanol	Isoprene	Acetonitrile	Benzene	Toluene	Xylene
	<b>TT34</b>	-	-	-	-	-	-	-	-	-	-
<b>Biogenic sites</b>	<b>SMEAR</b>	0.97	0.89	0.72	-	0.90	0.84	-	-	-	-
	<b>ATTO</b>	0.89	0.62	0.75	0.75	0.51	0.77	0.49	0.07	0.27	0.04
	<b>O<sub>3</sub>PH</b>	0.61	0.62	0.12	0.41	0.57	0.14	0.19	0.03	0.15	0.00
<b>Anthropogenic sites</b>	<b>T2</b>	0.64	0.21	-	0.41	0.27	0.06	0.27	0.11	0.07	0.27
	<b>CYPHEX</b>	0.45	0.42	0.07	0.10	0.25	0.08	0.00	0.58	0.09	-



## 9. Figures

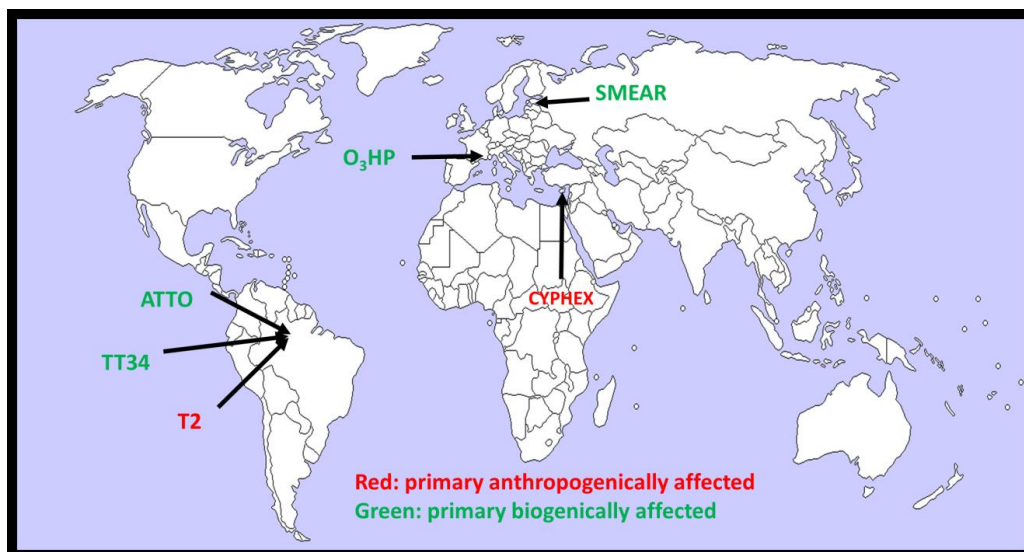


Figure 1: World map showing the location of the different sites. The names are colour coded depending on if they have primarily biogenic influence (green) or a primarily anthropogenic influence (red). Wikimedia Foundation, 2016.

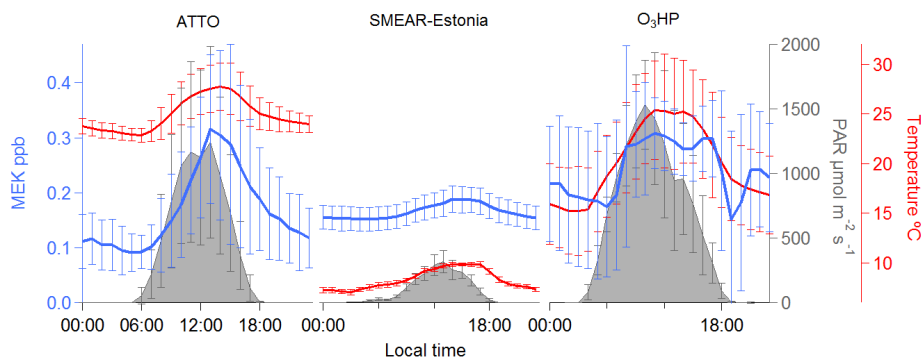


Figure 2: Hourly average diel cycles of MEK at the ATTO (left), SMEAR-Estonia (middle) and O<sub>3</sub>HP (right) sites, for the period of measurements (wet season 2014 for ATTO at 38 m, May and June 2014 for O<sub>3</sub>HP at 2 m, and October 2014 for SMEAR-Estonia at 16 m). Hourly mean diel cycles of temperature and PAR are also shown in red and grey, respectively. Error bars represent the standard deviations.

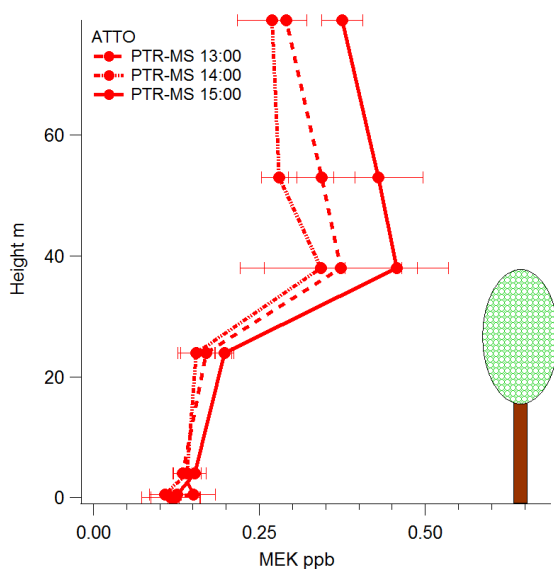


Figure 3: Hourly average vertical profiles of MEK mixing ratios at ATTO for the 7<sup>th</sup> of March 2014 for 13:00 LT (dashed lines), 14:00 LT (dotted and dashed lines) and 15:00 LT (thick lines). Error bars of vertical profiles are the standard deviations.

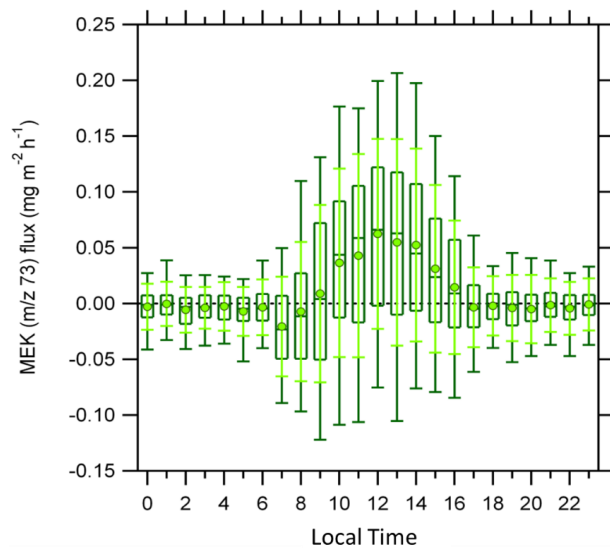


Figure 4: Hourly average MEK fluxes at the TT34 tower for the period Sept 2013 - July 2014. The light green circles represent means and associated error bars are one standard deviation. The central line of the box plots (dark green) indicates the median, bottom and top lines the 25<sup>th</sup> and 75<sup>th</sup> percentile respectively and whiskers are the 5<sup>th</sup> and 95<sup>th</sup> percentiles.

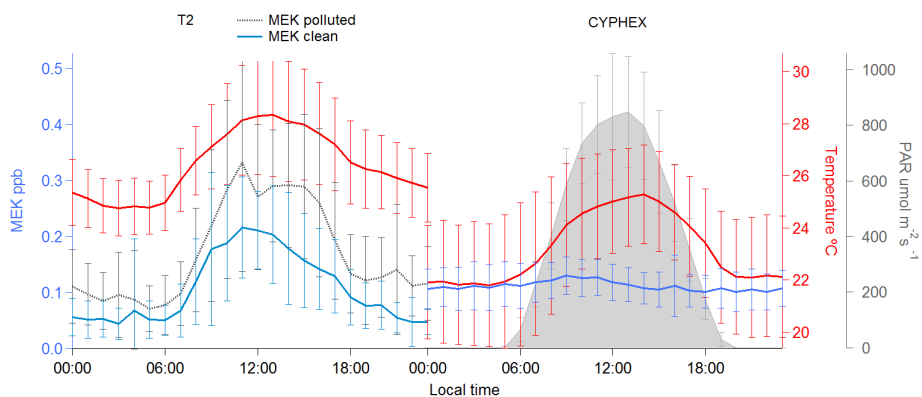


Figure 5: Hourly average diel cycles of MEK at the T2 (left) and CYPHEX (right) sites, for the period of measurements (wet season 2014 for T2 at 14 m, July and August 2014 for CYPHEX at 12 m). For T2 a separation between polluted (dotted black line) and clean (thick blue line) air masses was done. Hourly mean diel cycles of temperature and PAR are also shown in red and grey, respectively. Error bars represent the standard deviations.

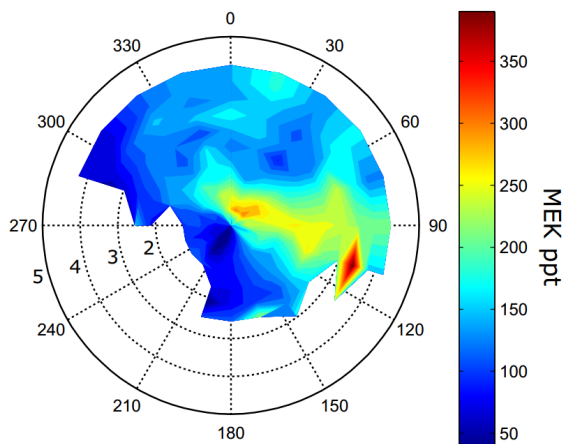


Figure 6: Polar surface plot for average MEK mixing ratios at a given wind direction (angle,  $1-5 \text{ m s}^{-1}$ ) and wind speed (radius).

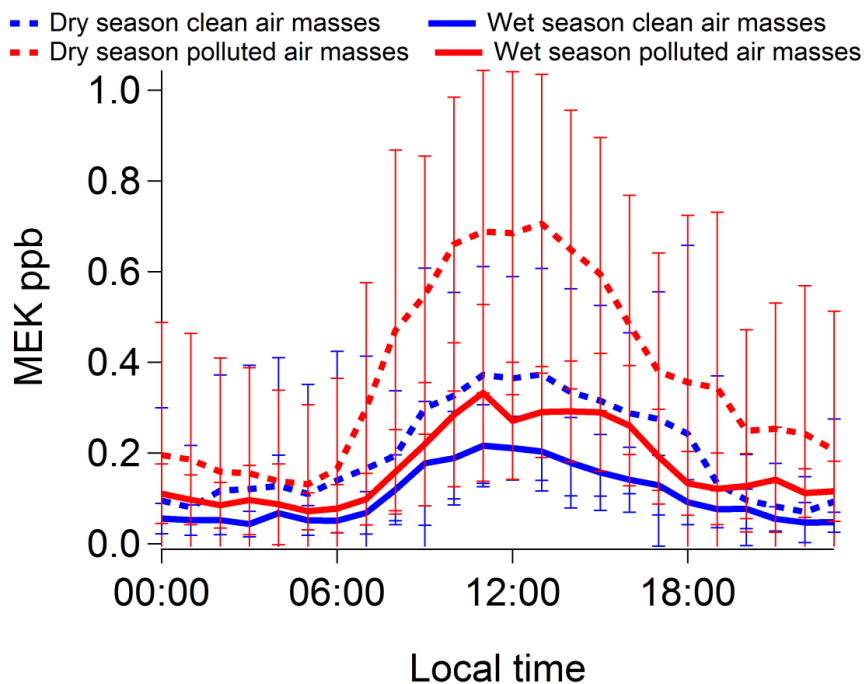


Figure 7: Hourly average concentrations of MEK in ppb for the clean conditions (blue) and the polluted conditions (red) at the T2 site. Dashed lines represent the dry season and thick lines represent the wet season. Error bars represent the standard deviation.

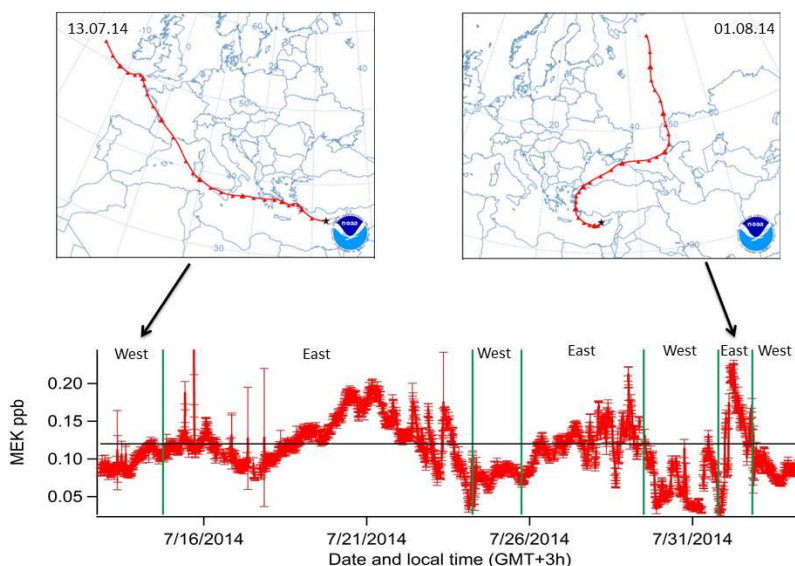


Figure 8: Timeline of MEK mixing ratios divided into periods when the air was coming either from Eastern or Western Europe. The HYSPLIT backward trajectories from 13 July and 1 August, 2014 to show the origin of the air masses. The black line represents the average of the whole campaign.