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

A. M. Yáñez-Serrano<sup>1,2,a</sup>, A. C. Nölscher<sup>1,b</sup>, E. Bourtsoukidis<sup>1</sup>, B. Derstroff<sup>1</sup>, N. Zannoni<sup>3</sup>, V. Gros<sup>3</sup>, M. Lanza<sup>4</sup>, J. Brito<sup>5</sup>, S. M. Noe<sup>6</sup>, E. House<sup>7</sup>, C. N. Hewitt<sup>7</sup>, B. Langford<sup>8</sup>, E. Nemitz<sup>8</sup>, T. Behrendt<sup>1,c</sup>, J. Williams<sup>1</sup>, P. Artaxo<sup>5</sup>, M. O. Andreae<sup>1,9</sup>, and J. Kesselmeier<sup>1</sup>

<sup>1</sup>Biogeochemistry and Air Chemistry Departments, Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany

<sup>2</sup>Instituto Nacional de Pesquisas da Amazônia (INPA), Av. André Araújo 2936, Manaus-AM, 69083-000, Brazil

<sup>3</sup>Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, 91191 Gif-sur-Yvette, France

<sup>4</sup>IONICON Analytik GmbH, Eduard-Bodem-Gasse 3, 6020, Innsbruck, Austria

<sup>5</sup>Instituto de Física, Universidade de São Paulo (USP), Rua do Matão, Travessa R, 187, CEP 05508-900, São Paulo-SP, Brazil

<sup>6</sup>Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 1, 51014 Tartu, Estonia

<sup>7</sup>Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK

<sup>8</sup>Centre for Ecology & Hydrology, Penicuik, EH26 0QB, UK

<sup>9</sup>Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92037, USA

<sup>a</sup>now at: Department of Ecosystem Physiology, University of Freiburg, 79085 Freiburg, Germany

<sup>b</sup>now at: Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

<sup>c</sup>now at: Department of Biogeochemical Processes, Max Planck Institute for Biogeochemistry, Hans-Knöll-Str. 10, 07745 Jena, Germany

Correspondence to: A. M. Yáñez-Serrano (a.yanezserrano@mpic.de)

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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 hemiboreal forest in Tartumaa, Estonia, and  $r^2 = 0.89$  at the ATTO pristine tropical rainforest site in central Amazonia). Under polluted conditions, we observed strongly enhanced MEK mixing ratios. Overall, the MEK mixing ratios and flux data presented here indicate that both biogenic and anthropogenic sources contribute to its occurrence in the global atmosphere.

## 1 Introduction

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

There are several known but poorly characterised sources of MEK to the atmosphere. Terrestrial vegetation (Bracho-Nunez et al., 2013; Brillì et al., 2014; Davison et al., 2008; De Gouw et al., 1999; Isidorov et al., 1985; Jardine et al., 2010; Kirstine et al., 1998; König et al., 1995; McKinney et al., 2011; Ruuskanen et al., 2011; Song and Ryu, 2013; Steeghs et al., 2004; Wilkins, 1996; Yáñez-Serrano et al., 2015), fungi (Wheatley et al., 1997) and bacteria (Song and Ryu, 2013; Wilkins, 1996) are known to emit MEK. It is also emitted directly by several anthropogenic sources, including anthropogenic biomass burning (Andreae and Merlet, 2001), solvent evaporation (Kim et al., 2015; Legreid et al., 2007) and vehicle exhaust (Bon et al., 2011; Brito et al., 2015; Liu et al., 2015; Verschueren, 1983). In addition, MEK can be formed via the atmospheric oxidation of other compounds (de Gouw et al., 2003; Jenkin et al., 1997; Neier and Strehlke, 2002; Sommariva et al., 2011).

Looking in more detail at biogenic sources, MEK emissions have been observed from different types of vegetation, including forest canopies (Brillì et al., 2014; Jordan et al., 2009b; Yáñez-Serrano et al., 2015), pasture (Davison et al., 2008; De Gouw et al., 1999; Kirstine et al., 1998) and clover (De Gouw et al., 1999; Kirstine et al., 1998). The MEK production and release mechanisms are manifold but poorly un-

derstood. Studies show higher MEK emissions after cutting and drying of leaves than under no-stress conditions (Davison et al., 2008; De Gouw et al., 1999). Due to the water solubility of MEK in leaves and on surfaces (Sander, 2015), Jardine et al. (2010) suggested MEK emissions to be dependent on evaporation from storage pools in leaves. It has been suggested that MEK takes part in tri-trophic signalling following herbivore attack (Jardine et al., 2010; Song and Ryu, 2013). The roots of plants have also been found to release MEK in root–aphid interactions (Steeghs et al., 2004). Decaying plant tissue may also act as a source of MEK to the atmosphere (Warneke et al., 1999). Furthermore, some studies indicate the importance of MEK emissions by microbes, such as *Brevibacterium linens*, *Bacillus* spp. and thermophilic Gram-positive actinomycetes bacteria (Song and Ryu, 2013; Wilkins, 1996), and fungi such as *Trichoderma* spp. (Wheatley et al., 1997).

MEK not only enters the atmosphere via direct emissions but also results from the atmospheric photooxidation of VOCs such as *n*-butane, 2-butanol, 3-methyl pentane and 2-methyl-1-butene (de Gouw et al., 2003; Jenkin et al., 1997; Neier and Strehlke, 2002; Sommariva et al., 2011). Although butane in the atmosphere comes predominantly from anthropogenic sources (Kesselmeier and Staudt, 1999), some studies have reported emission of *n*-butane from vegetation (Donoso et al., 1996; Greenberg and Zimmerman, 1984; Hellén et al., 2006; König et al., 1995; Zimmerman et al., 1988). The MEK yield from *n*-butane oxidation is ~80% (Singh et al., 2004). It is important to note that no mechanistic pathways have been found for atmospheric MEK production from the dominant biogenic VOCs isoprene,  $\alpha$ -pinene and  $\beta$ -pinene, as well as from methyl butenol oxidation (Rollins et al., 2009; Singh et al., 2004).

In the atmosphere MEK reacts mainly with OH ( $k_{\text{OH}} = 1.15 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ) (Chew and Atkinson, 1996), while reactions with O<sub>3</sub> and NO<sub>3</sub> are very slow during the day and hence negligible (Atkinson and Arey, 2003). MEK has a lifetime of 5.4 days at an OH concentration of  $1.6 \times 10^6 \text{ radicals cm}^{-3}$ , whereas isoprene and acetone have lifetimes of 8.2 h and 38 days, respectively, under the same conditions (Grant et al., 2008). The atmospheric degradation of MEK leads to acetaldehyde and formaldehyde formation. In the presence of NO<sub>x</sub>, MEK can lead to peroxyacetyl nitrate (PAN) and ozone formation (Grosjean et al., 2002; Pinho et al., 2005). In the upper troposphere, MEK photolyses and regenerates OH (Atkinson, 2000; Baeza Romero et al., 2005; De Gouw et al., 1999), as does acetone, potentially increasing ozone formation.

Anthropogenic biomass burning leads to significant MEK emissions of about 2 Tg a<sup>-1</sup> globally (Andreae and Merlet, 2001, and unpublished updates; Schauer et al., 2001). Furthermore, about 9 Tg a<sup>-1</sup> of other C<sub>4</sub> compounds is emitted by biomass burning, which may act as MEK precursors. Another strong source of MEK is biofuel and charcoal combustion, with emissions of ~830 mg kg<sup>-1</sup> of dry

biomass (compared to an emission rate of  $\sim 260 \text{ mg kg}^{-1}$  of dry mass for biomass burning of savannah and grassland vegetation types; Andreae and Merlet, 2001). Despite the fact that biomass burning emission rates have been fairly well characterised, vehicular emissions, food cooking, industrial activities, cigarette smoke and other anthropogenic sources have not been characterised. Even though MEK is present in urban atmospheres, there are no observations of MEK emissions from vehicles. Most of the urban MEK is released to the atmosphere via evaporation from chemical plants and industrial and household applications, as it is widely used as a solvent (e.g. in glues and as a paint thinner). It has a low toxicity and is not carcinogenic (National Center for Biotechnology, 2015). As its manufacturing has been increasing in the last 10 years, global atmospheric mixing ratios have probably increased as well.

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

## 2 Sites and methodology

The field sites compared in our study cover areas from pristine to remote anthropogenically influenced tropical forests, as well as boreal and Mediterranean regions. Measurements were performed using proton-transfer-reaction mass spectrometry (PTR-MS) and partly complemented by gas chromatography–flame ionisation detection (GC-FID) and gas chromatography–mass spectrometry (GC-MS) analytical techniques (Fig. 1, Table 1).

Online MEK measurements were performed with quadrupole PTR-MSs (Ionicon Analytic GmbH, Austria; Lindinger et al., 1998) at all sites except for CYPHEX, where a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytic GmbH, Austria; Jordan et al., 2009a) was used. The PTR-MSs were operated at standard conditions (2.2 mbar drift pressure, 600 V drift voltage, 142 Td for ATTO and SMEAR Estonia; 2.0 mbar drift pressure, 550 V drift voltage, 129 Td, for TT34; 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 voltage, 132 Td for T2; and 2.2 mbar drift pressure, 600 V drift voltage, 137 Td for CYPHEX).

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

### 2.1 The Amazon Tall Tower Observatory, ATTO: pristine tropical rainforest (Amazon, Brazil)

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

Measurements for this study took place 18 February–15 March 2014. They were carried out at seven different heights (0.05, 0.5, 4, 24, 53 and 79 m) with the PTR-MS switching sequentially between each height in 2 min intervals. The inlet lines were made of PTFE (9.5 mm OD), insulated and heated to 50 °C, and had PTFE particle inlet filters. More information about the gradient system and PTR-MS operation at ATTO can be found elsewhere (Nölscher et al., 2016; Yáñez-Serrano et al., 2015). The limit of detection (LOD) and uncertainty in the PTR-MS were 0.05 ppb and 34 %, respectively.

Additionally, ambient samples for offline measurements with GC-FID were taken on 11 March 2014 from 08:30 to 11:00 LT. They were collected at 24 m using a GSA SG-10-2 personal sampler pump and adsorber tubes (130 mg of Carbograph 1 ( $90 \text{ m}^2 \text{ g}^{-1}$ ) followed by 130 mg of Carbograph 5 ( $560 \text{ m}^2 \text{ g}^{-1}$ )). The size of the Carbograph particles was in the range of 20–40 mesh. Carbograph 1 and 5 were provided by Lara s.r.l. (Rome, Italy). Samples were collected for 20 min with a flow of  $167 \text{ mL min}^{-1}$  passing about 3.3 L of ambient air through the adsorbent. Cartridges were transported to the laboratory for analysis by a Perkin Elmer Autosystem XL GC-FID. These samples generally matched the results of the PTR-MS. For details on sampling see Kesselmeier et al. (2002).

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

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

**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 of-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 hemiboreal forest	16–20 m dense veg.	Jun, Jul, Oct 2012 Oct 2012	GC-MS (samples for of-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–Apr 2014 Jul–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

Measurements for this study were made from 1 September 2013 to 20 July 2014 at 41 m, at a fast rate (0.5 Hz) for virtual disjunct eddy covariance (vDEC) flux derivations techniques (Karl et al., 2002; Langford et al., 2009; Rinne et al., 2002). The high-resolution data were further averaged to give 30 min concentration and flux data. Wind vector data were obtained with a sonic anemometer (Gill R3, USA) mounted at the top of the tower close to the PTR-MS inlet. The PTR-MS inlet line was made of PFA (12.7 mm OD) (PFA-T8-062-100, Swagelok) and was insulated and heated to 40 °C inside the air-conditioned cabin. The LOD and uncertainty averaged 30 min concentrations measurements were 0.18 ppb and 6 %, respectively.

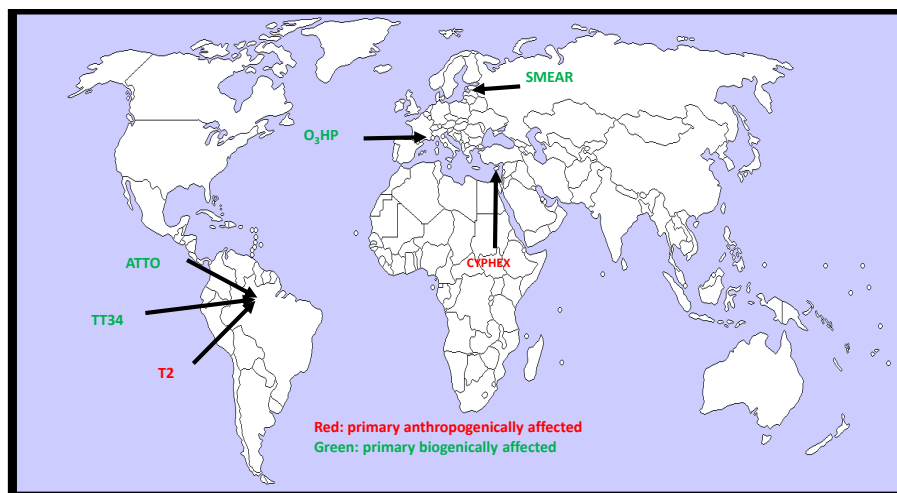
### 2.3 Station for Measuring Ecosystem-Atmosphere Relations, SMEAR Estonia: remote hemiboreal forest (Tartumaa, Estonia)

The Station for Measuring Ecosystem-Atmosphere Relations (SMEAR Estonia) site is located in the Järvselja Experimental Forestry station in Tartumaa, SE Estonia (58°16′N 27°16′E), within a remote hemiboreal zone, far from major anthropogenic disturbances (Noe et al., 2011; Fig. 1). The site is equipped with a tower of 24 m height. The surrounding canopy is about 16–20 m in height and the remote hemiboreal forest consists of a mixture of tree species, with Norway spruce (*Picea abies*) dominating. The climate is boreal

with a growing season of 170–180 days. More information about the site can be found elsewhere (e.g. Bourtsoukidis et al., 2014a; Noe et al., 2011, 2016).

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

Furthermore, at SMEAR Estonia, offline measurements with a GC-MS were carried out for periods of 3 days each in June and July 2012, with samples taken every 4 h at two heights (2 and 20 m). Samples for GC-MS analysis were also taken from cuvettes enclosing some common plant species at the site (Table 1). In addition, VOC emissions from soil litter were monitored monthly. The air samples were drawn into multi-bed stainless steel cartridges (10.5 cm length, 3 mm inner diameter, Supelco, Bellefonte, PA, USA) filled with Carbotrap C 20/40 mesh (0.2 g), Carbopack C 40/60 mesh (0.1 g) and Carbotrap X 20–40 mesh (0.1 g) adsorbents (Supelco). Even though the site usually experiences low ozone mix-



**Figure 1.** World map showing the location of the different sites. The names are colour-coded to show whether they have primarily biogenic influence (green) or a primarily anthropogenic influence (red). Source: outline world map, <http://www.outline-world-map.com/political-white-world-map-b6a>, last access: 1 September 2016.

ing ratios of 10–30 ppb (Noe et al., 2012), a catalytic Cu(II) ozone scrubbing system (Sun et al., 2012) was applied. Three constant-flow air sample pumps (1003-SKC, SKC Inc., Huston, TX, USA) and one multisample constant-flow air sample pump (224-PCXR8, SKC Inc., Huston, TX, USA) allowed four samples to be collected at the same time. Each sample took 30 min with a flow of  $200 \text{ mL min}^{-1}$  concentrating 6 L of ambient air onto the adsorbent. More information can be found elsewhere (Noe et al., 2012).

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

The oak observatory (O<sub>3</sub>HP, <https://o3hp.obs-hp.fr>) at the “Observatoire de Haute Provence” (OHP, <http://www.obs-hp.fr/welcome.shtml>) is located within a rural Mediterranean temperate forest in the French Mediterranean region, 60 km north of Marseille, the closest large city ( $43^{\circ}55'54.0'' \text{ N}$ ,  $5^{\circ}42'43.9'' \text{ E}$ ; Fig. 1). A 10 m mast was set up inside the oak forest with a canopy height of approximately 5 m. The O<sub>3</sub>HP site is dominated by *Quercus pubescens* Willd. (75 % of trees) and *Acer monspessulanum* L. (25 %) forming a sparse canopy, while *Cotinus coggygria* Scop. and other grass species constitute the understorey canopy. The climate at the site is typical Mediterranean, with dry and hot summers and humid and cool winters. More information about the site can be found elsewhere (Genard-Zielinski et al., 2015; Kalogridis et al., 2014).

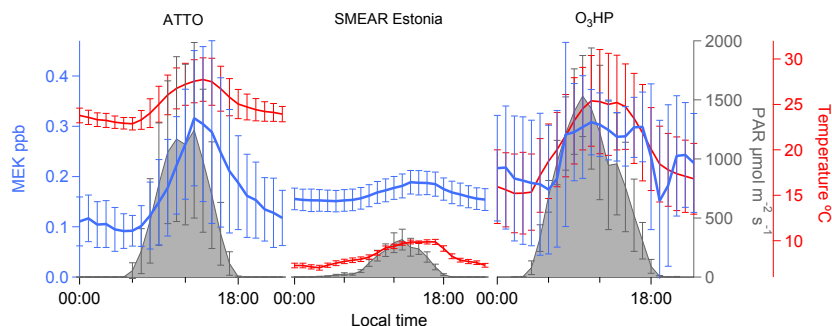
The measurements took place during 29 May–12 June 2014 as part of the CANOPÉE project (Biosphere-atmosphere exchange of organic compounds: impact of intra-canopy processes). Ambient measurements were carried out at 2 m (inside the canopy) on consecutive days in intervals of 5 min. The 9.5 mm OD Teflon inlet lines were

insulated and heated above ambient temperature and had no particle filter. The LOD and uncertainty of the PTR-MS were 0.11 ppb and 20 %, respectively. In addition, light non-methane hydrocarbons (from ethane to hexane) were measured with a GC-FID (Chromatotec, Saint-Antoine, France) in line with the PTR-MS as described in Zannoni et al. (2016).

#### 2.5 T2: mixed urban- and rainforest-influenced environment (Amazon, Brazil)

The T2 site is part of a set of experimental sites within the GoAmazon project to study the effect of the pollution plume from the city of Manaus on the otherwise pristine Amazonian atmosphere. The T2 site is located 8 km downwind, i.e. to the west, of Manaus ( $3^{\circ}8'21.12'' \text{ S}$ ,  $60^{\circ}7'53.52'' \text{ W}$ ; Fig. 1). Given its location, near Manaus and across the Rio Negro, air mass transport to the sampling site is strongly modulated by a river breeze, alternating between mostly biogenic conditions, resulting from the surrounding forest, and the city emissions. The climate is tropical and similar to that at the ATTO and ZF2 sites.

The measurements for this study took place between 15 February and 15 November 2014. They were carried out at 12 m above the laboratory container with 30 min cycles. The inlet line was made of insulated Teflon (9.5 mm OD) without a PTFE particle filter. The LOD and uncertainty of the PTR-MS were 0.02 ppb and  $\sim 30$  %, respectively.



**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 October 2014 for SMEAR Estonia at 16 m, and May and June 2014 for O<sub>3</sub>HP 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.

## 2.6 CYPHEX: mixed marine, rural environment influenced by aged air masses (Cyprus)

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

The measurements took place during July and August 2014 without a single rain event. Instruments were installed inside containers and connected to a stack inlet that reached up 5 m above the container roofs. Air was drawn through the 8 m stack inlet of 0.5 m with high flow rate (10 L min<sup>-1</sup>) to minimise wall losses. The subsampling inlet line was made of Teflon (13 mm OD), was insulated and heated to 35 °C, and had a PTFE inlet particle filter. The LOD and uncertainty of the PTR-MS were 0.02 ppb and 11 %, respectively.

## 3 Results

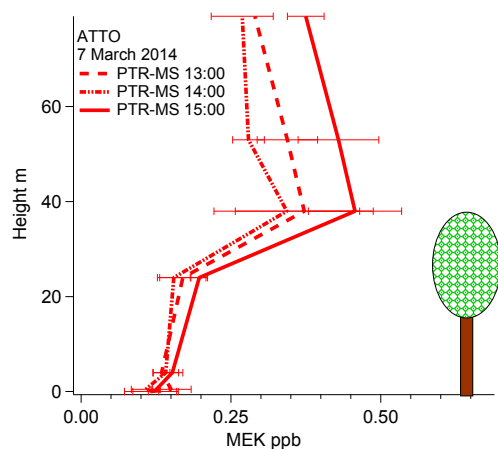
### 3.1 Sites dominated by biogenic emissions

All the pristine or remote sites studied were characterised by relatively low mixing ratios of nitrogen oxides (NO<sub>x</sub>) (< 3 ppb of nitrogen dioxide (NO<sub>2</sub>) for O<sub>3</sub>HP (Kalogridis et al., 2014; Zannoni et al., 2016), 0.2–0.8 ppb of NO<sub>x</sub> for SMEAR Estonia, and < 1 ppb NO<sub>x</sub> for the Amazon rainforest (Kuhn et al., 2010)). The diel cycles of MEK at these sites followed a comparable pattern (Fig. 2), where MEK mixing ratios were highest in the middle of the day, following the maxima of light and air temperature. The dominant source at these sites was considered to be biogenic. Mixing ratios of MEK correlated well with ambient temperature ( $r^2 = 0.57$  (ATTO),  $r^2 = 0.83$  (SMEAR),  $r^2 = 0.47$  (O<sub>3</sub>HP)), while it was less well correlated with photosynthetically active radiation (PAR) ( $r^2 = 0.23$  (ATTO),  $r^2 = 0.26$

(SMEAR),  $r^2 = 0.67$  (O<sub>3</sub>HP)). This suggests that ambient temperature predominantly influenced MEK emission rates from plants.

The vertical observations at ATTO revealed a strong diel variability in the magnitude and vertical distribution of MEK mixing ratios throughout the forest canopy and in the atmosphere above. Figure 3 shows an example of an hourly vertical profile of MEK for 1 day (7 March 2014) from 13:00 to 15:00 LT, from the ground to the atmosphere, suggesting that the canopy top is the major source of MEK at the site on such days. Similar concentration gradients were found for 83 % (for the afternoon hours) and 45 % (for the morning hours) of all days of measurements. In addition, MEK mixing ratios decreased significantly beneath the canopy towards the forest floor, possibly due to dry deposition or generally smaller vegetation emissions due to less light and temperature. However, a possible production from the ozonolysis of alkanes or bidirectional plant exchange cannot be ruled out. For a seasonal comparison, Yáñez-Serrano et al. (2015) reported 0.43 ppb of MEK for the dry season (September 2013) and 0.13 ppb of MEK for the wet season (February–March 2013) at 38 m. Curiously, at 24 m, MEK mixing ratios for the wet season were 0.38 ppb, very close to the measured values for this study. Possible differences in canopy structure temperature and solar radiation among years may be the cause for this discrepancy.

At the TT34 rainforest site, ecosystem-scale fluxes were directly calculated from the PTR-MS measurements using the method of virtual disjunct eddy covariance (vDEC) (Karl et al., 2001; Fig. 4). The fluxes averaged over the entire 11-month measurement period (covering parts of both the dry and the wet season) clearly demonstrate an emission of MEK by the rainforest during daytime with the highest emissions around noon, and no emissions during nighttime. In terms of seasonal variation, MEK mixing ratios were observed to be higher during the dry season (September–October 2013, ~ 0.6 ppb) and lower during the wet season (January–April, ~ 0.2 ppb) (data not shown).

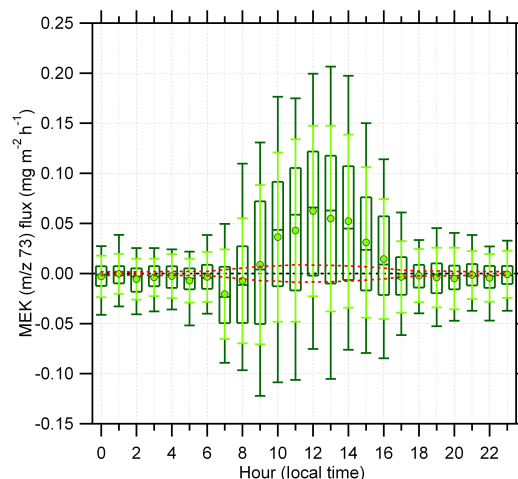


**Figure 3.** Hourly average vertical profiles of MEK mixing ratios at ATTO for 7 March 2014 for 13:00 LT (dashed lines), 14:00 LT (dotted and dashed lines) and 15:00 LT (thick lines). Error bars of vertical profiles are the standard deviations.

Online ambient mixing ratios of MEK, as measured by the PTR-MS in the hemiboreal forest at the SMEAR Estonia site during autumn 2012, were on average  $0.15 \pm 0.04$  ppb (range 0.09–0.25 ppb). These mixing ratios are almost a factor of 2 lower than ATTO and O<sub>3</sub>HP during daytime hours. This difference among boreal forests, with growing season ending in October, broadleaved tropical (ATTO) and temperate (O<sub>3</sub>HP) forests could be partly related to the temperature dependence of MEK emissions apparently common among all biogenic sites.

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

During the CANOPÉE campaign at the O<sub>3</sub>HP site, additional GC-FID samples were taken at 2 m, allowing measurements of several anthropogenic light hydrocarbons, including *n*-butane. This sampling was performed in parallel to the PTR-MS measurements. All samples contained *n*-butane, which typically has an anthropogenic origin with an average mixing ratio of  $0.071 \pm 0.09$  (much lower mixing ratios than MEK), indicating there is no significant source of *n*-butane nearby. Hence, MEK at the O<sub>3</sub>HP site could not be related to



**Figure 4.** Hourly average MEK fluxes at the TT34 tower for the period September 2013–July 2014. The light-green circles represent means and associated error bars are 1 standard deviation. The central line of the box plots (dark green) indicates the median, the bottom and top lines are 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).

the atmospheric oxidation of *n*-butane. Furthermore, the absence of a correlation with other anthropogenic tracers leads us to conclude that MEK at this site was predominantly of biogenic origin.

The measurements obtained by PTR-MS at the presented sites dominated by biogenic emissions were occasionally confirmed by GC-FID and GC-MS, which are compound-selective. At ATTO the same range of MEK mixing ratios for the same hour of the day and height for the GC-FID and the PTR-MS measurements was found, indicating that the PTR-MS signal was only or at least dominated by MEK. To identify sources, canopy measurements at SMEAR Estonia were complemented by emission measurements using cuvettes with GC-MS identification. Common hemiboreal forest species, such as *Quercus robur*, *Tilia cordata*, *Sorbus aucuparia*, *Betula pubescens* and *Picea abies*, were screened for VOC emissions. The highest emissions of MEK were found from *Tilia cordata* and *Picea abies* (Table 2). The data are consistent with those reported by Bourtsoukidis et al. (2014b), who measured an emission rate of MEK of  $2.6 \pm 2.2 \text{ ng g}_{(\text{dw needles})}^{-1} \text{ s}^{-1}$  from *Picea abies* using PTR-MS. The GC-MS technique obtained a very similar value of  $2.3 \text{ ng g}_{(\text{dw needles})}^{-1} \text{ s}^{-1}$ . MEK emissions from *Picea abies* were relatively small compared to other VOCs emitted by the same plant species such as total monoterpenes and acetone, which reached 93.2 and 27.6  $\text{ng g}_{(\text{dw needles})}^{-1} \text{ s}^{-1}$ , respectively (Bourtsoukidis et al., 2014b). In addition to plant sources, the emissions rates of MEK from leaf litter were quantified using a GC-MS. MEK litter emissions, with a monthly av-



**Table 2.** Emission rates of MEK for typical hemiboreal 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

erage of  $7 \mu\text{g m}^{-2} \text{h}^{-1}$ , were of comparable magnitude to the emissions rates of MEK from the screened hemiboreal forest tree species, including *Quercus robur* or *Sorbus aucuparia*, which emitted  $8\text{--}9 \mu\text{g m}^{-2} \text{h}^{-1}$  of MEK (Table 2).

### 3.2 Anthropogenically influenced sites

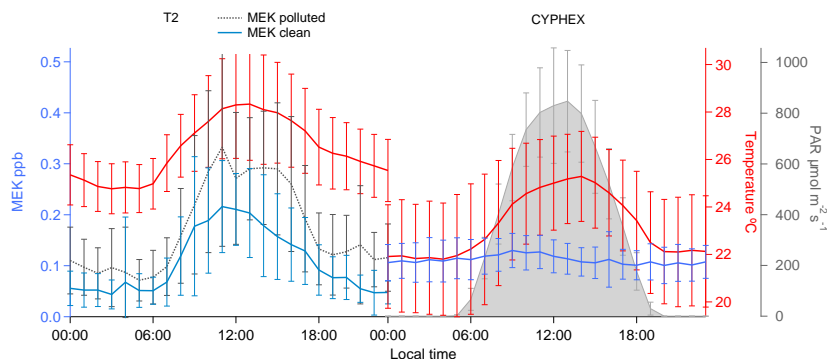
Anthropogenically influenced sites are characterised by air masses that have passed over polluted cities or industrialised regions. This air typically has elevated mixing ratios of  $\text{NO}_x$ , other products of fossil fuel combustion such as aromatic compounds, and carbon monoxide (CO), as well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

The T2 dataset was sorted for polluted periods (air masses loaded with CO, black carbon, high aerosol loading, aromatic compounds) and non-polluted periods. Periods with CO higher than 130 ppb during the tropical wet season and higher than 160 ppb during the dry season were considered polluted. As shown in Fig. 5, MEK mixing ratios strongly increase with pollution. The T2 site in Brazil is located on the bank of the Rio Negro and is affected by both the tropical rainforest (biogenic) and the megacity of Manaus (anthropogenic). The location of the T2 site downwind of Manaus and upwind of the rainforest minimises the biogenic influence. MEK mixing ratios were generally lower for the clean conditions at T2 than mixing ratios found at ATTO or TT34 (Figs. 2 and 5). Nevertheless, the mixing ratios of MEK during polluted conditions ( $0.7 \pm 0.33$  ppb during dry season at 13:00 LT) reached or even exceeded those at the other tropical rainforest sites ( $0.32 \pm 0.13$  ppb at 13:00 LT for ATTO and  $0.45 \pm 0.28$  ppb at TT34; Figs. 2 and 5). Presumably, anthropogenically affected air as transported across the Rio Negro from the city of Manaus ( $\sim 2$  million inhabitants; IBGE, 2014) generated a plume with a mixture of anthropogenic MEK directly emitted in Manaus or MEK formed by oxidation of, for example, *n*-butane during transport. The general trend observed in Fig. 6 is an increase in MEK mixing ratios when easterly winds came from Manaus (located to the east of T2). However, there were times when winds blew from the north, and incident air masses passed through large rainfor-

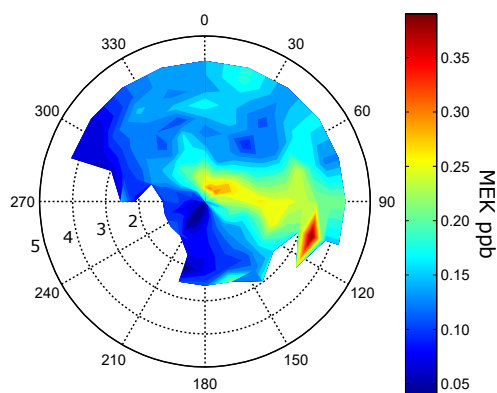
est areas, in which TT34 is included; these air masses then crossed the river and arrived at the site. During these times, when air masses were mostly dominated by biogenic emissions, MEK enhancement reached on average 0.2 ppb.

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

The CYPHEX campaign took place at Ineia, north-west Cyprus, at a location that has very little significant vegetation nearby. The air masses that pass through the site are either from western Europe, passing across France and Spain and then the Mediterranean Sea, or from south-eastern Europe (e.g. Turkey, Greece). During the CYPHEX campaign, the hourly median MEK mixing ratios did not show any distinct diel cycle or relations to temperature or net radiation (Fig. 5), strongly suggesting that no significant local sources were present. Furthermore, backward air mass trajectories, as calculated by the HYSPLIT model (NOAA Air Resources Laboratory, USA; Stein et al., 2015) (Fig. 8), can be used to delineate times when Cyprus was affected by easterly and westerly flow. These trajectories were started at 650 m height with the ensemble mode. The periods (east, west) were chosen on the basis of the FLEXPART model. Further information can be found in Derstroff et al. (2016). On average, easterly air masses contained  $0.13 \pm 0.03$  ppb, whereas westerly masses contained  $0.08 \pm 0.02$  ppb. This difference can be due to differences in source strength, to the greater duration of boundary layer transport from the west and hence marine uptake, or to photochemical loss during transport.



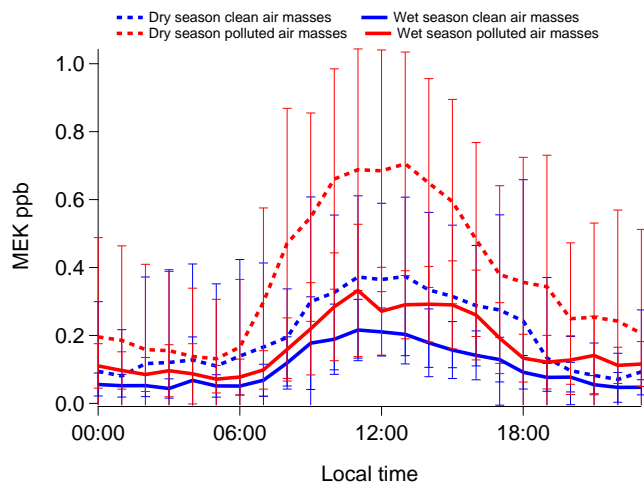
**Figure 5.** Hourly average diel cycles of MEK at the T2 (left) and CYPHEX (right) sites, for the period of measurements (wet season 2014 for T2 at 14 m, July and August 2014 for CYPHEX at 12 m). For T2 a separation between polluted (dotted black line) and clean (thick blue line) air masses was done. 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,  $1\text{--}5\text{ m s}^{-1}$ ) and wind speed (radius).

### 3.3 Compilation of measurement data

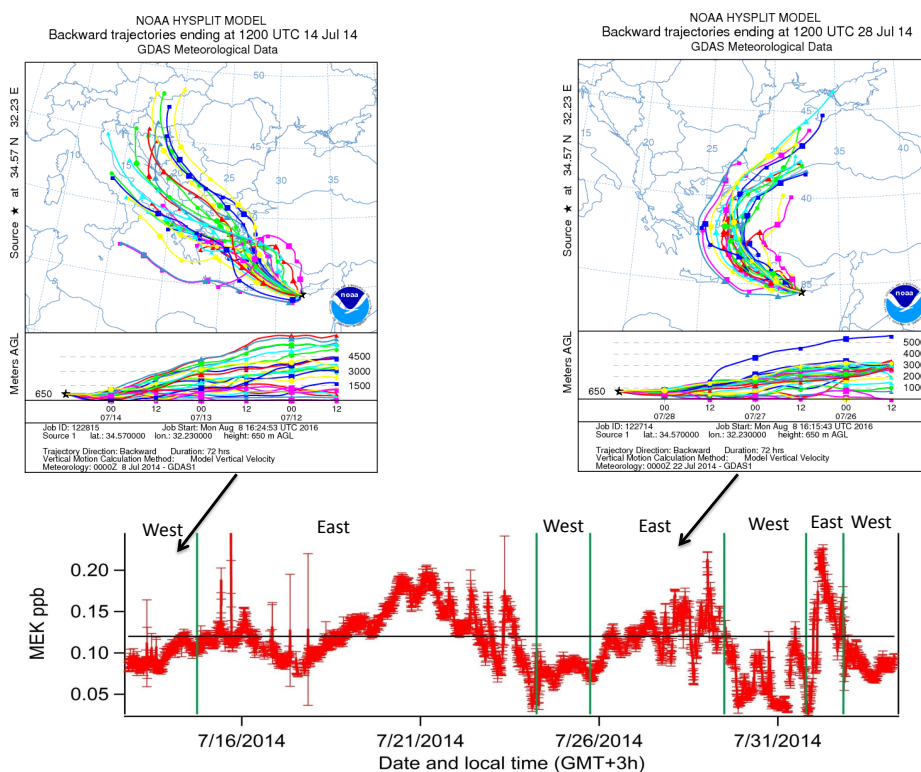
In order to investigate the origin and characteristics of MEK in the atmosphere, we calculated the correlation coefficient ( $r^2$ ) between the mixing ratios of MEK and other co-measured VOC species for each site (Table 3). This coefficient is the ratio of the variability in the MEK mixing ratios to the variability in the other VOC mixing ratios available for each site. The correlation between MEK and other VOC helps to identify possible similarities such as common sources, sinks, chemical mechanisms, or transport processes. However, this comparison does not necessarily claim links between the various compounds. Acetone, acetaldehyde, monoterpenes, isoprene, isoprene oxidation products and methanol are regarded as being mainly of biogenic origin especially in forested areas (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009). Nevertheless, acetone, acetaldehyde and methanol may have additional sources including direct and secondary anthropogenic emissions that cannot be neglected even at clean environments (Goldstein



**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.

and Schade, 2000; Yáñez-Serrano et al., 2015). Compounds such as benzene, toluene, xylene and acetonitrile are considered typical anthropogenic tracers (Andreae and Merlet, 2001; Finlayson-Pitts and Pitts Jr., 1997).

In general, biogenic sites, namely ATTO, SMEAR Estonia, and O<sub>3</sub>HP, showed relatively high correlations between MEK and almost all biogenic VOCs ( $r^2 > 0.5$ ). Exceptions appear in the  $r^2$  values for O<sub>3</sub>HP. For instance, the highest correlation coefficient ( $r^2$ ) was found for MEK and acetone at the SMEAR site ( $r^2 = 0.97$ ). A high correlation coefficient could indicate that the atmospheric processes governing acetone and MEK abundance are likely very similar (Zhou and Mopper, 1993). In SMEAR Estonia, overall high correlations were found between MEK and the oxygenated compounds, acetone, acetaldehyde and methanol, as



**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.

well as with monoterpenes and isoprene. At ATTO, correlations were only slightly lower. The correlation coefficient ( $r^2$ ) calculated for the  $O_3$ HP observations were generally lower than for ATTO and SMEAR Estonia, further influenced by the higher turbulent mixing due to sparser vegetation, leading to fastest transport to the atmosphere. Nevertheless, the good correlations of MEK with typical biogenically emitted compounds, such as isoprene, isoprene oxidation products, monoterpenes, methanol and acetone, corroborated the biogenic origin of MEK emissions at the biogenic sites.

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

## 4 Discussion

### 4.1 PTR-MS measurements

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

**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.

$r^2$		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	-

Methyl glyoxal is a likely contributor to the observed signal at the PTR-MS protonated mass  $m/z$  73, especially in areas where there are high levels of isoprene. It is formed following the oxidation of methyl vinyl ketone and methacrolein, which are both isoprene oxidation products (Calvert and Madronich, 1987; Lee et al., 2006). Supported by GC-FID measurements and relatively low isoprene levels during the wet season (Yáñez-Serrano et al., 2015), we can assume that the contribution of methyl glyoxal to this mass was insignificant at the rainforest sites (ATTO and TT34). Despite the high isoprene emissions at O<sub>3</sub>HP, the correlation between MEK and the isoprene oxidation products was low ( $r^2 = 0.41$ ), suggesting that methyl glyoxal did not significantly contribute to the signal at  $m/z$  73. During the CYPHEX campaign the PTR-ToF-MS could unambiguously distinguish between MEK and methyl glyoxal (at 73.0648 and 73.0284 amu, respectively).

Even though a contribution of butanal to  $m/z$  73 of up to 65 % (Lindinger et al., 1998) and 20 % (Williams et al., 2001) has been reported previously, most butanal fragments on  $m/z$  57 (Ionicon Analytic GmbH). Acrylic acid, a marine compound (Liu et al., 2016) that may interfere at  $m/z$  73, was probably not of relevance at sites under biogenic influence. However, in the case of anthropogenically influenced sites, such as T2, interferences may have been of relevance. Karl et al. (2007) and Ciccioli et al. (2014) measured tropical biomass burning emissions and found that  $m/z$  73 is comprised of 74 % MEK and 23 % 2-methyl propanal (73.1057 amu). Even though none of the sites presented in this study was severely influenced by biomass burning, we cannot completely rule out a possible direct emission of 2-methyl propanal by plants, which is of lower magnitude than from biomass burning (Hafner et al., 2013; Jardine et al., 2010; Karl et al., 2005a). Due to the standard operation conditions of the PTR-MS under our measurement conditions, we neglected water clusters as they are regarded to

be insignificant (McKinney et al., 2011; Yáñez-Serrano et al., 2015). To summarise these issues, we note that several studies have concluded  $m/z$  73 to originate from MEK only (Bourtsoukidis et al., 2014b; Crutzen et al., 2000; De Gouw et al., 1999, 2000; Holzinger et al., 2000; Karl et al., 2001, 2005a; Kim et al., 2015; Millet et al., 2015; Steeghs et al., 2004). Based on these considerations and the similarity of magnitudes measured by the PTR-MS as compared with the GC results, we assume  $m/z$  73 is representative of the atmospheric MEK present.

## 4.2 The biogenic MEK

The data obtained at the biologically influenced sites demonstrated that MEK was emitted by vegetation. This is clearly supported by the canopy-scale net flux observations of MEK at the TT34 rainforest site (Fig. 4) as well as the diel cycles of the mixing ratios at the other biogenically influenced sites (Fig. 2). Furthermore, the leaf-level cuvette measurements at SMEAR Estonia also corroborated the MEK emission by vegetation. In addition, a contribution by other biogenic sources such as dead and decaying plant matter was also observed at SMEAR Estonia to be of similar magnitude to boreal plant species emissions and indicative of a source from plant litter, in accordance with the results from Warneke et al. (1999) that measured MEK emission from the abiotic processes of plant decaying matter. This is not the case for the tropical sites where vertical profiles show that canopy emissions dominate.

High correlation coefficients suggested strong relations between the emission processes for MEK and other biogenic compounds (Table 3). A similar approach has been used previously by Goldstein and Schade (2000) to unveil the sources of acetone. Similarly, Davison et al. (2008) found a high correlation coefficient between MEK and acetone of  $r^2 = 0.87$  and a relatively poor correlation between MEK

and monoterpenes ( $r^2 = 0.54$ ). They surmised that good correlations indicated a common origin for biogenically emitted compounds. Furthermore, a resemblance of the pattern of acetone and MEK has been reported for the ATTO site before (Yáñez-Serrano et al., 2015). In our study, we found high correlation coefficients ( $r^2$ ) for MEK with acetone and MEK with temperature, and lower  $r^2$  for MEK and compounds such as isoprene and monoterpenes for all the biogenic sites (Table 3). This could indicate that MEK forest emissions are more related to processes resembling acetone emissions and temperature-dependent processes, rather than light- and temperature-dependent emission mechanisms, as for isoprene and monoterpenes (Jardine et al., 2015; Kesselmeier and Staudt, 1999).

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

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

Due to its relatively long atmospheric lifetime ( $\sim 5$  days for the reaction with OH; Grant et al., 2008), MEK is expected to accumulate in the atmosphere until removal. Hence, atmospheric mixing ratios can reflect seasonality and changes in dominating sources, affected by radiation, temperature and phenology, from more biogenic dominance during the wet season to transport phenomena and oxidation processes of primarily emitted compounds from regional biomass burning, as was seen in 2013 at the ATTO site

(Yáñez-Serrano et al., 2015). Moreover, a possible production from certain terpenes through ozonolysis cannot be excluded (Holzinger et al., 2005). Additionally, the canopy structure seems to be important for air mixing and transport, as seen for the O<sub>3</sub>HP site with an apparently faster mixing due to sparser vegetation and consequent dampening of the amplitude of the diel cycle. Furthermore, due to its oxygenated nature, partitioning to and from aqueous surfaces is likely, including deposition and surface reactions. Its high water solubility might allow dissolution within leaf water (Sander, 2015), triggering bidirectional exchange of MEK (Karl et al., 2005b; McKinney et al., 2011; Niinemets et al., 2014). Due to its high solubility in water and its relatively long lifetime, MEK could potentially influence gas–aqueous reactions on aerosol surfaces (Nozière, 2005). This has been shown indirectly by the production of methyl glyoxal after its oxidation by OH, having implications for the formation of organics in the aerosol aqueous phase (Rodigast et al., 2016).

### 4.3 The anthropogenic MEK

A clear difference could be observed between the anthropogenic and biogenic influenced sites presented in this study. The T2 site represented a site with mixed influence by urban area and tropical rainforest. Affected by anthropogenic and biogenic sources, ambient mixing ratios of MEK were higher than at the pristine ATTO rainforest site. Polluted episodes (from the Manaus plume) with an increase in 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 (Fig. 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 which was 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 long distances (10 days) is lost by photochemical aging or

**Table 4.** 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 Sea	Cruise data, total average	10 m	October 1988
Ho et al. (2002)	0.14	Hong Kong urban centre	Annual average	6 m	April 2000–April 2001
Cecinato et al. (2002)	0.15	Algerian rural residential site	Daytime average	Not specified	January 2001
Cecinato et al. (2002)	0.23	Algerian rural residential site	Daytime average	Not specified	August 2001
Feng et al. (2004)	2.11	Chinese urban site	Evening time	Not specified	August–September 2002
Hellén 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	Not specified	0–2 km	February–April 2001
Legreid et al. (2007)	0.2 <sup>a</sup>	Swiss urban site	Annual average	8 m	Throughout 2005
Davison et al. (2008)	0.8 <sup>b</sup>	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. (2009b)	0.13	USA mixed rural site	Interannual median from 2005 to 2008	12 m	From 2005 to 2008
Kim et al. (2015)	~ 4	South Korean 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	Hemiboreal forest site (SMEAR Estonia)	Daytime average	16 m	October 2012
This study	0.30	French Mediterranean forest (O <sub>3</sub> 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

<sup>a</sup> Average from different seasons reported. <sup>b</sup> Average of different conditions cutting, a day after cutting and removing hay and a day after removing hay.

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. To summarise, Table 4 aims to provide a numerical comparison of MEK mixing ratios reported around the globe. While MEK mixing ratios in our study are relatively constant, MEK has been measured in many different ecosystems ranging from 0.073 ppb to 4 ppb. Therefore, it is important to consider the variability in this compound as MEK can lead to PAN and ozone formation in the atmosphere (Pinho et al., 2005). Photochemical odd-hydrogen production in the upper troposphere (Atkinson, 2000; Baeza Romero et al., 2005; De Gouw et al., 1999) can further enhance the MEK ozone forming potential (Folkens et al., 1998; Prather and Jacob, 1997). Of the widely used atmospheric chemistry models, only GEOS-Chem explicitly computes MEK but only with regard to anthropogenic origin. On the basis of the data presented here from forest sites, it is necessary for atmospheric chemistry models to also include biogenic MEK emissions to better estimate its effects on the environment. Sites under biogenic influence showed marked diel variability, matching biogenic VOC emissions and temperature. Structural forest features seem to affect turbulent mixing and diluting of trace gases like MEK, as in the case of O<sub>3</sub>HP with patchy vegetation. MEK seemed to be produced in plants in a similar fashion to acetone, likely released during mechanical stress. Possible pathways for productions in plants are oxidation of fatty acids, cyanogenesis, production from pyruvic acid leading to acetyl-CoA, and light-dependent and independent processes that can be associated with the decarboxylation of acetoacetate occurring in microorganisms and animals.

This study presents the first compilation and comparison of ambient measurements of MEK at different sites. MEK patterns and mixing ratios differ around the globe depending on sources and transport. Vegetation and litter have been identified as sources of MEK and magnitude of sources varied among the tropical rainforest, the Mediterranean temperate forest and the hemiboreal forest following a likely temperature dependence. However, via different filtering methodologies (CO filtering and backward trajectories), the anthropogenic input from polluted regions, such as the mixed urban and tropical rainforest and mixed marine environment, is often found to be the dominant contribution.

## 6 Data availability

Even though the data are still not available in any public repository, as the authors are still working on other parts of the data collected during the campaigns, the data are available upon request from the main author.

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