

Reply to reviewer 1:

All authors acknowledge the work and time provided by this reviewer as all comments truly made the manuscript more consistent and clearer.

1. Comment: Introduction, line 71/72: I think it is unfair to characterize all biomass burning as anthropogenic since a substantial fraction of it is not man-made; naturally occurring fires can be caused by triggers such as lightning.

Response: This is true and we will change it accordingly.

Change in manuscript: Line 71-72: ...“It is also emitted directly by several anthropogenic sources, including man-made biomass burning (Andreae and Merlet, 2001)...”.

2. Comment: line 93: I fail to see how MEK can be produced by cis-2-butene or cis-2-pentene. I also did not find that in the cited literature. Please elaborate or drop.

Response: This is true and we have eliminated cis-2- butane/pentene from the text.

3. Comment: line 121: MEK is of rather low toxicity; it is widely used as a solvent in the US, both in the chemical industry, and commercially. It is known as “paint-thinner”, and available over the counter in home improvement stores such as “Lowes”. Aside from its contents in paints and varnishes, it is also used in other household products, such as glues. As the result of such uses, its major fate is evaporation to the atmosphere. Here are some useful sources: <https://www.americanchemistry.com/ProductsTechnology/Ketones/Methyl-EthylKetone-MEK.html>, <https://www3.epa.gov/ttn/atw/hlthef/methylet.html> MEK manufacturing and use have been increasing in the last ten years, such that emissions very likely have as well.

Response: We have taken into consideration this information and have expanded the text with additional information.

Change in the manuscript: Line 120: “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 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.”

4. Comment: Results section, line 262f.: While the interpretation that higher MEK mixing ratios near the canopy stem from direct canopy emissions is attractive, a chemical production through fast chemical reactions of emitted terpenes with ozone cannot strictly be excluded. A similar situation was presented by Holzinger et al. (ACP 5, 67-75, 2005). While it would be unusual that MEK, not acetone, is produced from certain terpene structures, the possibility cannot be excluded using the evidence presented. Of course, this origin discussion makes no difference with respect to MEK entering the lower atmosphere. With respect to deposition (and mixing ratios where given), the authors may want to cite Karl et al. (ACP 5, 3015-3031, 2005) and Schade et al. (Biogeochemistry, 106, 337-355, 2011).

Response: Even though at ATTO there are low ozone values, the possibility mentioned by the reviewer, although unknown, cannot be totally excluded. Thus, we have decided to incorporate it to the text. In addition, we have included the references mentioned in the text when considering bidirectional VOC exchange and interpretation of temperature to extrapolate MEK as well as acetone.

Change in the manuscript: Line 267: “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.”; and line 488:

Moreover, a possible production from certain terpenes through ozonolysis cannot be excluded (Holzinger et al., 2005)."

5. Comment: line 356: the HYSPLIT citation is incorrect; it should be NOAA not NASA. In fact, the HYSPLIT webpages give concrete instructions on how to cite the model use, which should obviously be followed. The model's use in this case also appears incomplete: several back trajectories for each case should be shown if the preferred ensemble is not used, trajectory heights need to be given, and weather maps should be consulted as a sanity check. This is a major shortcoming in the manuscript.

Response: We acknowledge the mistake in the citation and we have modified it in the text. Furthermore, we now provide the trajectory heights and the ensemble mode used. Weather maps have also been checked. We have also changed Figure 8 to add more information about the settings.

Change in manuscript: Line 355: "Furthermore, backward air mass trajectories, as calculated by the HYSPLIT model (NOAA Air Resources Laboratory, USA, Stein et al., 2015) (Figure 8), can be used to delineate times when Cyprus was affected by easterly and westerly flow."; in Line 589: "For CYPHEX: The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>) used in this publication."; and line 357: "These trajectories were modelled starting 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., in preparation."

6. Comment: line 361f., section 3.3: This is a poor analysis. It should either be dropped or expanded properly. Simple correlations are not always meaningful, especially in the given setting. Instead, a multi-variate analysis such as a factor analysis (see citation used in line 449) could be

performed to evaluate sources, but even in that case, their interpretation may be difficult unless well-defined tracers are available and separated into different factors.

In the author's case, the interpretation of acetone, acetaldehyde, and methanol as "biogenic" is questionable since all three compounds, especially acetone and acetaldehyde, have substantial anthropogenic sources. In the case of acetone, its sources are likely very similar to MEK, which makes the exploitation of the MEK to acetone correlation a potentially much more useful variable to explore. The authors barely touch on that in line 375 and 384/385.

Response: We agree with the reviewer that further statistical analysis would be more enriching, but we also agree with the difficulty of doing so with the variable data sets available. However, we insist on keeping the correlations as the comparison of various compounds to MEK seems interesting to us. However, we have clarified in the text that this comparison does not necessarily claim links between the various compounds. A comment on acetone and MEK similarity was also added.

Change in the manuscript: Line 365 "...site. Using this method, we compare similar compounds to MEK, as this information could indicate some similarities, but this comparison does not necessarily claim links between the various compounds. Acetone, acetaldehyde, monoterpenes, isoprene, isoprene oxidation products and methanol are regarded as being of biogenic origin especially in forested areas (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009). Nevertheless, acetone, acetaldehyde and methanol may have additional sources."; and in line 375: "Since sources of both compounds are likely very similar, a high coefficient could indicate similarity in the processes involved in acetone and MEK emission and abundance (Zhou and Mopper, 1993)."

7. Comment: line 463: "mechanical stress" is undefined. In the particular use here it actually means cutting", i.e. physically injuring, the plant, which, in nature, is either due to herbivores (common) or infrequent events such as strong storms or heavy snow/frost load (less common). In this respect, I question the formulation of "close agreement" (line 479), since branches or

leaves were not cut to enable “the installation of the branch enclosure”, or were they? (see also line 546) anthropogenically cause “wounding” (e.g. deGouw et al. papers) is typically related to crop harvesting.

Response: We agree with the reviewer that such example given in line 479 was not adequate, as the branches were not cut. In this sense, we have decided to remove that part.

8. Comment: line 515: lowest MEK abundance at CYPHEX? According to your Figure 5, MEK in “clean” air masses was lower at the T2 site at night. Did you mean averages or medians were lowest at CYPHEX? Also, revise the following section (lines 517f.) after reviewing air mass origins and “correlations”.

Response: Yes, we meant lowest averages and have modified in text. We did the same for the correlations.

Change in the manuscript: Line 515: “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.”

9. Comment: line 528: What are “night-time anthropogenic activities”? The Guha paper does not list those, but rather links MEK abundances dominantly to soil and agricultural sources.

Response: We agree with the reviewer that the Guha paper (10.5194/acp-15-12043-2015) links MEK abundances dominantly to soil and agricultural sources, so we have decided to remove such reference.

10. Comment: line 538: It seems the Le Calvé reference is outdated, see above.

Response: We agree and we have excluded the comment about human exposure.

129

130 **11. Comment:** It would be useful to present a comparison of the MEK data listed in this
131 manuscript and published measurements, such as in Jordan et al and McKinney et al, which the
132 authors already cite.

133 **Response:** We agree with the comment of the reviewer and we will add a table like sug-
134 gested in the text.

135 **Change in the manuscript:** Line 533: “Summarizing, Table 4 aims to provide a numerical
136 comparison of MEK mixing ratios reported around the globe. While MEK mixing ratios in our
137 study are relatively constant, MEK has been measured in many different ecosystems ranging from
138 0.073 ppb to up to 4 ppb. Therefore it is important to account for the variability of this compound.”

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140

141 **Reply to reviewer 2:**

142 We acknowledge the work and time provided by this reviewer as all comments truly made
143 the manuscript more consistent and clearer.

144

145 **1. Comment:** It would be interesting to know detection limits and uncertainties for the
146 different instruments.

147 **Response:** We have added a bracket with LOD and uncertainty next to each site descrip-
148 tion when available.

149

150 **2. Comment:** Could you add some comments on seasonal variation of MEK? For example,
151 you mention on lines 275-279 and in discussion that MEK levels were significantly lower at
152 SMEAR-Estonia, but there you were measuring only in October, which is clearly not a high growing

season anymore at this site. How was the seasonal variation at the sites where you were measuring for longer period?

Response: Most of the sites only have measurements for the periods stated in the manuscript. However, there are some seasonal measurements for ATTO, TT34 and T2. For ATTO there is a paper published commenting on MEK seasonal variation which we have added to the text (Yañez Serrano et al., 2015). For TT34 we were able to have a look at the seasonal change in the mixing ratio raw data to report an approximate seasonal variation. For T2, we already comment about the possible difference in source and sink among seasons when commenting figure 7.

Change in manuscript: Line 269: (Holzinger et al., 2005; Karl et al., 2005a). For a seasonal analysis, Yañez-Serrano et al., 2015 reported 0.43 ppb of MEK for the dry season and 0.13 ppb of MEK for the wet season at 38m. Curiously, at 24m, MEK mixing ratios for the wet season were 0.38 ppb, very close to the measured values for this study. Possible differences in temperature and solar radiation among years may be the cause for this variation.”; line 274: “In terms of seasonal variation, MEK mixing ratios were observed to be higher during the dry season (~0.6 ppb) and lower during the wet season (~0.2 ppb) (data not shown).”; and line 278: “This difference among boreal forests, with growing season ending in October, and broad-leafed tropical (ATTO) and temperate (O₃HP) forests could be partly related to the temperature dependence of MEK emissions apparently common among all biogenic sites.”

3. Comment: Lines 293-297: You state that MEK did not show any covariance with butane and therefore it cannot be related to butane. However, I was wondering, if there is a constant local source or anthropogenic butane emissions are long range transported, then MEK would be produced during the day and lost on surfaces during the night while at the same time butane is not going on surfaces. Then you would not detect any covariance. Maybe you could mention the mixing ratio of butane and it is so low that butane cannot be the main source.

Response: We acknowledge that interesting point raised by the referee and changed the text accordingly as follows below.

Change in the manuscript: Line 292: “All samples contained n-butane, which was of anthropogenic origin with an average mixing ratio of 0.071 ± 0.09 (much lower mixing ratios than MEK), indicating there is no significant source of n-butane nearby.”

4. Comment: Line 340: change 200 ppt to 0.2 ppb

Response: We have changed it to 0.2 ppb.

5. Comment: Lines 365-367: Acetone is regarded as biogenic origin. It has also direct anthropogenic sources and it is produced from the reactions of anthropogenic VOCs also.

Response: We have modified the text to account for extra sources.

Change in the manuscript: Line 365 “...site. Using this method, we compare similar compounds to MEK, as this information could indicate some similarities, but this comparison does not necessarily claim links between the various compounds. Acetone, acetaldehyde, monoterpenes, isoprene, isoprene oxidation products and methanol are regarded as being of biogenic origin particularly in forested areas (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009). Nevertheless, acetone, acetaldehyde and methanol may have additional sources.”

6. Comment: Lines 418-420: Something missing from this sentence?

Response: We do not think there is anything missing from this sentence, we are reporting that butanal can fragment on m/z 73, thus influencing the MEK signal, but the manufacturer of the machine has reported to most account for m/z 57.

7. Comment: Lines 516-518: Is determination coefficient same as correlation coefficient?

Response: The determination coefficient is the same as the correlation coefficient r^2 . We just wanted to make sure it was not confused with the pearson coefficient r . For consistency, we will modify all determination coefficient with correlation coefficient (r^2).

8. Comment: Figure 6. Use ppb as a unit also here.

Response: We have modified the figure to ppb.

9. Comment: Table 3: No mean noon mixing ratios are shown and colour codes for the sites are missing.

Response: This is right; we have removed it from table label.

Reply to reviewer 2:

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1. Comment: It would be interesting to know detection limits and uncertainties for the different instruments.

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

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Abstract

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

Keywords: Methyl ethyl ketone, plant emission, anthropogenic sources, air quality, rainforest, boreal forests.

1. Introduction

Methyl ethyl ketone (C_4H_8O ; MEK, also known as 2-butanone, butanone, methyl acetone, butan-2-one, methylpropanone, ethylmethylketone and methylacetone) 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

Mannozzi, 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_x) regime (Ciccioli and Mannozzi, 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 characterized sources of MEK to the atmosphere. Terrestrial vegetation (Bracho-Nunez et al., 2013; Brilli 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 man-made 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 (Brilli 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 understood. 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 does not only enter the atmosphere via direct emissions, but also results from the atmospheric photooxidation of VOCs such as *n*-butane, 2-butanol, ~~*cis*-2-butene/pentene~~, 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, α - and β -pinene and methyl butenol oxidation (Rollins et al., 2009; Singh et al., 2004).

In the atmosphere MEK reacts mainly with OH ($k_{OH}=1.15\times10^{-12}$ cm³ s⁻¹) (Chew and Atkinson, 1996), while reactions with O₃ and NO₃ 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 1.6×10^6 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_x, MEK can lead to peroxyacetyl nitrate (PAN) and ozone formation (Grosjean et al., 2002; Pinho et al., 2005). In the upper troposphere, MEK photolyzes 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⁻¹ globally (Andreae and Merlet, 2001 and unpublished updates; Schauer et al., 2001). Furthermore, about

9 Tg a⁻¹ of other C₄ compounds are 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⁻¹ of dry biomass (compared to an emission rate of ~260 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 characterized, vehicular emissions, food cooking, industrial activities, cigarette smoke and other anthropogenic sources have not been characterized. 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 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 by proton transfer reaction – mass spectrometry (PTR-MS) and partly complemented by gas chromatography - flame ionization detector (GC-FID) and gas chromatography - mass spectrometry (GC-MS) analytical techniques (Figure 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 PTR-Time-of-Flight-MS (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 O₃HP; 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 O₃HP 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 (Figure 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 ≥ 10 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 minutes 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 of the PTR-MS were 0.05 ppb and 34% respectively.

Additionally, ambient samples for off-line 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 (Carbograph 1, Carbograph V 130 mg of Carbograph 1 (90 m² g⁻¹) followed by 130 mg of Carbograph 5 (560 m² 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 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 Auto-system 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 Biologica 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 (Figure 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).

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 was further averaged to give 30-minute 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-minute concentrations measurements were 0.18 ppb and 6 % respectively.

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

The Station for Measuring Ecosystem-Atmosphere Relations (SMEAR-Estonia) site is located in the Järvselja Experimental forest station in Tartumaa, SE Estonia (58°16'N 27°16'E), within a remote hemi-boreal zone, far from major anthropogenic disturbances (Noe et al., 2011, Figure 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 hemi-boreal 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 seconds. 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, off-line measurements with a GC-MS were carried out for periods of three days each in June and July 2012, with samples taken every 4 hours at two heights (2 m 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), Carboxen 1000/60 mesh (0.1 g) and Carbotrap X 20-40 mesh (0.1 g) adsorbents (Supelco). Even though the site usually experiences low ozone mixing 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 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, O₃HP: rural Mediterranean temperate forest (Provence, France)

The oak observatory (O₃HP, <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°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 height of approximately 5 m. The O₃HP 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 CANOPEE 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 minutes. 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°8'21.12" S, 60°7'53.52" W, Figure 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 minute cycles. The inlet line was made of insulated Teflon (9.5 mm OD) without PFTE particle filter. The LOD and uncertainty of the PTR-MS were 0.02 ppb and ~30% respectively.

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) (Figure 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 (105 l min^{-1}) to minimize 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 characterized by relatively low mixing ratios of nitrogen oxides (NO_x) (< 3 ppb of nitrogen dioxide (NO_2) for O₃HP (Kalogridis et al., 2014; Zannoni et al., 2016), 0.2-0.8 ppb of NO_x for SMEAR-Estonia, and <1 ppb NO_x for the Amazon rainforest (Kuhn et al., 2010)). The diel cycles of MEK at these sites followed a comparable pattern (Figure 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), $r^2=0.47$ (O₃HP)), while it was less well correlated with photosynthetically active radiation (PAR) ($r^2=0.23$ (ATTO), $r^2=0.26$ (SMEAR), $r^2=0.67$ (O₃HP)). This suggests that ambient temperature predominantly influenced MEK emission rates from plants.

The vertical observations at ATTO revealed a strong diel variability of the magnitude and vertical distribution of MEK mixing ratios throughout the forest canopy and in the atmosphere above. Figure 3 shows an example of one day (7th of March 2014) hourly vertical profile of MEK from 13:00-15:00 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, Yañez-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 38m. Curiously, at 24m, 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., 2001b; Figure 4). The fluxes averaged over the entire 11-month measurement period (covering both parts of dry and 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).

Online ambient mixing ratios of MEK, as measured by the PTR-MS in the hemi-boreal forest at the SMEAR-Estonia site during autumn 2012, were on average 0.15 ± 0.04 ppb (range 0.09 - 0.25 ppb). These mixing ratios are almost a factor of two lower than ATTO and O₃HP during daytime hours. This difference among boreal forests, with growing season ending in October, broad-leafed tropical (ATTO) and temperate (O₃HP) 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 O₃HP differs significantly from the tropical rainforest (ATTO, TT34) or the hemi-boreal forest (SMEAR-Estonia, Figure 1). The trees at O₃HP 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 Figure 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 hardly be explained by gas-phase chemistry or the reduced nocturnal boundary layer height.

During the CANOPEE campaign at the O₃HP 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±0.09 (much lower mixing ratios than MEK), indicating there is no significant source of n-butane nearby. Hence, MEK at the O₃HP site could not be related to the atmospheric oxidation of n-butane. Furthermore, the absence of a correlation with other anthropogenic tracers lets us 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 hemi-boreal 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 $2.6 \pm 2.2 \text{ ng g(dw needle)}^{-1} \text{ s}^{-1}$ from *Picea abies* using PTR-MS. The GC-MS technique obtained a very similar value of $2.3 \text{ ng g(dw needle)}^{-1} \text{ s}^{-1}$. 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 $27.6 \text{ ng g(dw needle)}^{-1} \text{ s}^{-1}$, 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 average of $7 \mu\text{g m}^{-2} \text{ h}^{-1}$, were of comparable magnitude to the emissions rates of MEK from the screened hemi-boreal forest tree species, including *Quercus robur* or *Sorbus aucuparia*, which emitted 8 - 9 $\mu\text{g m}^{-2} \text{ h}^{-1}$ of MEK (Table 2).

3.2. Anthropogenically influenced sites

Anthropogenically influenced sites are characterized by air masses that have passed over polluted cities or industrialised regions. This air typically has elevated mixing ratios of NO_x, other products of fossil fuel combustion such as aromatic compounds, carbon monoxide (CO), and higher

aerosol loading. Regional biomass burning plumes can also be a source of anthropogenic input to air masses and are here considered as anthropogenic.

The T2 data set 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 Figure 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 minimizes the biogenic influence. MEK mixing ratios were generally lower for the clean conditions at T2 than mixing ratios found at ATTO or TT34 (Figure 2 and 5). Nevertheless, the mixing ratios of MEK during polluted conditions (0.7 ± 0.33 ppb during dry season at 13:00 LT) reached or even exceeded those at the other tropical rainforest sites (0.32 ± 0.13 ppb at 13:00 LT for ATTO and 0.45 ± 0.28 ppb at TT34; Figure 2 and 5). Presumably, anthropogenically affected air as transported across the Rio Negro from the city of Manaus (~2 million inhabitants; IBGE, 2014) generated a plume with a mixture of anthropogenic MEK directly emitted in Manaus or MEK formed by oxidation of e.g. *n*-butane during transport. The general trend observed in Figure 6 is an increase of 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 rainforest 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 (Figure 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 of 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 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 (Figure 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) (Figure 8), can be used to delineate times when Cyprus was affected by easterly and westerly flow. These trajectories were started modelled starting 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., in preparation a.d.). On average, easterly air masses contained 0.13 ± 0.03 ppb whereas westerly masses contained 0.08 ± 0.02 ppb. This difference can be due to differences in source strength, the greater duration of boundary layer transport from the west and hence marine uptake, or to photochemical loss during transport.

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 of the MEK mixing ratios over the variability of 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 of biogenic origin especially in forested areas (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009). Compounds such as benzene, toluene, xylene and acetonitrile are considered as typical anthropogenic tracers (Andreae and Merlet, 2001; Finlayson-Pitts et al., 1997).

The correlation coefficients (r^2) between MEK and other VOCs may indicate similarities of production and consumption pathways. In general, biogenic sites, namely ATTO, SMEAR-Estonia, and O₃HP, showed relatively high correlations between MEK and almost all biogenic VOCs ($r^2 > 0.5$). Exceptions are the r^2 of isoprene, monoterpene and isoprene oxidation products for O₃HP.

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 well as with monoterpenes and isoprene. At ATTO, correlations were only slightly lower. The correlation coefficient (r^2) calculated for the O₃HP 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) for MEK and acetone was high, 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 et al., 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.

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 O₃HP, 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 amu 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). Summarizing 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., 2001b, 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 (Figure 4) as well as the diel cycles of the mixing ratios at the other biogenically influenced sites (Figure 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 indicating 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), oxidation of fatty acids leading to ketone emissions (Niinemets et al., 2014), from pyruvic acid leading to acetyl-CoA (Kesselmeier and Staudt, 1999), or produced from uncharacterized 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 (~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 it has been 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 O₃HP 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., 2015).

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

We regarded CYPHEX as an anthropogenically influenced site with weak or no apparent direct sources, but affected by anthropogenic air masses after long range transport over marine areas. Losses by transport over the sea and chemical decomposition led to the lowest averaged MEK mixing ratios of all compared sites. Correlation coefficients (r^2) of MEK with the biogenic tracers were relatively poor for T2 and CYPHEX. However, correlations were also poor for the anthropogenic tracers, although slightly better than at the biogenic sites. MEK showed highest correlation with acetone, indicating similar sources and fate in air mixing and chemistry processes. MEK transported over a long distances (10 days) is lost by photochemical aging or deposition as

evidenced by the lowest values reported from CYPHEX. This is despite known secondary photochemical sources, i.e. *n*-butane oxidation (Katzenstein et al., 2003; Kwok et al., 1996). Interestingly, even under polluted conditions, MEK did not correlate with aromatic compounds, except during CYPHEX, although this correlation deteriorated in the more aged westerly air masses. This can only be understood as a result of a very complex mixture of anthropogenic sources of MEK which vary from direct emission by industry (Legreid et al., 2007), gasoline combustion (Verschueren, 1983), biomass burning (Andreae and Merlet, 2001) ~~night-time anthropogenic activities~~—and vehicular emissions (Brito et al., 2015). Furthermore, chemical processing during transport may contribute, such as oxidation of *n*-butane, however, the longer transport times during CYPHEX from the west corresponded to lower values.

5. Remarks and conclusions

The comparison of MEK mixing ratios in different parts of the world is necessary in order to understand how this ubiquitous compound occurs and behaves in the atmosphere. Summarizing, 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 up to 4 ppb. Therefore, it is important to consider the variability of this compound as: MEK can lead to PAN and ozone formation in the atmosphere (Pinho et al., 2005). P-and photochemical odd-hydrogen production in the upper troposphere (Atkinson, 2000; Baeza Romero et al., 2005; De Gouw et al., 1999) ~~which~~ can further enhance the MEK ozone forming potential (Folkins et al., 1998; Prather and Jacob, 1997). ~~Furthermore, as higher mixing ratios of MEK have been found under polluted conditions, human exposure to this toxic compound should be considered (Le Calvé, et al., 1998).~~ 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 O₃HP 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, 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 hemi boreal 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 environmentis, is often found to be the dominant contribution.

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8. Tables

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

| Site | Characteristics | Canopy height | Time of Sampling | Technique | Type of measurement | Measurement heights |
|----------------------------|---|----------------------------|---------------------------------|---|--|--|
| ATTO (Brazil) | Pristine tropical rainforest | 35 m dense veg. | Feb/Mar 2014 | PTR-MS GC-FID (samples for off-line analysis, collected volume=3.34 L) | Ambient | 0.05, 0.5, 4, 24, 38, 53, 79 m 24 m |
| TT34 (Brazil) | Remote tropical rainforest | 30 m dense veg. | Sep 2013 – Jul 2014 | PTR-MS | Ambient, including canopy-scale fluxes | 41 m |
| SMEAR (Estonia) | Remote hemi-boreal forest | 16-20 m dense veg. | Jun, Jul, Oct 2012 Oct 2012 | GC-MS (samples for off-line analysis, collected volume=6 L) PTR-MS | Ambient, plant, soil enclosure Ambient, plant enclosure | 2, 20 m 16 m |
| O ₃ HP (France) | Rural temperate forest | 5 m sparse veg. | May-Jun 2014 | PTR-MS | Ambient | 2 m |
| T2 (Brazil) | Mixed urban and rainforest influenced environment | Influence from veg. nearby | Feb-April 2014 July-Oct 2014 | PTR-MS | Ambient | 14 m |
| CYPHEX (Cyprus) | Mixed marine, rural environment influenced by aged air masses | None, on top of a hill | Jul-Aug 2014 | PTR-TOF-MS | Ambient | 8 m |

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

| Plant species and soil cuvettes | Mean $\mu\text{g m}^{-2} \text{h}^{-1}$ | 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: 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 |
| Biogenic sites | TT34 | - | - | - | - | - | - | - | - | - | - |
| | SMEAR | 0.97 | 0.89 | 0.72 | - | 0.90 | 0.84 | - | - | - | - |
| | ATTO | 0.89 | 0.62 | 0.75 | 0.75 | 0.51 | 0.77 | 0.49 | 0.07 | 0.27 | 0.04 |
| | O₃PH | 0.61 | 0.62 | 0.12 | 0.41 | 0.57 | 0.14 | 0.19 | 0.03 | 0.15 | 0.00 |
| Anthropogenic sites | T2 | 0.64 | 0.21 | - | 0.41 | 0.27 | 0.06 | 0.27 | 0.11 | 0.07 | 0.27 |
| | CYPHEX | 0.45 | 0.42 | 0.07 | 0.10 | 0.25 | 0.08 | 0.00 | 0.58 | 0.09 | - |

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

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

| | | | | | |
|--|-----------------------|---|---|----------------------|---|
| Grant et al., 2008 | ~ 0.5 | Senegalese rural site | Daytime average | 6 m | September 2006 |
| Jordan et al., 2009 | 0.13 | USA mixed rural site | Interannual median from 2005-2008 | 12 m | From 2005 to 2008 |
| Kim et al., 2015 | ~4 | South Korea semi rural site | Diel average | 15 m | June 2013 |
| Yáñez-Serrano et al., 2015 | 0.43 | Brazilian tropical rainforest site (ATTO) | Daytime average | 38 m | September 2013 |
| Yáñez-Serrano et al., 2015 | 0.13 | Brazilian tropical rainforest site (ATTO) | Daytime average | 38 m | February-March 2013 |
| This study | 0.39 | Brazilian tropical rainforest site (ATTO) | Daytime average | 38 m | February-March 2014 |
| This study | 0.39 | Brazilian tropical rainforest site (TT34) | Daytime average | 41 m | September 2013- July 2014 |
| This study | 0.19 | Hemi boreal forest site (SMEAR-Estonia) | Daytime average | 16 m | October 2012 |
| This study | 0.30 | French Mediterranean forest (O₃HP) | Daytime average | 2 m | May-June 2014 |
| This study | 0.13 | Brazilian mixed Tropical rainforest site(T2) | Daytime average | 14 m | February - October 2014 |
| This study | 0.11 | Cyprian rural site (CYPHEX) | Daytime average | 8 m | July -August 2014 |

[*average from different seasons reported. **average of different conditions cutting, a day after cutting removing hay and a day after removing hay.](#)

9. Figures

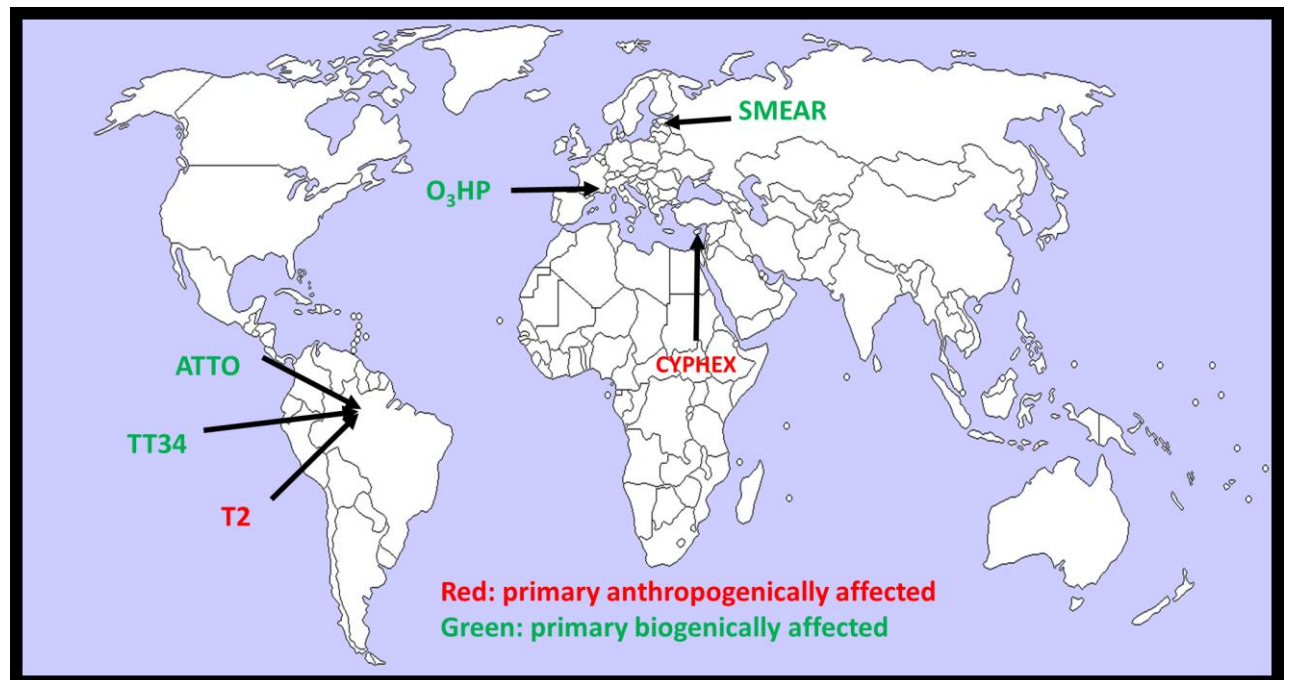


Figure 1: World map showing the location of the different sites. The names are colour coded depending on [whether](#) they have primarily biogenic influence (green) or a primarily anthropogenic influence (red). Wikimedia Foundation, 2016.

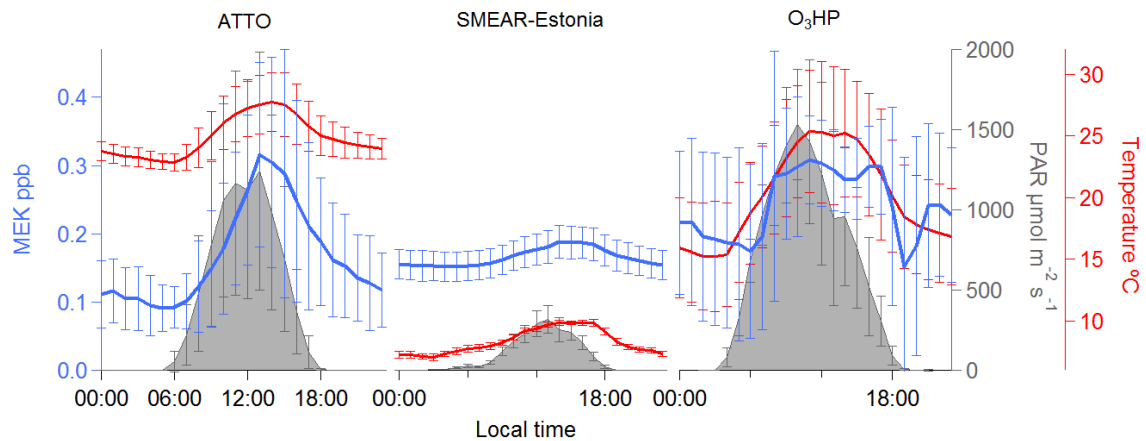


Figure 2: Hourly average diel cycles of MEK at the ATTO (left), SMEAR-Estonia (middle) and O₃HP (right) sites, for the period of measurements (wet season 2014 for ATTO at 38 m [October 2014](#) for SMEAR-Estonia at 16 m, and May and June 2014 for O₃HP at 2 m). Hourly mean diel cycles of temperature and PAR are also shown in red and grey, respectively. Error bars represent the standard deviations.

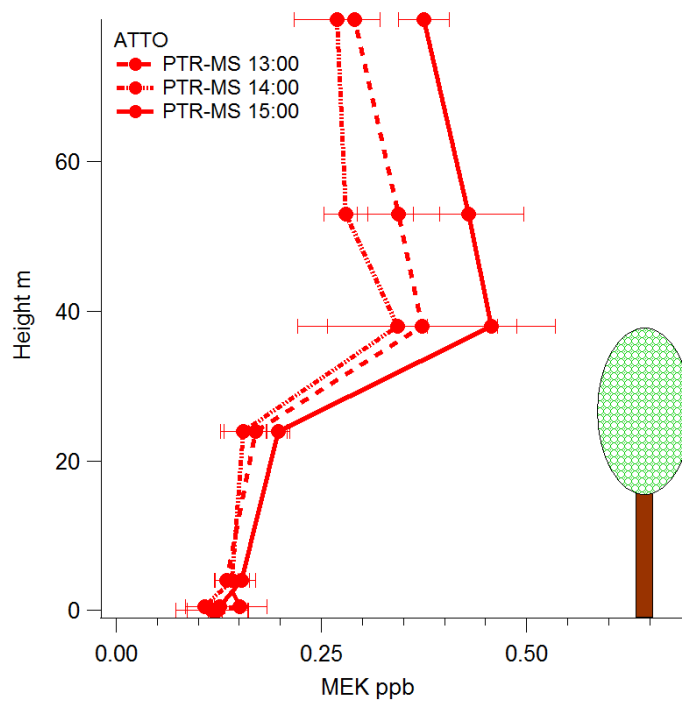


Figure 3: Hourly average vertical profiles of MEK mixing ratios at ATTO for the 7th of March 2014 for 13:00 LT (dashed lines), 14:00 LT (dotted and dashed lines) and 15:00 LT (thick lines). Error bars of vertical profiles are the standard deviations.

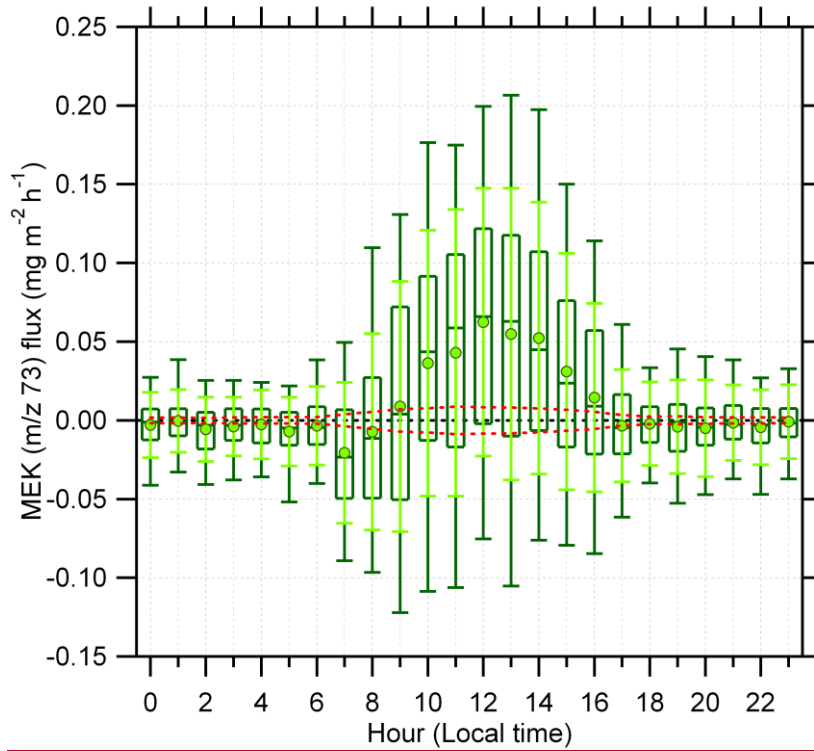


Figure 4: Hourly average MEK fluxes at the TT34 tower for the period Sept 2013 - July 2014. The light green circles represent means and associated error bars are one standard deviation. The central line of the box plots (dark green) indicates the median, bottom and top lines the 25th and 75th percentile respectively and whiskers are the 5th and 95th percentiles. Red dashed lines indicate the propagated limit of detection calculated according to the method outlined by (Langford et al., 2015).

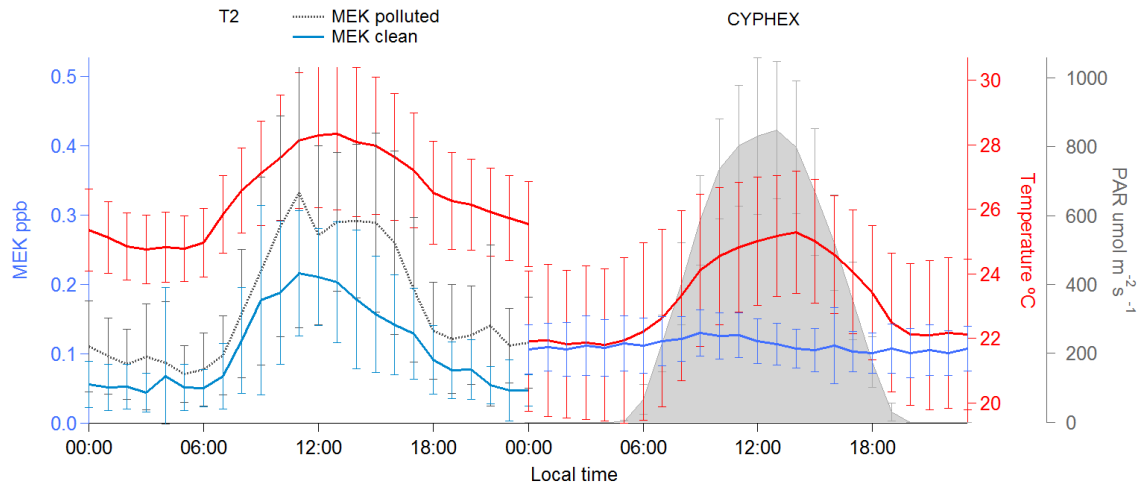


Figure 5: Hourly average diel cycles of MEK at the T2 (left) and CYPHEX (right) sites, for the period of measurements (wet season 2014 for T2 at 14 m, July and August 2014 for CYPHEX at 12 m). For T2 a separation between polluted (dotted black line) and clean (thick blue line) air masses was done. Hourly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

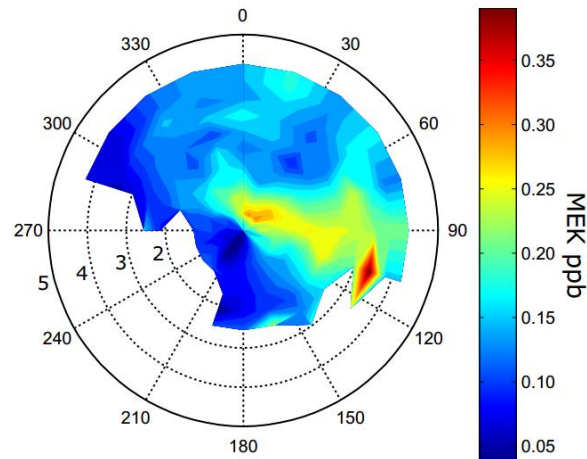


Figure 6: Polar surface plot for average MEK mixing ratios at a given wind direction (angle, $1-5 \text{ m s}^{-1}$) and wind speed (radius).

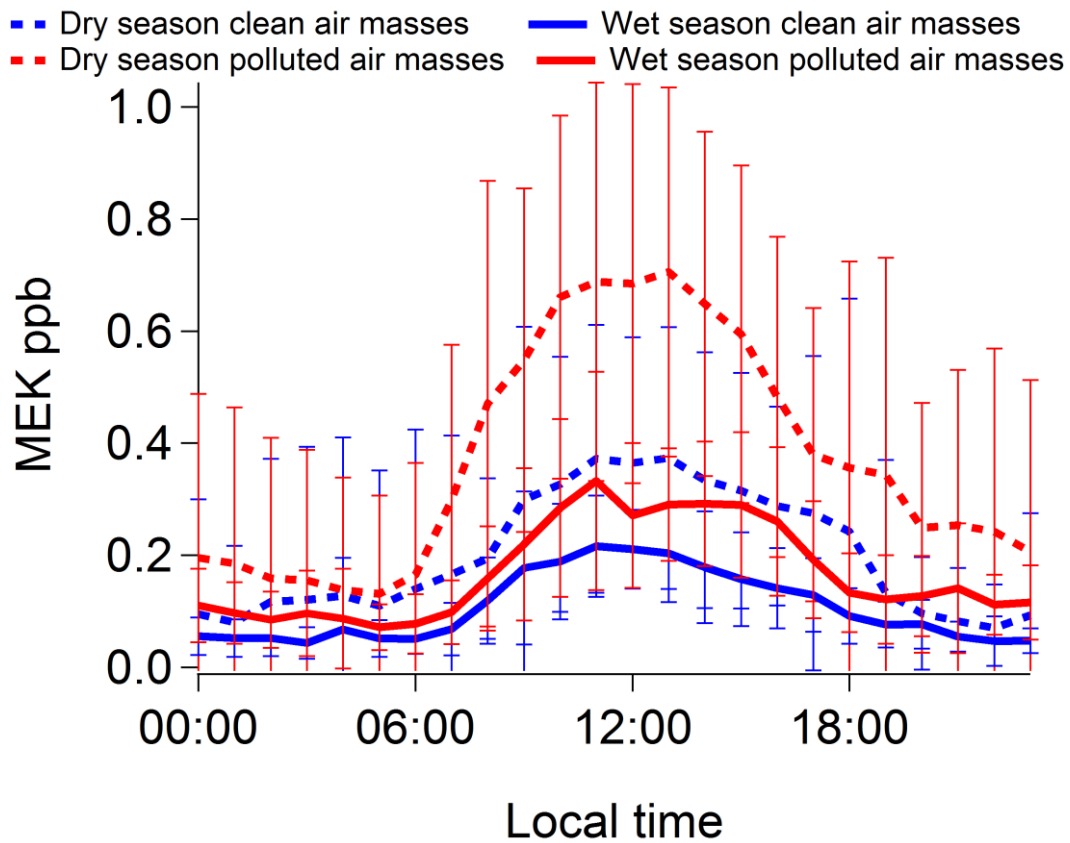


Figure 7: Hourly average concentrations of MEK in ppb for the clean conditions (blue) and the polluted conditions (red) at the T2 site. Dashed lines represent the dry season and thick lines represent the wet season. Error bars represent the standard deviation.

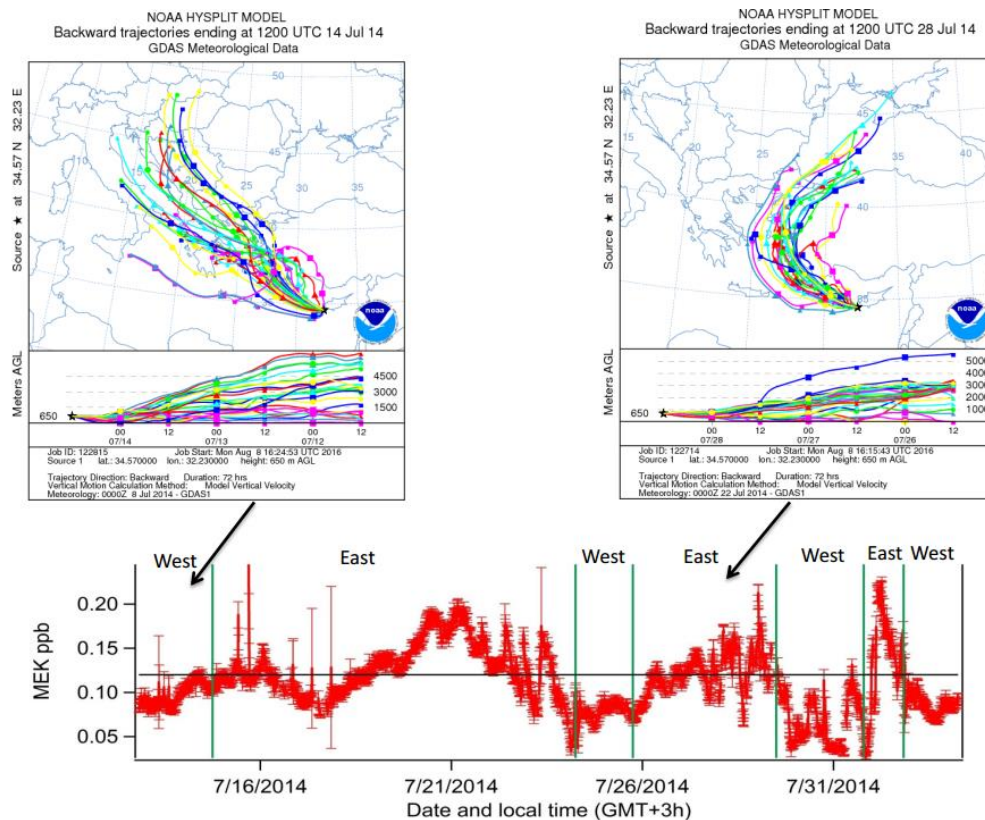


Figure 8: Timeline of MEK mixing ratios divided into periods when the air was coming either from either Eastern or Western Europe. The HYSPLIT backward trajectories from 14 July and 28 August 2014 are shown based on the origin of the air masses. The black line represents the average of the whole campaign.