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Diel and seasonal changes of Biogenic Volatile Organic Compounds within and above an Amazonian rainforest site

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Abstract

The Amazonian rainforest is a large tropical ecosystem, and is one of the last pristine continental terrains. This ecosystem is ideally located for the study of diel and seasonal behaviour of Biogenic Volatile Organic Compounds (BVOC) in the absence of local human interference. In this study, we report the first atmospheric BVOC measurements at the Amazonian Tall Tower Observatory (ATTO) site, located in Central Amazonia. A quadrupole Proton Transfer Reaction Mass Spectrometer (PTR-MS) with 7 ambient air inlets, positioned from near the ground to about 80 m (0.05, 0.5, 4, 24, 38, 53 and 79 m above the forest floor), was deployed for BVOC monitoring. We report diel and seasonal (February/March 2013 and September 2013) ambient mixing ratios for isoprene, monoterpenes, methyl vinyl ketone (MVK) + methacrolein (MACR), acetaldehyde, acetone, methyl ethyl ketone (MEK), methanol and acetonitrile. Clear diel and seasonal patterns were observed for all compounds during the study. In general, lower mixing ratios were observed during night, while maximum mixing ratios were observed with the peak in solar irradiation at 12:00 LT during the wet season (February/March 2013), and with the peak in temperature at 16:00 LT during the dry season (September 2013). Isoprene mixing ratios were highest within the canopy with a median of 7.6 ppb and interquartile range (IQR) of 6.1 ppb (dry season at 24 m, from 12:00–15:00). Monoterpene mixing ratios were higher than previously reported for any Amazonian rainforest ecosystem (median 1 ppb, IQR 0.38 ppb during the dry season at 24 m from 15:00–18:00). Oxygenated Volatile Organic Compound (OVOC) patterns indicated a transition from dominating forest emissions during the wet season to a blend of biogenic emission, photochemical production, and advection during the dry season. This was inferred from the high mixing ratios found within the canopy, and those obtained above the canopy for the wet and dry season, respectively. Our observations reveal strong seasonal BVOC patterns and oxidation capacity, reflected in the different vertical profiles obtained between the dry and wet season, most likely driven by insolation, temperature and phenology. In addition, significant differences to other reports

of Amazonian BVOC demonstrate the need for long-term observations and more standardized measurement procedures in order to better understand the natural exchange of BVOC between the Amazonian rainforest and the atmosphere.
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1 Introduction

The Amazonian rainforest is one of the last pristine continental areas. Low atmospheric concentrations of nitrogen oxides (NO_x) $\leq$ 1 ppb (Andreae et al., 2002; Kuhn et al., 2007) indicate little human interference. Tropospheric ozone levels of $\leq$ 15 ppb for the wet season (Rummel et al., 2007) are considered natural and the influence from seasonal biomass burning can be observed only occasionally during the dry season (Andreae, 2007; Kesselmeier et al., 2009; Kuhn et al., 2010; Davidson et al., 2012; Artaxo et al., 2013). Understanding this ecosystem's interactions between the biosphere and the atmosphere is of vital importance to be able to predict how it will respond to future climate change. The emission of Biogenic Volatile Organic Compounds (BVOC), a part of these interactions, can influence the ecosystem at different levels. At the leaf level, plants emit BVOCs as a result of signalling, thermo-tolerance, protection against pathogens, wound-sealing and prevention against cellular damage (Laothawornkitkul et al., 2009). In the atmosphere, BVOCs influence photochemistry and radiative forcing by the formation of secondary oxidants (such as tropospheric ozone) and by contributing to the Secondary Organic Aerosol (SOA) budget (Kesselmeier et al., 2002b; Williams, 2004; Artaxo et al., 2009). In the Amazonian rainforest, the high amount of biomass (93 ± 23 Pg C (Malhi et al., 2006)), in conjunction with the high year-round temperatures (26 °C mean (Araujo et al., 2002)), the high insolation due to the equatorial geographic location (33.7 MJ J m^{-2} day^{-1}) and the high humidity (70 % relative humidity, annual mean), makes the atmosphere similar to a photochemical reactor with a strong light source, filled with reactive gases (Andreae et al., 2002). As such, the atmospheric composition, in terms of OH, O_3, CO_2 and aerosols, is modulated by the

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biogenic emissions as well as uptake by the forest (Kesselmeier et al., 2000; Andreae et al., 2002), which can significantly influence the atmospheric oxidation capacity.

In the Amazonian rainforest, as well as on the global scale, the compound most copiously emitted by vegetation is isoprene (Crutzen et al., 2000; Karl et al., 2004; Kuhn et al., 2010), with emissions being circa four times the total of all anthropogenic VOCs (Boucher et al., 2013). Isoprene accounts for almost half of the world's biogenic emissions and its emission represents a few percent of the assimilated carbon in tropical regions (Kesselmeier et al., 2002a). Due to its high emission rates and reactivity, isoprene is a key-player in the oxidative capacity of the atmosphere (Lelieveld et al., 2008). Furthermore, evidence of SOA originating from isoprene has been observed in recent years in several different ecosystems (Claeys et al., 2004; Paulot et al., 2009; Carlton et al., 2009; Surratt et al., 2010; Chan et al., 2010; Pye et al., 2013). Despite the expected low particulate mass yield of isoprene relative to other natural VOCs such as monoterpenes and sesquiterpenes (Claeys et al., 2004; Surratt et al., 2010), its high abundance could potentially produce enough aerosols to significantly impact radiative forcing (Hallquist et al., 2009). The seasonality of isoprene in the Amazon is well established. Atmospheric mixing ratios may vary throughout the year by a factor of 4 (Kesselmeier et al., 2002b). During the wet season, the emission of isoprene is much lower, due to reduced sunshine from cloud cover, and slightly lower temperatures compared to the dry season, when high temperatures and radiation stimulate stronger biogenic emissions. In addition, strong seasonal cycles of vegetation growth, as observed by dendrochronology, may contribute to seasonal VOC fluctuations (Kesselmeier et al., 2009).

Monoterpenes comprise a class of well-known SOA precursor isoprenoids (Sakulyanontvittaya et al., 2008). These compounds also influence global atmospheric chemistry due to high OH reactivity (Kesselmeier and Staudt, 1999; Atkinson and Arey, 2003). Similar to isoprene, monoterpene emissions are regulated by light and temperature (Kesselmeier and Staudt, 1999), a feature which has also been specifically demonstrated for Amazonian monoterpene emitting plant species (Kuhn et al., 2002).

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Oxygenated volatile compounds are also present in the Amazonian atmosphere. Their atmospheric abundance has been observed to be determined by the balance between their sources (direct plant emissions as well as secondary formation though oxidation) and sinks (reaction with oxidants and surface uptake) (Karl et al., 2009). For instance, methanol is known to have multiple sources (Folkers et al., 2008). Its biogenic origin is primarily the reaction of pectin in plant cell walls during periods of leaf growth, but it could also be released by plant wounding, and decomposition of soil and leaf litter (Fall and Benson, 1996). The second most highly emitted VOC in terms of carbon after isoprene is methanol (Koppmann and Wildt, 2007), and its impact on atmospheric oxidation can be large, influencing the HOx budget, especially due to its long lifetime, which allows it to be transported over longer distances (Galbally and Kirstine, 2002).

Acetaldehyde has already been reported to have a 4–5 fold increase from the wet to the dry season, possibly due to vegetation fires, or due to an increase of secondary biogenic sources (i.e. oxidation of other BVOC) (Kesselmeier et al., 2002b). Several biological formation mechanisms for acetaldehyde exist. During root anoxia and fermentation in plants, acetaldehyde is formed as a by-product of ethanol production and is released via the transpiration stream (Kesselmeier et al., 2009; Bracho-Nunez et al., 2012, 2013). Another source of biological production of acetaldehyde occurs during the light-to-dark transition in plants, where as an outflow mechanism, acetaldehyde is leaked from intracellular space after conversion from pyruvate (Fall, 2003; Rottenberger et al., 2004). An interesting feature is the bidirectional exchange of acetaldehyde by plants, such that when high ambient concentrations in comparison to plant cellular space occur, acetaldehyde can also be taken-up (Rottenberger et al., 2004; Jardine et al., 2008). Furthermore, acetaldehyde has an important atmospheric source due to the oxidation of other BVOCs and long lived VOCs such as ethane in the atmosphere (Seco et al., 2007).

Acetone is also a very abundant oxygenated BVOC, which is known to have a variety of sources. In the troposphere, acetone is relevant due to its photolytic sink, which could eventually lead to PAN, under sufficient NOx levels, influencing tropospheric ozone and

HOx radicals (McKeen et al., 1997; Pöschl et al., 2001; Karl et al., 2002). On the other hand, acetone can also be emitted by vegetation. It is released after leaf wounding, with special importance for cyanogenic plant species. It is also emitted due to light dependent and independent responses, which may be related to the decarboxylation of acetoacetate, that occurs in soil microorganisms, animals or other processes (Fall, 2003).

Methyl ethyl ketone, MEK (or 2-butanone) is an oxygenated BVOC which has rarely been reported (Williams et al., 2001; Davison et al., 2008; Bracho-Nunez et al., 2013). MEK can be emitted from vegetation (Isidorov et al., 1985; Kirstine et al., 1998; de Gouw et al., 1999; Davison et al., 2007; Jardine et al., 2013). However, it is also an oxidation product of isoprene and butane (Gouw et al., 2003a; Bracho-Nunez et al., 2013). Additionally, methyl vinyl ketone and methacrolein (MVK + MACR) are oxygenated compounds thought to be predominantly produced after oxidation of other VOCs, particularly, isoprene (Warneke et al., 2001; Kesselmeier et al., 2002b; Karl et al., 2009; Kuhn et al., 2010). Ambient mixing ratios of such compounds are controlled by the oxidation rate of isoprene, however there is new evidence of isoprene oxidation within plants, possibly leading to direct emission of MVK + MAC (Jardine et al., 2012).

Another interesting compound is acetonitrile, which is related uniquely to biomass burning (Lobert et al., 1990; Andreae and Merlet, 2001), although it has also been reported to be emitted by plants (Nyalala et al., 2011) and by soil (Bange and Williams, 2000). It has a long OH lifetime of approx. 900 days (Williams et al., 2001) and it is considered an anthropogenic VOC since most regional biomass burning events are man-made (Crutzen and Andreae, 1990).

The objective of this study is to provide a detailed description of the aforementioned BVOC in-canopy fluctuations, which can be related to the exchange between the forest and the atmosphere under dry and wet season conditions. Within this context, we present the first measurements of BVOC reported from the "INSTANT" tower (80 m) recently installed at the new Amazonian Tall Tower Observatory (ATTO) site.

2 Methodology

2.1 Site description

The ATTO site is located in central Amazonia, 135 km NE from Manaus, the closest populated area. The reserve in which ATTO is embedded comprises 424 430 ha of mainly non-flooded closed forest vegetation (*terra firme*), but also black-water flood-plain forests (*igapó*), old non-flooded alluvial terraces (*paleoigapó*) and open forest vegetation on white sands (*campina*). The main wind direction at the site is NE and therefore most of the air masses arriving at the site, have passed through 1500 km of undisturbed *terra firme* rainforest, with negligible intrusion of air masses from Manaus. This unique situation makes this site very suitable for long-term measurements of the chemical exchanges between biosphere and atmosphere in the Amazon region. The site, with a mean canopy height of 35 m, is equipped with an 80 m walk-up tower (IN-STANT tower; 02°08′38.8″ S 58°59′59.5″ W). Measurements cover several research areas such as meteorology, micrometeorology, phenology, dendrochronology, hydrology and atmospheric chemistry/physics and are performed continuously for O_3, NO, NO_2, CO_2, CO, CH_4, H_2O, and aerosol particle size, number and composition. These studies were complemented by the periodic determination of total OH reactivity and VOC measurements during the campaigns.

2.2 Trace gas sampling

Measurements of Volatile Organic Compound (VOC) mixing ratios were accompanied by the determination of total OH reactivity, nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), and water vapour (H_2O) at 7 heights in and above the rainforest canopy. The lower part of the vertical profile (0.05, 0.5 and 4 m above the forest floor) was set up in undisturbed vegetation adjacent to the INSTANT tower (distance 12 m). The upper part of the vertical profile (24, 38, 53 and 79 m above the forest floor) was mounted on the north-west corner of the INSTANT tower. Seven Teflon tubes (OD 3/8″) of

different lengths were guided to a valve system which separated the flows every 2 min, completing a whole profile in 16 min. While a line was not being sampled from, it was kept flushed by a by-pass pump. The residence times were 24, 17, 13, 9, 4, 5, and 5 s for 79, 53, 38, 24, 4, 0.5 and 0.05 m, respectively, using a Teflon pump at a flow rate of 16 lpm. Heated (50 °C) and insulated transfer lines (PTFE) were connected to a PTR-MS (Proton Transfer Reaction Mass Spectrometer), which was housed in an air conditioned lab container 10 m away from the INSTANT tower (see Fig. 1).

2.3 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

Measurements of Volatile Organic Compounds (VOCs) were performed using a Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon Analytic, Austria) operated under standard conditions (2.2 mbar drift pressure, 600 V drift voltage, 127 Td) (Lindinger et al., 1998). Each level of the vertical profile was sampled for 2 min with 6 to 7 cycles (approx. 20 s each) of PTR-MS measurements. A catalytic converter (Supelco, Inc. with platinum pellets heated to 400 °C), was used to convert ambient VOC to $CO_2 + H_2O$ to determine the background signal for each compound once every hour. Background values were interpolated over the time of the measurements. Detection limits (LOD) were calculated as 2σ of the background averages (Kaser et al., 2013) (Table 1).

Humidity dependent calibrations (using bubbled synthetic air, regulated as close as possible to ambient humidity conditions) were performed using a gravimetrically prepared multicomponent standard of formaldehyde (detected as protonated mass m/z 31), methanol (m/z 33), acetonitrile (m/z 42), acetaldehyde (m/z 45), acetone (m/z 59), dimethyl sulphide, DMS (m/z 63), isoprene (m/z 69), MVK (m/z 71), MACR (m/z 71), benzene (m/z 79), toluene (m/z 93), o-xylene (m/z 107), α-pinene (m/z 137 and m/z 81) (Ionimed and ApelandRiemer). Monoterpenes were monitored at m/z 81 (mass calibrated independently for α-pinene, Pearson coefficient for m/z 81 against m/z 137 : 0.71), its main fragment, instead of the unfragmented m/z 137, to

improve LOD due to higher quadrupole transmission (Tani et al., 2003; Rinne et al., 2005; Misztal et al., 2011).

The PTR-MS technology allows for fast sampling at very low mixing ratios, but the system relies solely on mass-over-charge (m/z) for compound specification. As such, cross validation with another compound selective technique, such as Gas Chromatography is strongly advised. This was performed using the GC-FID (Gas Chromatography-Flame Ionisation Detector) technique for monoterpenes (α-pinene, camphene, 1-octen-3-ol, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α-terpinene, ρ-cymene, limonene and δ-terpinene) and isoprene. On chosen days, samples were collected continuously at selected heights using a GSA SG-10-2 personal sampler pump. Ambient air was drawn through absorbent filled tubes (Carbograph I, Carbograph V 130 mg of Carbograph 1 ($90\,m^2\,g^1$) followed by 130 mg of Carbograph 5 ($560\,m^2\,g^1$)). The size of the Carbograph particles was in the range of 20–40 mesh. Carbographs 1 and 5 were provided by Lara s.r.l. (Rome, Italy) (Kesselmeier et al., 2002b). Cartridges were analysed by GC-FID in the laboratory in order to validate the measurements by the PTR-MS. The uncertainty of the measurements by GC-FID was less than 10 %. The sampling error was determined to be less than 20 %. The uncertainty of the PTR-MS involved the uncertainty of the calibration, of the PTR-MS itself and the background error. These uncertainties for the PTR-MS measurements added up to 9.9 % for isoprene, 10.4 % for monoterpenes, 16.5 % for acetaldehyde, 15.2 % for acetonitrile, 6.2 % for acetone, 10.8 % for methyl vinyl ketone and methacrolein, 26.1 % for methyl ethyl ketone, and 37.7 % for methanol.

Nevertheless, not all compounds could be cross validated by GC-FID. For PTR-MS detected masses such as m/z 33, m/z 42, m/z 45, m/z 59, m/z 71 and m/z 73, we relied on an identification which has been generally agreed on by reasonable exclusion of some species (Williams et al., 2001; Warneke et al., 2003; de Gouw et al., 2007; Kajos et al., 2015). It should be noted that recent research has shown the possibility of ISOPOO (isoprene peroxy radicals) which could interfere in m/z

71. This is why MVK + MACR within this study should be considered in reality as MVK + MACR + ISOPOO (Liu et al., 2013).

There could be multiple contributors to the mass for m/z 73. It has been reported that methyl ethyl ketone (hereby referred to as MEK) represents 74 % of this signal in most air masses (Karl et al., 2007b; Warneke et al., 2003). The most likely other contributors to this m/z would be butanal, methyl glyoxal and acrylic acid. However, acrylic acid and methyl glyoxal would not have been able to make it through the 12–90 m length inlet lines, due to their sticky nature. A possible interference from water clusters on the MEK signal was tested by calculating correlations between water and MEK. A poor correlation ($r < 0.5$) was observed, suggesting the absence of an interference from water clusters in m/z 73. Methyl glyoxal is a compound which results from isoprene oxidation, and therefore it closely follows the isoprene patterns. However MEK mixing ratios from the wet to the dry season did not change in magnitude, only in patterns, whereas the isoprene difference between seasons was by a factor of 4 (Sects. 3.3 and 3.5). For this reason, methyl glyoxal could also be eliminated as a contributor. Furthermore, in this precise case, the pattern obtained is consistent with the stability and relatively long lifetime of MEK (5.4 days), since mixing ratios remained relatively constant higher up in the canopy and above the canopy (Grant et al., 2008; Williams et al., 2001). Finally, butanal could also have been a contributor, but GC-FID values for butanal had a mean of 0.01±0.04 ppb ($n = 104$) and thus we considered it as negligible. Therefore, we regarded m/z 73 as representing MEK.

3 Results

Firstly we present the cross validation of the measurements between PTR-MS and GC-FID. Secondly, all measured BVOC mixing ratios are reported linking their diurnal and the seasonal cycles to sources and/or atmospheric processes. The medians were calculated from the dry (20–30 September 2013) and wet (20 February to 6 March 2013) season measurement periods. The dates expressed herein are all in local time. In all

cases, variability is represented as the interquartile range (IQR) which is the 75 % percentile minus the 25 % percentile. This is the range where 50 % of the data lies.

3.1 Crossvalidation

A cross validation for isoprene and for the monoterpene data obtained by PTR-MS (in-situ) and GC-FID (off-line using absorbent tubes) was performed (Fig. 2). The temporal variation compared well. The coefficients of determination (r^2) were 0.88 and 0.58 for isoprene and the sum of monoterpenes, respectively, and a slope of 1.12 ($n = 30$) for isoprene and 0.64 ($n = 32$) for the sum of monoterpenes was calculated. The underestimation of monoterpenes (slope < 1) is regarded to be a result of missing monoterpene species which could be below the detection limit for the GC-FID technique (monoterpenes detected by the GC-FID technique: α-pinene, camphene, 1-octen-3-ol, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α-terpinene, ρ-cymene, limonene and δ-terpinene), while the PTR-MS detects the sum of all monoterpenes. In addition, monoterpenes might diffuse inside the adsorbent tube to stronger adsorbents during the transport from the forest to the laboratory. For other measured masses such as m/z 33 (methanol), m/z 42 (acetonitrile), m/z 45 (acetaldehyde), m/z 59 (acetone), m/z 71 (methyl ethyl ketone and methacrolein) and m/z 73 (MEK) we adopted compound identifications based on atmospheric chemistry and emission inventories reported in the literature in which acknowledgment of possible compound contribution and GC cross-checks were performed (Gouw et al., 2003; de Gouw et al., 2007; Warneke et al., 2003; Williams et al., 2001).

3.2 Time series

Four campaigns were performed in the course of one year, i.e. in November 2012, February–March 2013, June 2013 and September 2013. Two intensive measurement periods cover the two extremes of seasonality: 20 February to 6 March of 2013 (during the wet season) and 20 to 30 September 2013 (during the dry season), which

will be termed as typical wet and dry season data, respectively. Meteorological conditions between the dry and wet season varied significantly (Fig. 3). This site generally experiences dry season conditions from August to October, during which cumulative precipitation is less than 100 mm month^{-1} (Restrepo-Coupe et al., 2013). For September 2013, ambient temperature and net radiation measured at the tower were higher ($\overline{T} = 26.56 \pm 2.78\,°C$ and $\overline{Q^*} = 147 \pm 282\,W\,m^{-2}$), and rain events less frequent when compared with the February–March period ($\overline{T} = 25.55 \pm 2.50\,°C$ and net radiation mean of $\overline{Q^*} = 103 \pm 220\,W\,m^{-2}$). Transition periods represent the times with mixed features from both the wet and dry seasons as can be observed in June, where rainfall events are quite frequent and exhibit the largest discharge of water in the whole measurement period (Fig. 3). Interestingly, temperature during the period of November 2012 further increased almost every day to a maxima of 35 °C ($\overline{x} = 28.20 \pm 3.29\,°C$) as compared to the wet season (i.e. February/March 2013), where it barely reached 30 °C on some days. During the dry season (i.e. September 2013) temperatures only reached maximums of 33 °C (maximum temperature observed for September = 36 °C). Of special interest is the comparison of solar radiation for November 2012 and September 2013. During the dry season more solar radiation was available at the canopy top (reaching at noon 1000 W m^{-2} and low cloud cover overall), whereas in November 2012 the net radiation rarely reached 800 W m^{-2} due to the more extended cloud cover, despite the higher temperature. More detailed information about Amazonian seasonality can be found elsewhere (Araujo et al., 2002; Restrepo-Coupe et al., 2013).

3.3 Isoprenoids

During the daytime isoprene had the highest mixing ratios within the canopy reaching a median of 7.6 (IQR 6.1) ppb at 24 m for the period of 12:00 to 15:00. During the night (median of the period of 00:00–03:00 LT), the vertical profiles changed, having higher mixing ratios above the canopy (Fig. 4). Strong gradients towards the ground could be seen, especially for the dry season, which could suggest a deposition towards the

ground or plants (Fig. 5). The vertical profiles of isoprene revealed the highest mixing ratios for both day and night during the dry season. In addition, the variability increases during the dry season, as observed in the difference of IQR of 1.9 ppb during the wet season to 6.1 ppb during the dry season, at 24 m for the period 12:00–15:00. Both seasons had similar vertical profiles: at night the highest values were found at the highest inlet, at day maximum isoprene was observed inside the canopy. However, the vertical profiles for isoprene during the wet season had a relatively stronger night-to-day variability at 24 m despite the overall lower mixing ratios during this period. The less pronounced vertical gradient during the dry season could be due to a stronger turbulent mixing (Fig. 5).

Total monoterpene mixing ratios were extremely low during the wet season period and rarely above the detection limit ($LOD_{MT} = 0.23$ ppb, Table 1). For the dry season, within the 24 m level the highest mixing ratios were found, with a median of 1 (IQR 0.38) ppb between 15:00–18:00. The mixing ratios at 79 m as well as at the ground (0.5 m) were significantly lower than at 24 m between 15:00–18:00 (about more than a factor of 2). During the night, total monoterpene mixing ratios decreased but never reached zero values (Fig. 4). Daily patterns of the total monoterpenes seemed to follow the diel cycle of temperature rather than the diurnal variation of insolation as supported by emission estimates according to Tingey et al. (1980) and Guenther et al. (1995). A correlation analysis between the dynamics of the measured total monoterpenes and the calculated light and temperature dependent emission capacity for monoterpenes showed a correlation coefficient (r) of 0.61. The calculation of temperature-only dependent emissions according to the Tingey's algorithm improved the correlation coefficient for the measured total monoterpenes to 0.82. These correlations were calculated using mixing ratios instead of emissions, for which additionally, transport and chemistry need to be taken into account.

3.4 Oxidation products of Isoprenoids

Methyl vinyl ketone and methacrolein (hereby referred to as MVK + MACR) are key compounds for use in the analysis of the oxidation processes in the forest atmosphere as their predominant source is from the oxidation of isoprene, the compound most copiously emitted by tropical forests. A noticeable seasonality was found in comparing the dry to the wet season for MVK + MACR with a strong difference in magnitudes (Fig. 6).

During the wet season, the highest median mixing ratios were found above the canopy with 0.22 (IQR 0.34) ppb around 13:00 at 79 m. This coincided with the peak of isoprene at 24 m during the same time of the day, suggesting that MVK + MACR production is at its maximum when isoprene emissions are highest and that they are produced above the canopy shortly after the emission of isoprene. Mixing ratios for 24 and 0.5 m during the wet season remained almost constant during the night (≤ 0.05 ppb) and only increased during daylight hours. The difference between the lower inlets in comparison to above the canopy was approximately of 0.1 ppb lower (Fig. 6). After sunset, the 79 m level mixing ratios of MVK + MACR did not decrease immediately as those at the 24 m level did. This may indicate a lower depletion in the dark at the top levels.

During the dry season, median mixing ratios were higher by one order of magnitude above the canopy as compared to the wet season. For most times of the day, mixing ratios at 24 m matched those at 79 m. During this time of the year, the decrease of mixing ratios after sunset was similar at 24 and 79 m. This effect may be caused by a better turbulent mixing during the dry season, which allows for a faster oxidation of isoprene to MVK + MACR, as well as better mixing of the MVK + MACR formed within the profile. The ground levels showed a diurnal variability with respect to the wet season, though mixing ratios remained the lowest at this height.

An analysis of the ratio between isoprene and MVK + MACR indicated changes in the oxidative patterns between the seasons. During the wet season ratios never ex-

ceeded 0.2, indicating there was not much oxidation taking place. The minimum of the MVK + MACR-to-isoprene ratio was located inside the canopy, with the ratios at the ground and above the canopy being only slightly higher. During the dry season, ratios increased at all heights indicating a higher oxidative capacity during this period. The ratios increased above the canopy, suggesting a clear formation of MVK + MACR at this height. Ratios were highest at 53 m, however the high variability found at 53 m and at 79 m dampened any dominance. This variability was most likely due to the high inter-day variability (Fig. 7). It could be that above the canopy isoprene, which was emitted from the canopy, was rapidly converted into MVK + MACR by OH.

3.5 Acetaldehyde, acetone and Methyl Ethyl Ketone (MEK)

Oxygenated VOCs such as acetaldehyde, acetone and methyl ethyl ketone (MEK) were grouped together. They exhibited similar variations over the day and season. In the wet season, acetaldehyde, acetone and MEK (Fig. 8) showed the highest mixing ratios at 24 m at midday, reaching medians of 0.94 (IQR 1.61) ppb, 0.98 (IQR 0.93) ppb and 0.4 (IQR 0.58) ppb, respectively. Although the highest mixing ratios were found at the canopy top, the diurnal cycle with a pronounced increase around noon suggested a biogenic origin. The mixing ratios above the canopy and at the ground remained much lower throughout the measurement period, except for acetone. Of all three species, acetone was the only compound with higher mixing ratios above the canopy (up to 0.92 (IQR 0.53) ppb at 12:00 to 15:00), compared to the canopy top. For acetone, above canopy mixing ratios were always higher than inside the canopy during daytime except for the period of 11:00 to 14:00, where the canopy layer (24 m) dominated (Fig. 8).

Conditions during the dry season were markedly different, with mixing ratios peaking above the canopy, instead of inside. Interestingly, the mixing ratios of acetaldehyde, within the canopy during the dry season were comparable to those of the wet season, whereas the 79 m level showed a 3-fold increase. Such difference clearly indicated a seasonal change in the dominating sources for this species. In a comparable fashion,

acetone, during the dry season, was also more abundant above canopy than within. Similarly to acetaldehyde, MEK was observed to change from much higher mixing ratios in-canopy than above during the wet season, to comparable mixing ratios in and above the canopy during the dry season. Despite the 4-fold increase in the 79 m mixing ratios from the wet to the dry season, mixing ratios within the canopy remained similar ($\sim$ 400 ppt) from the wet to the dry season, suggesting that the MEK within the canopy does not come from isoprene oxidation, as was found for MVK + MACR. In addition, the vertical distribution of these oxygenated compounds during the dry season compared very well to the calculated MVK + MACR-to-isoprene ratio. Furthermore, for the dry season, it seemed that whereas isoprene peaked at 13:00, the oxygenated compounds peaked from 15:00 to 18:00. This suggested different processes involved in the formation of these compounds besides plant production.

3.6 Methanol

Up to 80 % of the methanol data during the wet season were below the detection limit ($LOD_{Methanol,\ wet}$ = 1.70 ppb, Table 1). In contrast, during the dry season, the median mixing ratios for methanol were higher at about 4.7 (IQR 1.35) ppb at 79 m during the period of 15:00 to 18:00 (Fig. 9). Mixing ratios at 79 and 24 m exhibited similar diurnal patterns with comparable magnitudes. Nevertheless, at 15:00 the within canopy mixing ratios slightly exceeded those above the canopy. This happened every day at the same time together with a peaking temperature. This suggests that the observed atmospheric methanol could be originated from a mixture of sources: one source above the canopy could be the photochemical oxidation of VOCs, another source could be the transport from other regions due to methanol's long lifetime, and another possible source is the emission from the canopy.

3.7 Acetonitrile

Acetonitrile mixing ratios during the wet season period were highest at 79 m with maximum mixing ratios of 0.1 (IQR 0.06) ppb during daytime (medians of the period from 12:00–15:00). During the dry season, median mixing ratios for acetonitrile increased to up to 0.25 (IQR 0.06) ppb at daytime (12:00 to 15:00 period), again with highest mixing ratios above the canopy and at the canopy crown. This compound typically originates from biomass burning which is more likely during the dry season. There were never spikes or events of increased acetonitrile, which is in good agreement with the CO data, indicating that there was no biomass burning close-by impacting our measurements. Constant levels above the canopy are characteristic of a well-mixed long lived VOC transported to the site, such as acetonitrile, with a decrease inside the canopy indicating a probable deposition or uptake by the ground and/or vegetation (Fig. 10).

4 Discussion

4.1 Diel and seasonal behaviour

A distinct seasonality in the magnitude of mixing ratios or the diel cycle patterns was observed for all monitored compounds. During the wet season the fluctuations and mixing ratio levels of detected BVOCs seemed to be solely of primary biogenic origin, as during the day mixing ratios for isoprene, acetaldehyde, acetone and MEK were always higher inside the canopy than above the canopy. The general behaviour strongly suggested a source at the forest canopy top height. This was not the case for MVK + MACR and acetonitrile, which exhibited the highest mixing ratios above the canopy. This observation was expected, as MVK + MACR are produced by the oxidation of isoprene released by vegetation and transported to above the canopy (Kesselmeier et al., 2002b). Furthermore, acetonitrile was also expected to be higher above the canopy as it may derive from regional biomass burning plumes that have been transported to the site

(Kuhlbusch et al., 1991; Andreae and Merlet, 2001). Finally the uptake of water soluble compounds by water surfaces might cause seasonality, as observed for the wet season period with methanol mixing ratios below detection limit.

During the dry season, a different situation was observed. Higher mixing ratios of acetaldehyde, acetone, MEK, methanol, MVK + MACR and acetonitrile were detected above the canopy both during the day and nighttime. Most likely, this increase above the canopy was due to higher production of secondary VOCs such as acetaldehyde, acetone, MVK + MACR or methanol via oxidation of BVOCs primarily emitted from the forest. In addition, an increase in the variability above the canopy was observed in the dry season, with mixing ratios inside the canopy sometimes reaching the above canopy levels. Most likely this was due to the higher insolation during the dry season which heated up the canopy top, increasing the turbulent mixing during the day, combining plant emissions with atmospheric production oxidation products and transport of air masses from other regions. This could be seen in the weak gradients above the canopy, except for those of isoprene which was additionally chemically depleted.

The main climatic difference between the dry and the wet season in the Central Amazonian rainforest is insolation, as the annual temperature variation is on average only 2 °C (da Rocha et al., 2004). During the wet season, the insolation is quite reduced due to the great cloud cover and rain events. As means of comparison, in boreal forest with a strong temperature annual variation from summer to winter, emissions of BVOCs significantly change during the growing season and are greatly reduced during wintertime (Hakola et al., 1998, 2001, 2003; Raisanen et al., 2009). In mid-latitude deciduous forests trees lose all the leaves during wintertime and leaf photosynthetic emissions cease (Holzke et al., 2006; Staudt et al., 2000). All these seasonal variations are mainly due to phenology and temperature (Abbot, 2003; Schnitzler et al., 2002).

In Central Amazonia, water limitation does not seem to be a problem in any season (Restrepo-Coupe et al., 2013). Since light and temperature are greatest during the dry season, at that time of the year photosynthesis, and probably related produc-

tion pathways allow for faster BVOC synthesis. Nevertheless, in the Amazon, the climatic changes during wet and dry season trigger seasonal growth rates which are mirrored in tree rings (Brienen and Zuidema, 2005; Restrepo-Coupe et al., 2013; Zuidema et al., 2012), indicating stronger growth during the wet season in *terra firme* rainforest (Dünisch et al., 2003) and there seems to be species-specific synchronous leaf flushing at the onset of the dry season.

During the dry season, long range transport from other regions, including biomass burning air masses, could have triggered a higher oxidative capacity of the air as indicated by higher ozone concentrations at the ATTO site during the dry season (S. Wolff, personal communication, 2014). The rise of ozone and NO_x during the dry season could have increased and speeded up atmospheric chemical reactions, due to the higher production of atmospheric oxidants such as OH and ozone itself (Rummel et al., 2007). These atmospheric conditions could have led to higher production of secondary BVOCs above the canopy as was observed for the dry season. Summarizing, the different mixing ratios and vertical patterns can be related to changes in insolation, temperature, external sources (i.e. biomass burning air masses during the dry season) and leaf phenology, all related to seasonality.

Isoprene peaked together with light intensity just after midday inside the canopy during the dry and the wet season. Interestingly, this was observed at 13:00 whereas other VOCs including oxygenated compounds and monoterpenes had the highest mixing ratios at 15:00 to 16:00 during the dry season. This suggested that isoprene emissions could to be more driven by radiation, which peaks at 12:00, whereas the oxygenated compounds, such as MVK + MACR, produced directly by the forest plant species or by chemical reactions in the atmosphere may have been more related to temperature (which peaks at the same time 15:00–16:00) than light. During both seasons, isoprene had the highest concentrations during the day at the top of the canopy where leaves received most of the radiation. During the night (Fig. 5), mixing ratios of isoprene decreased considerably towards the ground. This decrease just after sunset was too rapid to be explained exclusively by gas-phase chemistry due to a decrease in the levels of

OH which is the strongest isoprene sink since it does not have major sources in the dark (Goldan et al., 1995). At night, isoprene is not emitted due to the cessation in photosynthesis. In the dark, isoprene which has been emitted during the daylight can escape from the canopy via transport as its lifetime increases due to the decrease of OH production and the weak NO_3 chemistry in the Amazon. Ozonolysis of alkanes during the night can be neglected due to the low ozone levels (Paulot and Orlando, 1996; Andreae et al., 2002) but isoprene can be taken up or deposited onto surfaces. This potentially important process becomes more visible during the night, when the nocturnal boundary layer results in low transport rates (with a wind speed at 19 m of $0.23 \pm 0.17\,m\,s^{-1}$) with diffusion being the main trigger. Under these conditions, the profile of isoprene with lower mixing ratios to the ground during the night clearly indicated a sink at the surfaces (such as leaves, soil and/or litter) presumably due to isoprene microbial consumption (Goldan et al., 1995; Cleveland and Yavitt, 1997; Gray et al., 2014).

Total monoterpenes presented a very strong seasonality with mixing ratios during the wet season below 0.23 ppb and during the dry season up to 1.8 ppb (maximum value). A few Amazonian tree species have been monitored for monoterpene emissions in previous studies, suggesting that more factors than solely meteorological influence the seasonality of monoterpene emissions. Among those are the oxidative capacity of the atmosphere and phenological development, which may be accentuated during the dry season (Kuhn et al., 2004). In addition, during the dry season, total monoterpene mixing ratios peaked at the same time as the temperature peaked, at around 15:00. They seemed to more closely follow the diurnal temperature than the radiation cycle. The description of monoterpene mixing ratios by emission capacity algorithms was reasonable (see Sect. 3.3). Hence a significant temperature dependence cannot be ruled out. A switching of the metabolic processes to more temperature dependent processes might explain these observations. This would differ from previous plant studies that found Amazonian plant emissions of monoterpenes to be light and temperature dependant (Bracho-Nunez et al., 2003). Furthermore, as the PTR-MS measures the sum

of monoterpenes, it is possible that the monoterpene composition changes seasonally along with their reactivities and vertical patterns (Kesselmeier et al., 2002b; Kuhn et al., 2004).

The isoprene oxidation products MVK + MACR provide an indication of the oxidation capacity of the atmosphere. Patterns of MVK + MACR clearly indicated changes in the oxidation processes at the Amazonian rainforest over the year. During the wet season, a low MVK + MACR-to-isoprene ratio, suggested a weak oxidation regime above the canopy, in contrast to the dry season, where higher ratios indicated a higher oxidation capacity. Even though mixing ratios of MVK + MACR and isoprene rose during the dry season, they did not rise proportionally. Whereas isoprene had a 4-fold increase from the wet to the dry season, MVK + MACR had a 10-fold increase, possibly indicating a faster depletion of isoprene than MVK + MACR. This faster processing could also be observed in the more accentuated isoprene profiles despite the much higher variability observed during the dry season (Fig. 5). The MVK + MACR-to-isoprene ratios during the dry season increased to about 75 % compared to the wet season, and are comparable with ratios previously reported (Kesselmeier et al., 2002b) for Amazonian rainforest ecosystems (Fig. 7).

Regarding the vertical distributions of the other oxygenated VOCs above the canopy, a similarity of patterns became apparent. When MVK + MACR-to-isoprene ratio above the canopy is used as a proxy for atmospheric oxidation, OVOC vertical profiles in the dry season could suggest that the oxidation of emitted VOCs above the canopy efficiently produced secondary BVOCs such as acetaldehyde and acetone. Despite the high variability, a maximum of oxidation capacity was generally observed at 53 m.

The vertical profiles of acetone, MEK and acetaldehyde during the wet season showed a maximum inside the canopy at midday. Acetaldehyde is reported to be emitted by the forest crown as a by-product of fermentation processes within roots due to water flooding and root anoxia (Kesselmeier et al., 2009; Bracho-Nunez et al., 2013). If rain events cause such an anoxia, this would explain the observed mixing ratios below the LOD (LOD$_{acetaldehyde}$ 0.28 ppb) in the understory, a considerable increase at the

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crown, and a quick decrease towards the atmosphere during the wet season. A similar pattern, indicating plant production, was found for acetone and MEK, which is supported by other studies (Bracho-Nunez et al., 2013; Fall, 2003; Isidorov et al., 1985; Kirstine et al., 1998). However, for the vertical profile of acetone during the dry season, the peak was observed above the canopy, possibly due to a dominance of photochemistry just above the canopy (Seco et al., 2007). MEK showed a not so pronounced increase above the canopy. In fact, it seems that during the wet season MEK was only emitted by plants and not coming from isoprene oxidation. During the dry season, the higher mixing ratios above the canopy indicated possible production from isoprene oxidation, although plant emission could not be disregarded (Isidorov et al., 1985; Kirstine et al., 1998; de Gouw et al., 1999; Davison et al., 2007; Jardine et al., 2013). For all these compounds we should also consider a possible bidirectional exchange, where the canopy crown could be acting as a sink (Kesselmeier, 2001; Rottenberger et al., 2004; Karl et al., 2005; Park et al., 2013; Niinemets et al., 2014).

Methanol (MeOH) behaved similarly to other oxygenated compounds although at mixing ratios below the detection limit during the wet season, which could have been caused by lower plant production and deposition to wet surfaces. A strong seasonality was observed during the transition from the wet to the dry season. For the dry season, the overall higher mixing ratios above the canopy suggested chemical production from the oxidation of primarily emitted VOCs or transport from other regions. However, higher mixing ratios within the canopy in the afternoon (15:00) indicated a biogenic methanol emission due to pectin aging in cell walls during leaf growth (Galbally and Kirstine, 2002; Kesselmeier et al., 2009). Leaf area index (LAI) measurements demonstrated a growth of the canopy during the period of July 2013 to September 2013 (G. Martins, personal communication, 2014).

Acetonitrile is currently regarded to be primarily emitted from biomass burning sources with an oceanic and photochemical sink, but a biogenic source cannot be excluded (Bange and Williams, 2000; Andreae and Merlet, 2001; Nyalala et al., 2011). Our data differed significantly between the seasons with mixing ratios 2.5 times higher

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during the dry season than detected in the wet season, which is consistent with an influence from biomass burning in September 2013. As we did not observe distinct biomass burning plumes, long-range transport may be assumed. Such burning activities can be expected during this time of the year (Karl et al., 2007a). In addition the observation that levels decrease towards the ground could indicate a potential uptake by soil bacteria, although wet deposition cannot be excluded. The variability of the measurements especially inside the canopy occults a possible influence by plant emissions which has previously been reported (Bange and Williams, 2000; Nyalala et al., 2011).

4.2 Comparison to other observations in Amazonian rainforest ecosystems

Due to the immense area of the Amazonian ecosystem and the paucity of measurements, a great variability of plant species and atmospheric BVOC levels is observed. An overview of the investigated BVOCs was assembled from literature values (for isoprene, monoterpenes, acetaldehyde, acetone, MEK, MVK + MACR, methanol and acetonitrile) in Table 2 to be compared to this study. Isoprene has been the compound most measured, due to its high abundance and the ease of measuring it as compared to other more reactive compounds. Although isoprene values reported in this study generally agree with previously reported values, our values for isoprene in the wet season are the lowest reported. This was most likely due to the low sampling heights (i.e. 0.05 and 0.5 m), which were never reported for an Amazonian ecosystem before, but are needed to characterize the isoprene behaviour close to the ground. Monoterpene mixing ratios for this study were the highest ever reported for Amazonian ecosystem level measurements, although still within a similar range to some studies (Rinne et al., 2002; Jardine et al., 2011). This compares to ecosystems such as boreal forests, known to strongly emit monoterpenes. For instance, a mean mixing ratio of 1.1 ppb was observed in Hyytiälä, Finland during July, when the highest emissions occur (Raisanen et al., 2009), as compared to mean mixing ratio for monoterpenes of 1 ppb during the dry season in this study. In agreement with Kanakidou et al. (2005), further efforts on monoterpene characterization in terms of abundance and reactivity in Amazonia is

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needed for a better understanding of SOA growth and formation, regionally as well as worldwide. Oxidation capacity is reflected by higher values for MVK + MACR as was always found above the canopy (Table 2), especially when measured in the mixed layer by aircrafts (Karl et al., 2007b; Kuhn et al., 2007) or tethered balloons (Kesselmeier et al., 2000).

The reported values in the literature for acetaldehyde, methanol, acetone, and MEK are too scarce to make reliable conclusions. We report the highest mixing ratios for acetone and methanol. Acetonitrile seems to match previous measurements, and the lack of surface measurements of MEK does not allow a comparison. Therefore more continuous measurements with a better representation in space and height are needed to investigate the seasonality of within and above canopy interactions with the atmosphere to improve our understanding of BVOC over Amazonia (Greenberg and Zimmerman, 1984; Gregory et al., 1986; Rasmussen and Khalil, 1988; Helmig et al., 1998; Kesselmeier et al., 2000, 2002b; Warneke et al., 2001; Rinne et al., 2002; Greenberg et al., 2004; Rottenberger et al., 2004; Pöschl, 2005; Karl et al., 2007b; Kuhn et al., 2010, 2007; Rizzo et al., 2010; Jardine et al., 2011, 2012).

5 Conclusions

Our first BVOC measurements at the ATTO site provide unique information about the role of these compounds in the Central Amazon rainforest area within and above the canopy. Marked seasonality and diurnal behaviour is observed at the site, seen in the difference in mixing ratios and changes in vertical patterns. This is attributed to changing sources of these compounds mainly in relation to seasonal fluctuations of light, temperature and phenology. Whereas during the wet season, VOCs seem to be solely produced by vegetation, and mixing ratios are highest within the canopy, during the dry season additional BVOC sources from the atmosphere become apparent, where mixing ratios increased in magnitude and presented a different diurnal pattern with respect

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to the wet season. This indicates a mixture of sources such as vegetation emissions, oxidation from primary emitted BVOCs and regional atmospheric transport.

The summary of BVOC mixing ratios in the Amazonian ecoregion (Table 2) shows an enormous variation depending on sites, heights and seasons. Year-round continuous measurements are required in order to improve our understanding of the within canopy BVOC dynamics and their interaction with the atmospheric chemistry in such bio-diverse ecoregions forming the Amazonian rainforest.

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Table 1. Compounds calibrated for PTR-MS measurements with respective protonated mass-to-charge (m/z), PTR-MS dwell time and detection limit (LOD).

m/z	Compound	Dwell time	LOD Mar (ppb)	LOD Sep (ppb)
33	Methanol	200 ms	1.7	1.15
42	Acetonitrile	1 s	0.04	0.01
45	Acetaldehyde	1 s	0.28	0.17
59	Acetone	1 s	0.13	0.07
69	Isoprene	1 s	0.09	0.1
71	Methyl vinyl ketone + Methacrolein	1 s	0.03	0.05
73	Methyl ethyl ketone	1 s	0.09	0.06
81+137	Monoterpenes	5 s	0.23	0.05

Table 2. Mixing ratios of isoprene, methanol, acetaldehyde, acetone, acetonitrile, MEK, MVK + MACR and total monoterpenes measured at different Amazonian forest sites. In the second column different sites can be found: duke reserve is a scientific research site 25 km NE of Manaus (2°55′ S, 59°59′ W); Peru (4°35′15″ S, 77°28′00″ W); Balbina 100 km NE of Manaus (1°59′ S, 59.12′ W); C14 a tower in the Reserva Biologica de Cueiras, 50 km NW of Manaus (2°28′ S, 60°09′ W); Surinam (2–5° N, 54–57° W); Jaru-Rondonia: is the Rebio Jaru natural reserve in Rondonia, (10°04′55″ S, 61°55′48″ W); K34 is a tower located in the Reserva Biologica de Cueiras (2°35′33″ S, 60°12′27″ W); the TT34 is located in the same reserve (2°35.37′ S, 60°06.92′ W); the ATTO INSTANT tower is located in coordinates 2°08′39″ S, 58°59′59″ W. Seasons are specified together with the exact timing of sampling. Values are reported as medians and means during daylight periods as reported in the references. The values from this study are median values of the period from 12:00–15:00 during both seasons, except for total monoterpenes, methanol, acetaldehyde and MVK + MACR which in the dry season had higher median mixing ratios from 15:00–18:00. All values are in ppb.

Season	Site	Height	Iso-prene	Metha-nol	Acetal-dehyde	Ace-tone	Aceto-nitrile	MVK + MACR	MEK	Total Monoterpenes	Reference
Dry – Jul 2001	K34	52	3.40	–	–	–	–	–	–	0.34	Kuhn et al. (2007)
Dry – Jul 2001	K34	ML	4.70	–	–	–	–	0.50	–	0.23	Kuhn et al. (2007)
Dry – Jul 2001	Manaus	ML	1.80	–	–	–	–	–	–	–	Kuhn et al. (2010)
Dry – Aug/Sep 2004	C14	40	7.80	4.10	1.20	2.20	–	2.10	–	0.87	Karl et al. (2007)
Dry – Aug/Sep 2004	C14	ML	5.50	3.50	1.50	2.20	–	2.30	–	0.52	Karl et al. (2007)
Dry – Jul 2000	Santarem	47	4.50	–	–	–	–	–	–	0.90	Rinne et al. (2002)
Dry – Jun 1984	Manaus/Humaita	surface	2.40	–	–	–	–	–	–	0.27	Greenberg and Zimmerman (1984)
Dry – Sep 2013	ATTO	0.05	3.13	1.51	0.56	1.23	0.14	0.65	0.20	0.53	This study
Dry – Sep 2013	ATTO	0.5	3.77	1.63	0.45	1.22	0.15	0.61	0.19	0.55	This study
Dry – Sep 2013	ATTO	4	5.35	1.79	0.47	1.38	0.19	0.72	0.22	0.70	This study
Dry – Sep 2013	ATTO	24	7.62	5.04	0.82	1.68	0.25	2.34	0.43	1.02	This study
Dry – Sep 2013	ATTO	38	6.13	4.70	1.26	2.75	0.24	1.94	0.49	0.86	This study
Dry – Sep 2013	ATTO	53	5.72	5.44	2.04	3.48	0.25	2.80	0.53	0.89	This study
Dry – Sep 2013	ATTO	79	4.81	4.57	1.35	2.74	0.22	2.27	0.48	0.69	This study
Dry and D-t-W transition Sep–Dec 2010	TT34	2	2.20	–	–	–	–	–	–	0.55	Jardine et al. (2011)
Dry and D-t-W transition Sep–Dec 2010	TT34	2	–	–	–	–	–	0.80	–	–	Jardine et al. (2012)
Dry and D-t-W transition Sep–Dec 2010	TT34	11	3.20	–	–	–	–	–	–	0.76	Jardine et al. (2011)
Dry and D-t-W transition Sep–Dec 2010	TT34	11	–	–	–	–	–	1.15	–	–	Jardine et al. (2012)
Dry and D-t-W transition Sep–Dec 2010	TT34	17	3.20	–	–	–	–	–	–	0.82	Jardine et al. (2011)
Dry and D-t-W transition Sep–Dec 2010	TT34	17	–	–	–	–	–	1.20	–	–	Jardine et al. (2012)
Dry and D-t-W transition Sep–Dec 2010	TT34	24	2.90	–	–	–	–	–	–	0.80	Jardine et al. (2011)
Dry and D-t-W transition Sep–Dec 2010	TT34	24	–	–	–	–	–	1.30	–	–	Jardine et al. (2012)
Dry and D-t-W transition Sep–Dec 2010	TT34	30	2.80	–	–	–	–	–	–	0.75	Jardine et al. (2011)

Table 2. Continued.

| Season	Site	Height	Iso-prene	Metha-nol	Acetal-dehyde	Ace-tone	Aceto-nitrile	MVK + MACR	MEK	Total Monoterpenes	Reference
Dry and D-t-W transition Sep–Dec 2010	TT34	30	–	–	–	–	–	1.32	–	–	Jardine et al. (2012)
Dry and D-t-W transition Sep–Dec 2010	TT34	40	2.75	–	–	–	–	–	–	0.70	Jardine et al. (2011)
Dry and D-t-W transition Sep–Dec 2010	TT34	40	–	–	–	–	–	1.30	–	–	Jardine et al. (2012)
Dry and D-t-W transition Sep–Oct 1999	Jaru-Rondonia	52	15.0	3.00	∼ 3.5	0.30	–	∼ 0.7	–	∼ 0.5	Kesselmeier et al. (2002)
Dry – Jul/Aug 1985	Manaus	ML	2.30	–	–	–	–	–	–	0.23	Zimmerman et al. (1988)
Dry – Jun 1984	Guyana	ML	2.00	–	–	–	–	–	–	–	Gergory et al. (1986)
Dry – Jun 1996	Peru	2	3.31	–	–	–	–	1.24	–	0.22	Helmig et al. (1998)
Dry – Jun 1996	Peru	ML	1.69	–	–	–	–	0.87	–	0.22	Helmig et al. (1998)
Dry – Sep 2004	C14	53	7.80	3.50	< 1.5	1.75	0.20	–	–	0.29	Rizzo et al. (2009)
Dry – Jul/Aug 1985	Duke reserve	1	3.00	–	–	–	–	–	–	–	Rasmussen and Khalil (1988)
Wet – Feb 1999	Jaru-Rondonia	ML	6.68	–	–	–	–	–	–	0.69	Greenberg et al. (2004)
Wet – Feb/Mar 2013	ATTO	0.05	0.57	< 1.70	< 0.28	0.22	< 0.04	0.04	< 0.09	< 0.23	This study
Wet – Feb/Mar 2013	ATTO	0.5	0.57	< 1.70	< 0.28	0.22	0.04	0.04	< 0.09	< 0.23	This study
Wet – Feb/Mar 2013	ATTO	4	0.86	< 1.70	< 0.28	0.23	0.06	0.06	< 0.09	< 0.23	This study
Wet – Feb/Mar 2013	ATTO	24	2.29	< 1.70	0.94	0.98	0.09	0.15	0.38	< 0.23	This study
Wet – Feb/Mar 2013	ATTO	38	2.39	< 1.70	0.47	1.16	0.10	0.20	0.13	< 0.23	This study
Wet – Feb/Mar 2013	ATTO	53	1.85	< 1.70	0.33	0.94	0.08	0.20	0.12	< 0.23	This study
Wet – Feb/Mar 2013	ATTO	79	1.69	< 1.70	0.31	0.92	0.10	0.22	0.11	< 0.23	This study
Wet – Jan/Feb 1999	Tapajos	ML	0.54	–	–	–	–	–	–	0.08	Greenberg et al. (2004)
Wet – Mar 1988	Surinam	ML	3.30	4.00	–	–	–	∼ 1.5	–	–	Warneke et al. (2001)
Wet – Mar 1998	Surinam	ML	1.70	1.10	1.70	2.90	0.19	1.30	1.80	< 0.3	Williams et al. (2001)
Wet – Mar 1998	Surinam	ML	–	–	–	2.60	–	–	–	–	Pöschl et al. (2005)
Wet – Mar 1998	Balbina main	ML	2.30	–	–	–	–	–	–	0.20	Greenberg et al. (2004)
Wet – Mar 1998	Balbina 50 kmW	ML	2.90	–	–	–	–	–	–	0.21	Greenberg et al. (2004)
Wet – Mar 1998	Balbina 5 kmW	ML	2.10	–	–	–	–	–	–	0.25	Greenberg et al. (2004)
Wet – Mar/Apr 1998	C14	1.5	7.10	–	–	–	–	0.47	–	0.36	Kesselmeier et al. (2000)
Wet – Mar/Apr 1998	Balbina	1.5	6.00	–	–	–	–	0.43	–	0.68	Kesselmeier et al. (2000)
Wet – Mar/Apr 1998	C14	30	7.50	–	–	–	–	0.30	–	0.51	Kesselmeier et al. (2000)
Wet – Mar/Apr 1998	C14	50	6.13	–	–	–	–	0.62	–	0.46	Kesselmeier et al. (2000)
Wet – Mar/Apr 1998	Balbina	ML	3.00	–	–	–	–	1.90	–	0.14	Kesselmeier et al. (2000)
W-t-D transition – Apr/May 1999	Jaru-Rondonia	52	4.00	–	∼ 0.5	1.00	–	∼ 0.5	–	∼ 0.4	Kesselmeier et al. (2002)
W-t-D transition – Apr/May 1999	Jaru-Rondonia	52	–	–	4.00	–	–	–	–	–	Rottenberger et al. (2004)
W-t-D transition – May 1999	Jaru-Rondonia	25	8.00	–	–	–	–	–	–	–	Kuhn et al. (2002)
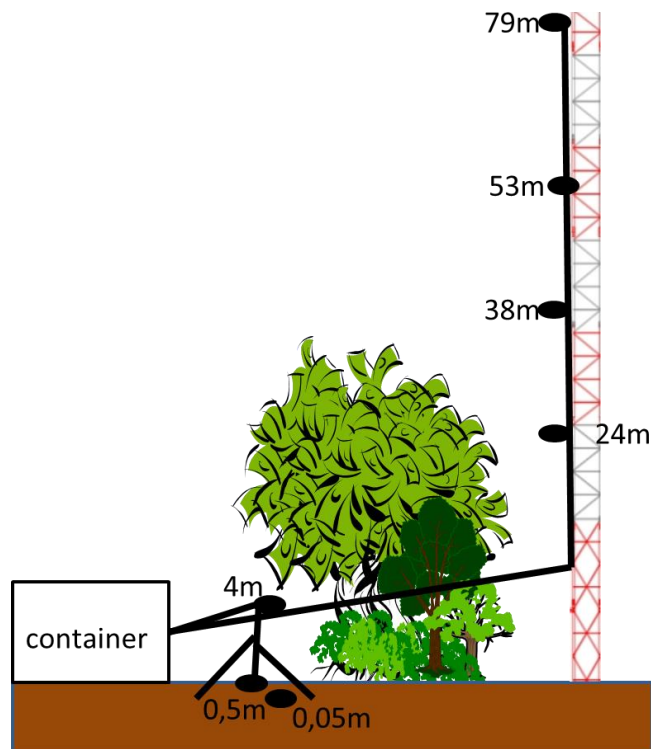
Figure 1. Schematic diagram of the experimental inlet set up. The various inlet heights at the tower and tripod are shown with respect to the canopy. The PTR-MS was housed in the air conditioned measurement container.
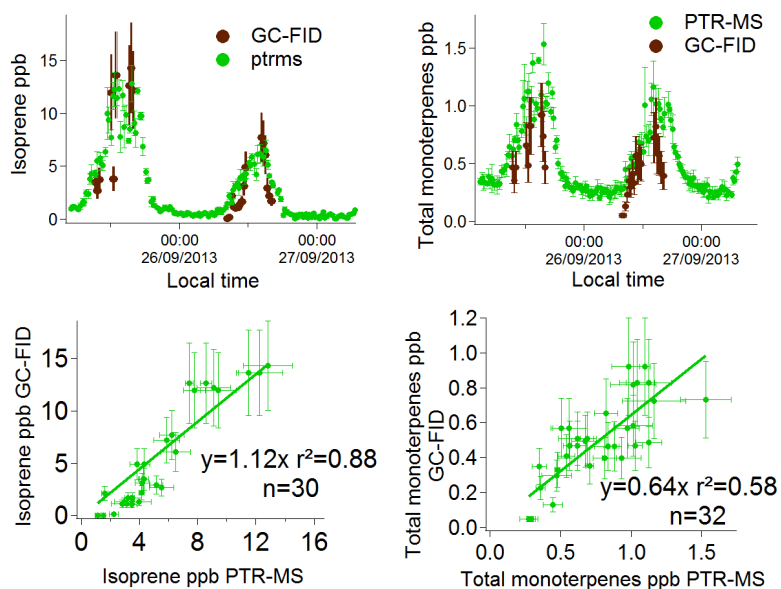
Figure 2. Top panels: example of PTR-MS and GC-FID time series data at the 25 and 26 September 2013 at 24 m for isoprene (left) and the total monoterpenes (right). Brown points are GC-FID measurements with an error of 30 % and green points are PTR-MS continuous measurements with SDs of the two-minute averages of the data. Bottom panel: correlation of isoprene (left) and total monoterpene (right) mixing ratios obtained by PTR-MS and GC-FID.
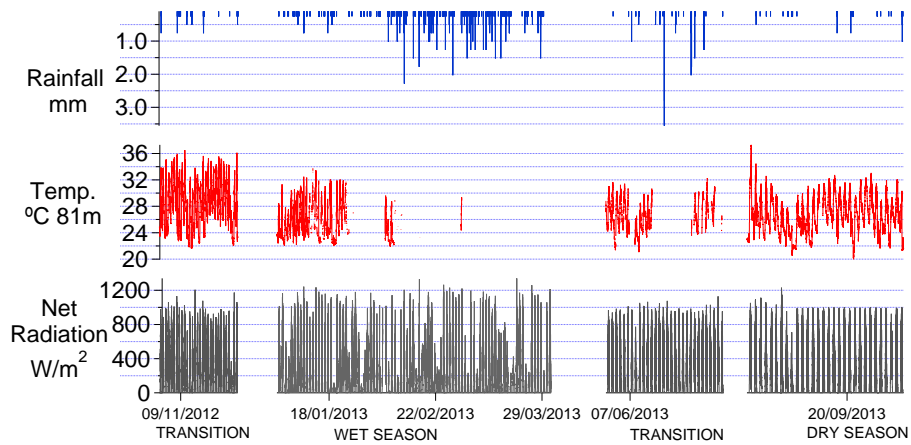
Figure 3. Meteorological data (two-minute averages) for the intensive measurement periods at the ATTO site for the 81 m level of the tower reporting rainfall (blue), temperature (red), and net radiation (grey).
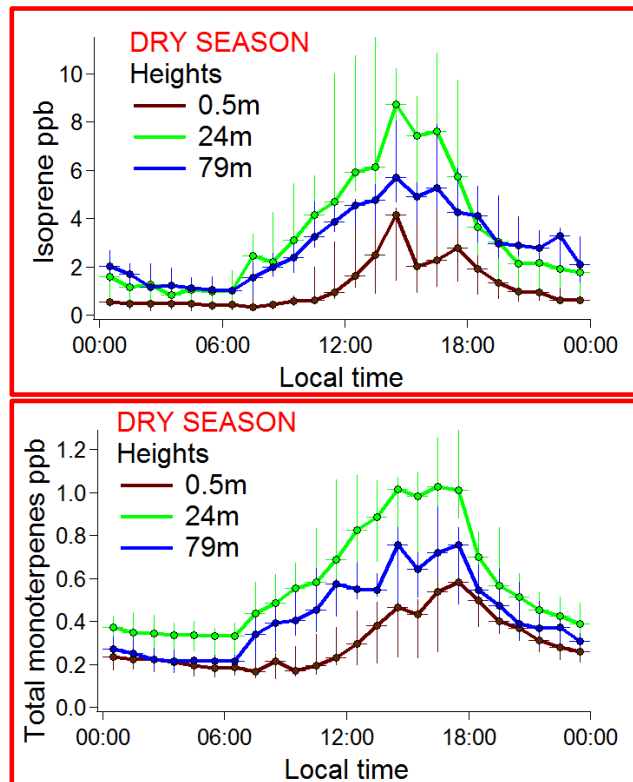
Figure 4. Diurnal hourly medians of isoprene (top) and the sum of monoterpenes (bottom) for the dry season. Range bars represent the 25 and 75 % percentiles.
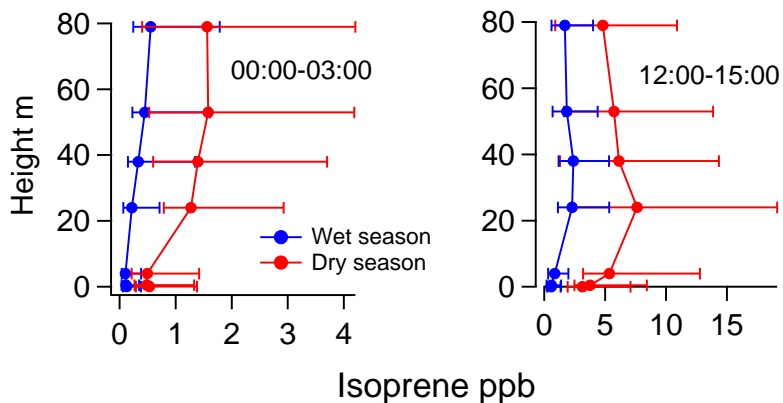
Figure 5. Vertical profiles for isoprene mixing ratios. Data is presented as medians over a period of 3 h between 00:00 and 03:00 (left) and 12:00 and 15:00 (right) (both LT). The 3 h medians are shown in red for the dry season and in blue for the wet season. Range bars represent the 25 and 75 % percentiles.
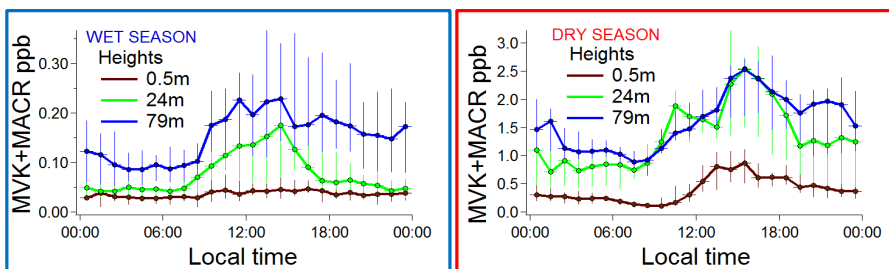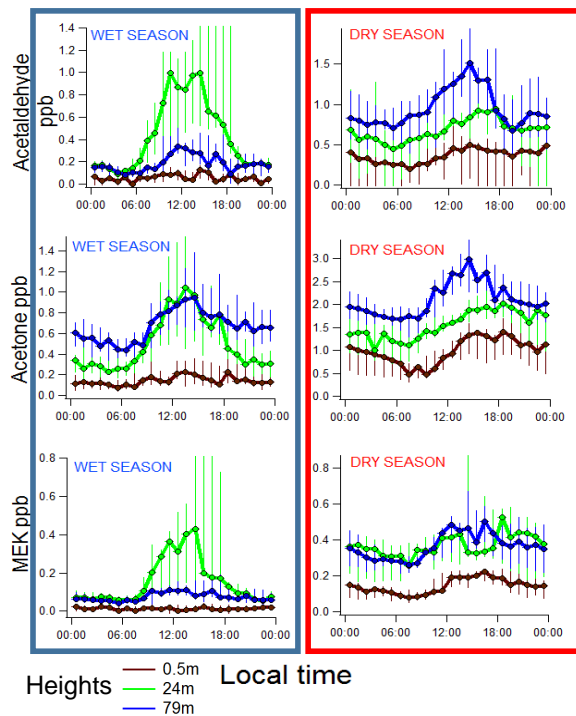
Figure 6. Diurnal hourly median MVK + MACR mixing ratios during the wet season (left) and the dry season (right) for different heights. Range bars represent the 75 % and the 25 % percentiles.
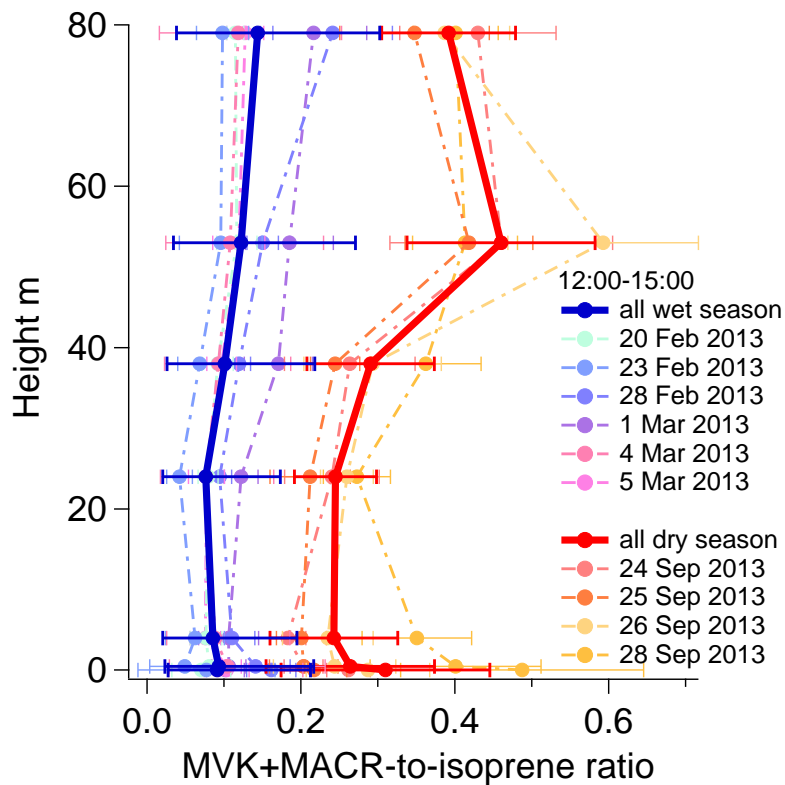
Figure 7. Average profiles of the MVK + MACR-to-isoprene ratio for the dry and wet season for the period of 12:00 to 15:00 for the whole measurement periods (thick lines) and as single day analysis (dashed lines).
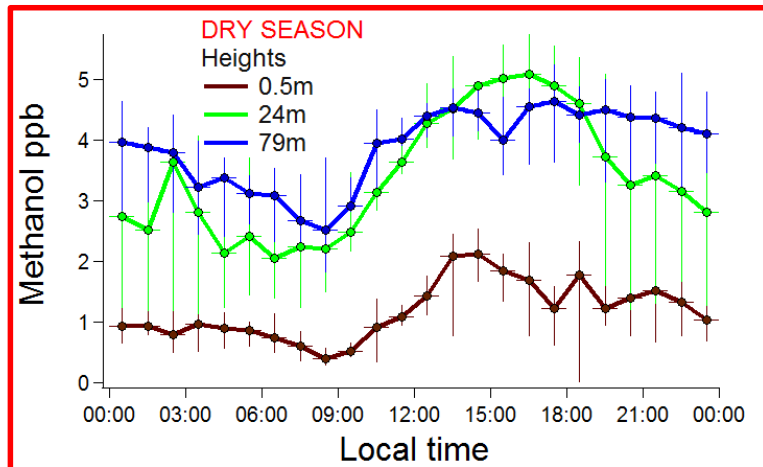
Figure 8. Diurnal medians for the wet season (left) and dry season (right), for acetaldehyde (top), acetone (middle) and methyl ethyl ketone (bottom) at different heights. Range bars are expressed as the 25 and 75 % percentiles.
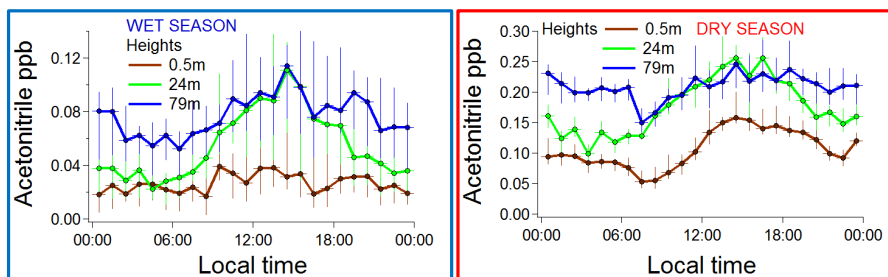
Figure 9. Diurnal hourly medians for methanol during the dry season at different heights. Range bars are expressed as the 25 and 75 % percentiles.

Figure 10. Diurnal hourly median acetonitrile mixing ratios during the wet season (left) and the dry season (right) for different heights. Range bars represent the 75 % and the 25 % percentiles.