Seasonality of isoprenoid emissions from a primary rainforest in central Amazonia

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Abstract

Tropical rainforests are an important source of isoprenoid and other Volatile Organic Compound (VOC) emissions to the atmosphere. The seasonal variation of these compounds is however still poorly understood. In this study, vertical profiles of mixing ratios of isoprene, total monoterpenes and total sesquiterpenes, were measured within and above the canopy, in a primary rainforest in central Amazonia, using a Proton Transfer Reaction – Mass Spectrometer (PTR-MS). Fluxes of these compounds from the canopy into the atmosphere were estimated from PTR-MS measurements by using an inverse Lagrangian transport model. Measurements were carried out continuously from September 2010 to January 2011, encompassing the dry and wet seasons. Mixing ratios were higher during the dry (isoprene – 2.68±0.9 ppbv, total monoterpenes - 0.67±0.3 ppbv; total sesquiterpenes – 0.09±0.07 ppbv) than the wet season (isoprene – 1.66±0.9 ppbv, total monoterpenes - 0.47±0.2 ppbv; total sesquiterpenes - 0.03±0.02 ppbv) for all compounds. Ambient air temperature and photosynthetically active radiation (PAR) behaved similarly. Daytime isoprene and total monoterpene mixing ratios were highest within the canopy, rather than near the ground or above the canopy. By comparison, daytime total sesquiterpene mixing ratios were highest near the ground. Daytime fluxes varied significantly between seasons for all compounds. The maximums for isoprene (2.53±0.5 μmol m^{-2} h^{-1}) and total monoterpenes (1.77±0.05 μmol m^{-2} h^{-1}) were observed in the late dry season, whereas the maximum for total sesquiterpenes was found during the dry-to-wet transition season (0.77±0.1 μmol m^{-2} h^{-1}). These flux estimates suggest that the canopy is the main source of isoprenoids emitted into the atmosphere for all seasons. However, uncertainties in turbulence parameterization near the ground could affect estimates of fluxes that come from the ground. Leaf phenology seemed to be an important driver of seasonal variation of isoprenoid emissions. Although remote sensing observations of changes in leaf area index were used to estimate leaf phenology, MEGAN 2.1 did not fully capture the behavior of seasonal emissions observed in this study. This could be a result of very local effects on the observed emissions, but also suggest that other parameters need to be better determined in Biogenic Volatile Organic Compound (BVOC) models. Our results support established findings that seasonality of isoprenoids are driven by seasonal changes in light, temperature and leaf phenology. However, they suggest that leaf phenology and its role on isoprenoid production and emission from tropical plant

species needs to be better understood in order to develop mechanistic explanations for seasonal variation in emissions. This also may reduce the uncertainties of model estimates associated with the responses to environmental factors. Therefore, this study strongly encourages long-term measurements of isoprenoid emissions, environmental factors and leaf phenology from leaf to ecosystem scale, with the purpose of improving BVOC model approaches that can characterize seasonality of isoprenoid emissions from tropical rainforests.

Key-words: Isoprene, monoterpenes, sesquiterpenes, leaf phenology, seasonal changes

1. Introduction

Terrestrial vegetation emits high quantities of biogenic volatile organic compounds (BVOCs) to the atmosphere (Guenther et al., 2006, 2012), which are removed by oxidation reactions, deposition of reaction products (Lelieveld et al., 2008) and consumption by surfaces (Gray et al., 2014). Emissions and subsequent transformations in the atmosphere have been widely explored by the scientific community. However, there is still a need for improving our understanding of how BVOC emissions and their reaction products vary seasonally and are involved in atmosphere chemistry, biogeochemical cycling and climate at local, regional and global scales.

Despite a large number of BVOC species that have been identified within plants and in emissions from plants, the largest part of the global biogenic emissions and subsequent effect on atmospheric chemistry are thought to be associated with isoprenoids (Laothawornkitkul et al., 2009). The isoprenoids are an important class of organic compounds that include isoprene (containing five carbon atoms - C_5), monoterpenes (10 carbon atoms - C_{10}), sesquiterpenes (15 carbon atoms - C_{15}) and diterpenes (20 carbon atoms - C_{20}) (Guenther, 2002).

Isoprene, as the building block of the higher order isoprenoids, is the dominant compound in emissions from many landscapes and has the single largest contribution to total global vegetation BVOC emission, with an estimated global annual emission of about

400─600 Tg C (see Table 1 of Arneth et al., 2008). Even though there are more than 1000 monoterpene compounds identified in plants, only a few (less than 12) monoterpenes comprise a large fraction of total monoterpene emissions into the atmosphere (Guenther, 2002). Compounds such as α-pinene, t-β-ocimene, β-pinene, limonene, sabinene, myrcene, 3-carene, camphene, β-phellandrene and terpinolene dominate monoterpene emissions globally (Guenther et al., 2012). However, at regional scales other monoterpene compounds may also be important (Geron et al., 2000; Jardine et al., 2015). Only a few (e.g., β-caryophyllene) of about 3000 sesquiterpenes and none of the 2000 diterpenes are known to be emitted into the atmosphere in considerable amounts (Guenther, 2002). However, there are many compounds in the atmosphere that are still unknown or unexplored (Goldstein et al., 2007, Park et al., 2013), suggesting that the characterization of sesquiterpene emissions and other trace gases is still an open question.

Although models indicate that tropical rainforests are the main source of isoprenoid emissions to the global atmosphere (Guenther et al., 2012), estimates of global annual emissions of isoprenoid still have large uncertainties (Guenther et al., 2006). One approach to constraining these estimates, specifically for isoprene, is the use of remotely sensed concentrations of BVOC oxidation products in the atmosphere in order to make top-down model estimates (Barkley et al., 2008, 2009, 2013; Stavrakou et al., 2009, 2015). This approach has also suggested seasonal patterns in the emissions of this organic compound (Barkley et al., 2009). In addition, seasonal variations of isoprene emissions in the Amazonian rainforest are suggested based on comparison of some studies with intensive campaigns *in situ* (Table 1). This seasonality may be driven by light and temperature seasonal variation and leaf phenology (Barkley et al., 2009), and seasonal changes in insolation is probably the main driver of leaf phenology (Jones et al., 2014).

Therefore, the objective of this study was to quantify the seasonal variation of mixing ratios and emissions of isoprene, total monoterpenes and total sesquiterpenes in a primary rainforest in central Amazonia and to correlate them to seasonal variations of environmental (temperature and light) and biological (leaf phenology) factors.

2. Material and methods

2.1 Site description

Isoprenoid vertical profiles were investigated at the triangular tower (TT34 tower - 2°35.37′S, 60°06.92′W) on a plateau of the Cuieiras Biological Reserve, a primary rainforest reserve located approximately 60 km northwest of Manaus city, in the central Amazonian Basin, in Amazonas, Brazil (Martin et al., 2010). The vegetation in this area is considered mature *terra firme* rain forest (Pires and Prances, 1985), with a leaf area index of 4.7 (Malhi et al., 2009). The diversity of tree species is above 200 species ha^{-1} (Oliveira et al., 2008). Annual precipitation is about 2500 mm (Fig. 1a), with December to May being the wetter period. Although severe droughts impacted part of the Amazon basin in 2005 and in 2010, those droughts did not affect central Amazonia (Marengo et al., 2008, 2011). However, micrometeorological measurements from 1999 to 2012 showed that from August to September the monthly cumulative precipitation can be less than 100 mm per month (Fig. 1a), characterizing this period as dry season. Average air temperature ranges between 24 °C (in April) and 27 °C (in September) (Fig. 1e). Soil moisture near the surface is slightly reduced (10%) during the dry compared to the wet season (Cuartas et al., 2012).

The period of this study (from September 2, 2010 to January 27, 2011) represents the second half of the dry season (September 2010 - October 2010), the dry-to-wet transition season (November 2010) and the beginning of the wet season (December 2010 - January 2011). The whole period of measurements includes the period of low precipitation and when precipitation is increasing (Fig. 1b), and when photosynthetically active radiation (PAR) (Fig. 1d) and air temperature (Fig. 1f) are at their peaks. As October 2010 had more precipitation only at the end of the month, for this study October 2010 is also considered as dry season. This is supported by the fact that the length and intensity of the dry season varies from year to year (da Rocha et al., 2009).

2.2. Isoprenoid measurements and data analysis

Ambient mixing ratio measurements of isoprene, total monoterpenes and total sesquiterpenes were carried out using a commercial high sensitivity proton-transfer reaction mass spectrometer (PTR-MS, IONICON, Austria). The PTR-MS was operated in standard conditions with a drift tube voltage of 600 V and drift tube pressure of 2.0 mbar (E/N, 136 Td). During each PTR-MS measurement cycle, the following mass-to-charge ratios (*m*/*z*) were monitored: 21 ($H_3{}^{18}O^+$), 32 ($O_2{}^+$), 37 (H_2O-H_3O^+) with a dwell time of 20 ms each; 69 (isoprene-H^+), 137 (total monoterpenes-H^+) and 205 (total sesquiterpenes-H^+) with a dwell time of 5 s each (Jardine et al., 2011, 2012; Lindinger et al., 1998). The isoprenoid vertical profile was installed with six ambient air inlets at different tower heights (2, 11, 17, 24, 30 and 40 m). Air was sequentially sampled during 10 min at each of the six heights, resulting in one complete profile every hour. Average mixing ratios were calculated for the daytime period (10:00 – 16:00, LT) and for the nighttime period (22:00 – 04:00, LT). Calibration slope (m, ppbv/normalized counts per second (PTR-MS signal)) for isoprene, total monoterpenes, and total sesquiterpenes were obtained twice in the field using the dynamic solution injection technique (Jardine et al., 2010). Solutions of isoprene, α-pinene, and β-caryophyllene standards (> 95% purity, Merk) in 100 mL of cyclohexane were injected into the mixing vial at 0.5, 1.0, 2.0, and 3.0 µL min^{-1} (30 min each flow rate) with a constant dilution flow of 1.0 slpm ultra high purity nitrogen passing through. The linearity of calibrations was significant, being r^2 of 0.92-0.97 for isoprene, r^2 of 0.98-0.99 for α-pinene, and r^2 of 0.90-098 for β-caryophyllene. Sample air isoprenoid mixing ratios were calculated by multiplying the calibration slope by normalized counts per second (PTR-MS signal) (average of two calibration slopes). Calibration slopes obtained on October 2010 were within 10 % relative to those from the calibration carried out in September 2010 (isoprene 7.2 %, α-pinene – 8.2%, and β-caryophyllene – 2.5%). For 4-7 days before each isoprenoid profile measurement period, ultra high purity nitrogen was run into the inlet of the PTR-MS for 2 h in order to obtain the background signals. The limit of detection for isoprene was 0.14 ppbv, 0.15 ppbv for total monoterpenes and 0.1 ppbv for total sesquiterpenes. More details about calibration and experimental design can be obtained in Jardine et al. (2011) and Jardine et al. (2012), in which a subset of these data are already described. While the previous study considered a subset of this data and time period (Jardine et al., 2011, 2012), this study examines the whole dataset and focuses on seasonality of mixing ratios and fluxes. Also, this is the first study in central Amazonia that correlates long-term measurements of isoprenoids, light and temperature, and leaf phenology.

2.3 Isoprenoid gradient flux, and modeled flux estimates - Model of Emissions of Gases and Aerosols from Nature (MEGAN 2.1)

Fluxes of isoprene, total monoterpenes and total sesquiterpenes - for dry, dry-to-wet transition and wet seasons - were estimated using the average daytime (10:00-14:00, LT) concentration vertical profile throughout the canopy and applying an inverse Lagrangian transport model (ILT) (Raupach, 1989; Nemitz et al., 2000; Karl et al., 2004; Karl et al., 2009). The source/sink distributions throughout the canopy were computed according to Eq. (1):

$$\vec{C} - C_{Ref} = \overleftrightarrow{D} . \vec{S} \qquad (1)$$

where $\vec{C}$ is the concentration (g m^{-3}) vector for the 6 levels, C_{Ref} is the concentration (g m^{-3}) at reference height (40 m), $\overleftrightarrow{D}$ (m) is a dispersion matrix, and $\overrightarrow{S}$ (mg m^{-2} h^{-1}layer^{-1}) is the resulting source/sink vector. $\overleftrightarrow{D}$ is expressed as a function of Lagrangian timescale and profiles of the standard deviation of the vertical wind speed (σ_w), which was normalized to friction velocity (u*). Integration over all source and sink terms ($\vec{S}$) yielded the canopy scale isoprenoid flux (mg m^{-2} h^{-1}). To parameterize $\overleftrightarrow{D}$, we use the Lagrangian timescale (Tl) parameterized according to Raupach (1989) and the vertical profile of the standard deviation of the vertical wind speed scaled to measured friction velocity. The normalized turbulence profile was taken from turbulence measurements inside and above the canopy at this site recorded as part of AMAZE-08 (Amazonian Aerosol Characterization Experiment 2008) (Karl et al., 2009). The friction velocity was averaged for each season using daytime data (10:00-14:00, LT) measured at a tower (K34 tower - 2° 36' 32.67" S, 60° 12' 33.48" W) that was 2 km away from the tower where isoprenoid profiles were measured (TT34 tower). The calculation of $\overleftrightarrow{D}$ was based on the far- and near-field approach described by Raupach (1989). As some model inputs (i.e., σ_w/ u*) were obtained during the wet season at the TT34 tower in 2008 (Karl et al., 2009), changes in canopy structure between the two studies could potentially affect the results of this study. However, previous work carried out at the K34 tower showed that u* along with other averaged turbulence data have quite similar daytime values in both wet and dry seasons (Ahlm et al., 2010; Araujo et al., 2002).

Once fluxes from the isoprenoid vertical profiles were obtained by the ILT, they were compared with the isoprenoid fluxes estimated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN 2.1). Isoprenoid emissions estimated by MEGAN 2.1 are based on a simple mechanistic model that takes into account the main processes driving variations in emissions (Guenther et al., 2012). As described by Guenther et al., (2012), the activity factor for isoprene, monoterpenes and sesquiterpenes (γ_i) considers the emission response to light (γ_P), temperature (γ_T), leaf age (γ_A), soil moisture (γ_{SM}), leaf area index (LAI) and CO_2 inhibition (γ_{CO2}) according to Eq. (2):

$$\gamma_i = C_{CE}\, LAI\, \gamma_P \gamma_T \gamma_A \gamma_{SM} \gamma_{CO_2} \qquad (2)$$

where C_{CE} is the canopy environment coefficient. For the present study, the canopy environment model of Guenther et al. (2006) was used. It has a C_{CE} of 0.57. MEGAN 2.1 was run with variation in light and temperature and LAI. Leaf age of the foliage was estimated by the model based on changes in LAI. Soil moisture and CO_2 inhibition activity factors were assigned a value $\gamma_{SM} = 1$ and $\gamma_{CO2} = 1$, respectively, which assumes no variation in these parameters. More details about the model settings can be obtained in Guenther et al. (2012).

Photosynthetic photon flux density (PPFD) and air temperature for all model runs were obtained from the K34 tower measurement time series (Program of Large Scale Biosphere-Atmosphere – LBA). LAI inputs were obtained by satellite observations from NASA MODIS during August 2010 to January 2011. The level-4 LAI product is composited every 8 days at 1-km resolution on a sinusoidal grid (MODIS-NASA, 2015).

2.4 Uncertainties associated with the ILT and BVOC emission modeling

The main source of errors for applying the ILT is related to the parameterization of two combined effects: (1) vertical diffusion coefficient which is based on measured σ(w)/u* profiles, and (2) Langrangian dispersion time scale (Tl). Moreover, some uncertainties may be due to systematic error sources with respect to (3) chemical losses, and (4) the number of source layers. The entire parameterization of combined effect (1) and (2) was tested using data from an earlier study (Karl et al., 2009, Karl et al., 2010), where a comparison with eddy covariance measurements was available. Taking the above conservative error assessment, the combined (effect 1 and 2) uncertainty is +/- 30%.

To account for chemistry (effect 3) we used a simple modification of the diffusion coefficient based on Hamba (1993), relying on the fact that the chemical loss will mainly influence the far field of the parameterization. Based on estimated OH and measured O_3 densities (Karl et al. 2009, Karl et al., 2010) calculated VOC fluxes were corrected accordingly. Due to low OH and O_3 densities in the canopy (<5 x 10^5 molecules cm^{-3} for OH and <10 ppbv for O_3) the chemical lifetime for isoprene and monoterpenes is considered large compared to the mixing timescale, leading to a chemistry correction on the order of <5% for isoprene and monoterpenes. This systematic error is included, but relies on an estimation of OH for isoprene. The overall uncertainty for isoprene is calculated as 0.3 – 4 % by varying in-canopy OH densities between 5 x 10^5 and 5 x 10^6 molecules cm^{-3}. It is noted that an in-canopy OH density of 5 x 10^6 molecules cm^{-3} is extremely unrealistic in such a dense canopy and only serves as a very conservative upper limit. Those assumptions were also considered for sesquiterpene flux estimates. However, a sensitivity test was carried out to show if the increasing ozone concentrations during the dry season could effectively affect sesquiterpene lifetime and then sesquiterpene flux estimates. For this test, sesquiterpene lifetime was changed in the ILT model using a range from 2 min to 8 hours (upper limit used for isoprene and monoterpene flux estimates). The lower limit (2 min) is based on the lifetime calculated for β-caryophyllene when it is exposed to 24-h average of 7 x 10^{11} molecules cm^{-3} of ozone (~30 ppb) (Atkinson and Arey, 2003). If all sesquiterpenes that occur in this site have similar reactivity with ozone as β-caryophyllene, the overall uncertainty for sesquiterpene flux estimates is calculated as up to 20% by varying sesquiterpene lifetime from 8 h to 2 min. It is noted that when considering a lifetime range from 8h to 10 min, the uncertainty for sesquiterpene flux estimates is calculated as up to 4%. The 20 % of uncertainty may be important only during the dry season, when ozone mixing ratios can eventually reach 30 ppbv above canopy (40 m) around noontime.

We have also investigated the effect of (4) - the number of source layers. If the number of selected source layers is too small, systematic errors of the calculated integrated fluxes arise. We have investigated this effect and found that in the present case, 6 source layers are sufficient to capture >90% of the flux. In the present setup, the ILT model does not converge for more than 9 layers and the numerical solution becomes unstable. If the ILT model would be initiated to only calculate two source layers, the integrated flux would be underestimated significantly (e.g. by up 50%). With 6 source layers we estimate a systematic error of <10% due to this effect. The combined effect of the systematic errors (3) and (4) is estimated to be 5-6%.

With respect to uncertainties in model estimates, one of the first quantitative estimates of biogenic VOC emissions (Lamb et al., 1987) included an estimate of uncertainty of 210% based on the propagation of uncertainties in emission factors, emission algorithms, amount of biomass, and land use distributions. This "factor of three" uncertainty has continued to be used as a rough assessment of the uncertainty of biogenic VOC emission model estimates applied on regional scales. A more recent study (Hanna et al., 2005) attempted a comprehensive assessment of each model component and concluded that the 95% confidence range on the calculated uncertainty in isoprene emission was about one order of magnitude while the calculated uncertainty for monoterpenes and other VOC was only ± 20%. Guenther (2013) suggests that the Hanna et al. (2005) study assigns isoprene a higher uncertainty only because more is known about isoprene, and so there are more parameters, and that the lack of observations for quantifying the uncertainties associated with individual model parameters limits the usefulness of this uncertainty estimation approach and instead recommends evaluations that consider the results of model comparisons with canopy scale observations. These studies indicate that models tend to agree with observations within ~30% for canopy scale studies with site specific parameters (Lamb et al., 1996) or for regional scale estimates with known land cover (Misztal et al., 2014) and differ by as much as a factor of two or more for other regional scale studies (Muller et al., 2008; Warneke et al., 2010).

2.5 Canopy light penetration and leaf phenology

The standard canopy environment model of MEGAN 2.1 was used to model light penetration into the canopy (Guenther et al., 2006). Model inputs included the above-canopy PAR measured (every 30 min) at 50 m on the K34 tower for the whole period of isoprenoid measurements as well as the estimated surface area density of the canopy (m^2 m^{-3}), with measurements carried out in March 2004 using a Light Detection and Ranging sensor (LIDAR) in a transect on the same plateau area of this study (Parker and Fitzjarrald, 2004).

The light penetration was modeled for five canopy layers distributed from the canopy top to the ground surface. The thickness of each of the five layers was determined based on the canopy surface area density estimated for every 50 cm from the ground surface to the top canopy (Parker and Fitzjarrald, 2004). The layers were distributed according to a Gaussian curve fit to the canopy surface area densities (from 0.5 m to 48 m). Light absorption was calculated as the difference in the model estimate of downward light at the top and bottom canopy levels. This light absorption corresponded to light that passed through the canopy vertically. Reflectance and scattering were not considered.

Leaf phenology was estimated based on the observation of leaf flushing events of the upper crown surfaces of 63 living trees around the K34 tower (~ 2 km far of TT34 tower). For this approach, it is assumed that the leaf phenology of the upper crown surfaces of trees around both towers is similar. For the monitoring, a system of data acquisition and storage, based on a Stardot (model Netcam XL 3MP) camera with a 1024 x 768 resolution CMOS sensor, was installed at K34 tower, at 15-20 m above the canopy. The camera viewing angle was south azimuth, perpendicular to the solar transit, centered on 32º of depression and pointing out to an area of plateau. Images were logged every 15 s to a passively cooled FitPC2i with heat-tolerant SSD drive. The whole system of data acquisition automatically rebooted after power outages. The images obtained by the camera covered approximately 66º horizontally and 57º vertically, fitting the forest canopy without including any area of sky in the image. The most distant trees in the image were located 150 m from the camera. The framework was fixed by monitoring the same 63 treetops over four months of observation (October 2010 – January 2011). The analysis of images was based on the number of treetops that showed leaf flushing within one month. For this, one image was selected at every six days, and then grouped for each month of this study.

2.6 Satellite-derived isoprene emission estimates

Top-down isoprene emission estimates over the 0.5 degree region around TT34 tower were obtained by using a grid-based source inversion scheme (Stavrakou et al., 2009) constrained by formaldehyde (HCHO) columns. HCHO is an intermediate product of the isoprene degradation process (e.g. Stavrakou et al., 2014). It is measured by UV-visible sensors, such as on the Global Ozone Monitoring Experiment (GOME-2)/MetOp satellite launched in 2006. The source inversion was performed using the global chemistry-transport model IMAGESv2 (Intermediate Model of Annual and Global Evolution of Species) run at a resolution of 2º × 2.5º and 40 vertical levels from the surface to the lower stratosphere (Stavrakou et al., 2014, 2015). The priori isoprene emission inventory is taken from MEGAN-MOHYCAN-v2 (Stavrakou et al., 2014, http://tropo.aeronomie.be/models/isoprene.htm), and includes updates regarding isoprene emission rates from Asian tropical forests. IMAGESv2 uses HCHO columns retrieved from GOME-2 sensor as top-down constraints and estimates the posterior biogenic isoprene emission on the global scale. Note that given the early morning (9:30) overpass time of the GOME-2 measurement, and the mostly delayed production of formaldehyde from isoprene oxidation, the top-down emission estimate is dependent on the ability of MEGAN to simulate the diurnal shape of isoprene emission and on the parameterization of chemical and physical processes affecting isoprene and its degradation products in IMAGESv2. For this study, we use daily (24 hours) mean satellite-derived isoprene emissions derived from January 2010 to January 2011. More details can be found in Stavrakou et al. (2009, 2014, 2015) and Bauwens et al. (2013).

3. Results and Discussion

3.1 Diurnal variation of isoprenoid mixing ratios

Vertical profiles of isoprenoids were analyzed for daytime and nighttime for all the seasons considered in this study. Isoprene (Fig. 2 a, b, c) and total monoterpenes (Fig. 2 d, e, f) had higher mixing ratios during daytime (10:00-16:00, LT) than during nighttime (22:00-04:00, LT) for all seasons, supporting the findings that emissions of isoprene (Alves et al., 2014; Harley et al., 2004) and monoterpenes (Bracho-Nunez et al., 2013; Kuhn et al., 2002, 2004a; Jardine et al., 2015) from Amazonian plant species, at least at this site, are primarily light-dependent and stimulated by increasing temperature.

During daytime, isoprene had a maximum mixing ratio within the canopy. By comparison, at nighttime maximum values occurred above the canopy, and the vertical profiles were similar to those of nighttime air temperature (Fig. 2 j, k, l). As isoprene is not emitted at night, this maximum nighttime abundance of isoprene above the canopy may be due to the daytime residual layer concentrations. In addition, isoprene lifetime increases during nighttime owing to the decrease of OH (hydroxyl radical) concentrations in the dark (Goldan et al., 1995) in light of the low concentrations of nitrogen oxides (NO_x) in Amazonia (≤ 3 ppb above the canopy during nighttime in the dry-to-wet transition season) (Andreae et al., 2002). Similar results found at another site in central Amazonia suggested that low isoprene concentrations near the ground after sunset could be due to deposition onto and consumption by surfaces (Yáñez-Serrano et al., 2015). Isoprene up-take in the soil has been suggested previously in central Amazonia (Silva, 2010), possibly because of isoprene microbial consumption (Cleveland and Yavitt, 1997; Gray et al., 2014). As with isoprene, higher mixing ratios of total monoterpenes were observed during daytime, indicating that they are light-dependent, which agrees with the evidence of recent photosynthetic origin of monoterpenes (Jardine et al., 2015; Loreto et al., 1996).

The vertical profile of total sesquiterpene mixing ratios differed from that of isoprene and total monoterpenes for all seasons. Total sesquiterpenes had higher mixing ratios near the ground and at the sub-canopy level (17 m) than above the canopy (Fig. 2 g, h, i) ($P < 0.05$). Daytime and nighttime vertical profiles had similar shape, but total sesquiterpene mixing ratios were higher during the nighttime. Even though sesquiterpene emissions for some plant species are both light- and temperature-dependent (Duhl et al., 2008), results reported here indicate that sesquiterpene emissions are not strongly light-dependent in this site, suggesting that their daily variation is driven primarily by temperature. Since some studies have shown that sesquiterpenes are found in the essential oil stored in Amazonian forest trees (e.g. Lima et al., 2005), emissions from these storage structures would not be expected to be light-dependent. In contrast, the monoterpenes, while also present in Amazonian tree essential oil (e.g. Fidelis et al., 2012; Lima et al., 2005), appear to be dominated by emissions that occur with no storage (e.g. Loreto et al., 1996; Jardine et al., 2015), similar to isoprene emission processes. Another reason for the higher total sesquiterpene mixing ratios at nighttime might be because the ozonolysis of sesquiterpenes during daytime can reduce ambient sesquiterpene concentrations, as previously reported for a subset of these data (Jardine et al., 2011). With daytime ozone mixing ratios up to 40 ppbv (40 m) during the dry season, sesquiterpene lifetime with respect to ozonolysis above the canopy (40 m) can be 2 min during the daytime and 5 min during the nighttime (Jardine et al., 2011). Additionally, sesquiterpene concentrations can build up near the surface, because during nighttime the storage in the forest dominates (80-90%) and is significantly larger than the turbulent flux (Karl et al., 2004).

3.2 Seasonal variation on isoprenoid mixing ratios and emissions

Vertical profiles of isoprene had higher mean mixing ratios in the dry season, followed by the dry-to-wet transition season and wet season (top panel of Fig. 3 a). The reduction of isoprene mixing ratios from the dry season to dry-to-wet transition season was up to 20% and from dry season to wet season was up to 65%. During the dry season, the higher mixing ratios and emissions of isoprene have been attributed to the higher insolation and higher temperatures compared to the wet season and, for this reason, higher isoprene concentrations at the top of the canopy are expected. Nevertheless, in contrast to the observations of Yañez-Serrano et al. (2015), who reported maximum daytime mixing ratios of isoprene at the top of the canopy for both dry and wet seasons, this study showed the highest isoprene mixing ratios inside the canopy (11 m) during the dry season, with this maximum moving to the upper canopy during the dry-to-wet transition season (24 m).

Isoprene emissions inferred from concentration vertical profiles were estimated to be highest in the sub-canopy (16 m) during the dry season and in the upper canopy (28 m) during the dry-to-wet transition season and the wet season (Fig. 4 a). Even though there were differences in which layer was the highest emitter of isoprene within the canopy, mean isoprene emissions into the atmosphere were about the same for the dry season and the dry-to-wet transition season (1.37 ± 0.7 mg m^{-2} $h^{-1}$and 1.41 ± 0.1 mg m^{-2} h^{-1}, respectively). Both of these seasons had higher isoprene emissions than during the wet season (0.52 ± 0.1 mg m^{-2} h^{-1}) (Fig. 4 b).

The maximum absorption of PPFD by canopy, calculated based on PPFD penetration profile modeled by the standard MEGAN 2.1 canopy environment model, occurred right above the maximum of estimated surface area density of the canopy, with the absorption of PPFD being higher during the dry season, followed by the wet season and the dry-to-wet transition season (Fig. 3 b). This maximum PPFD absorption at the upper canopy agreed with the maximum of isoprene mixing ratios (top panel of Fig. 3 a) and emissions (Fig. 4 a) during the dry-to-wet transition season. It differed, however, when compared to peaks of isoprene mixing ratios and emissions during the dry season and the wet season.

One reason for this difference could be the isoprene oxidation in the atmosphere and within plant, especially at the top of the canopy. During the dry season the ratio of methyl vinyl ketone + methacrolein + hydroperoxides (MVK+MAC+ISOPOOH) (Liu et al., 2013) to isoprene was higher compared to the dry-to-wet transition and the wet season (data not shown). This higher ratio may indicate an increased oxidative capacity of the atmosphere during the dry season. Moreover, a small source of MVK+MAC+ISOPOOH was observed at the top of the canopy (Jardine et al., 2012). Under conditions of high abiotic stress, as can occur in the dry season, elevated isoprene oxidation rates in plants can be observed and isoprene oxidation products might be directly emitted by plants (Jardine et al., 2012).

Another important factor might be leaf phenology and/or leaf demography. Different tree species have different isoprene emissions rates, and these rates depend upon the leaf ontogenetic stage. Isoprene emitters can flush at different canopy levels seasonally, and changes in within-canopy isoprene vertical profiles would be expected as a result. Moreover, as more leaf flushing was observed at the upper canopy during the wet-to-dry transition and early dry season, this caused leaves in the age group of 3-8 months to reach the highest abundance in late dry season and early wet season (Nelson *et al.*, 2014). The period with the high abundance of leaves in this age group is coincident with the period when gross ecosystem productivity and landscape-scale photosynthetic capacity is most efficient (Restrepo-Coupe et al., 2013). Here, results show maximum isoprene emission at the upper canopy during the dry-to-wet transition season (Fig. 4 a), which is coincident with the period of high abundance of healthy efficient leaves at the canopy top (Nelson et al., 2014) and also coincident with the maximum isoprene emission shown in young mature leaves in the dry-to-wet transition season (Alves et al., 2014). Similarly, higher isoprene emissions during the late dry season have also been related to the increase of active biomass in southern Amazonia (Kesselmeier et al., 2002; Kuhn et al., 2004a, 2004b).

Although the isoprene mixing ratios reported here are within the range of previously reported values in central Amazonia for the dry season and the dry-to-wet transition season (Greenberg and Zimmerman, 1984; Rasmussen and Khalil, 1988; Zimmerman et al., 1988) and for the wet season (Yáñez-Serrano et al., 2015), these results are the lowest observed fluxes of isoprene to atmosphere reported for the Amazonia. However, this could be due to the particular location of the site of this study, such as the relatively open canopy, caused by the proximity to a dirt road, and perhaps the site has a relatively low fraction of isoprene emitting species. Isoprene fluxes measured previously at the same tower site during the wet season were similar (Karl et al., 2009).

Total monoterpenes also showed a strong seasonal variation with maximum mixing ratios during the dry-to-wet season, followed by the dry season and the wet season (middle panel of Fig. 3 a). Taking mixing ratios of the dry-to-wet transition season as a reference, total monoterpene mixing ratios showed an increase of up to 20% from the dry season to the dry-to-wet transition season, and a decrease of up to 50% from the dry-to-wet transition season to the wet season. Although total monoterpene mixing ratios were somewhat higher in the dry-to-wet transition season than during the dry season, total monoterpene fluxes inferred by the vertical profiles were slightly higher during the dry season (1.47 ± 0.06 mg m^{-2} h^{-1}) compared to the dry-to-wet season (1.29 ± 0.2 mg m^{-2} h^{-1}) (Fig. 4 e), indicating that the production is higher in the dry season and losses are also higher, leading to lower mixing ratios. In comparison, emissions from these two seasons were considerably higher than during the wet season (0.36 ± 0.05 mg m^{-2} h^{-1}) (Fig. 4 e). This again indicates that higher insolation and air temperature during the dry season and dry-to-wet transition season compared to the wet season increased the atmospheric concentrations of monoterpenes and, considering the enhanced ozone mixing ratios during the dry season, this may influence the seasonal pattern in monoterpene ozonolysis loss rates (Jardine et al., 2015). These results agree with branch level measurements that showed higher monoterpene emissions during the dry-to-wet transition season compared to the wet-to-dry transition season (Kuhn et al., 2004a). However, results reported here differ from those presented for the southern Amazonia, where monoterpene mixing ratios were higher during the wet season than during the dry season (Kesselmeier et al., 2002). Although only a few studies have been carried out with the objective of investigating monoterpene seasonal variations, factors other than light and temperature might influence monoterpene emissions from vegetation, including the oxidative capacity of the atmosphere and leaf phenology (Kesselmeier et al., 2002; Kuhn et al., 2004a).

Total monoterpene mixing ratios and fluxes, during the dry season and the dry-to-wet transition season, were similar to values reported for other sites in central Amazonia (Karl et al., 2007; Yáñez-Serrano et al., 2015). However, the monoterpene comparison of reported studies is a difficult endeavor given that some techniques measured total monoterpenes and others measured some specific monoterpene compounds, and also because monoterpene fragmentation during measurements (PTR-MS) could affect the absolute values of these compounds. Therefore, further efforts are needed in order to characterize the seasonal abundance and the seasonal species-specific composition of monoterpenes in the Amazonia.

Average vertical profiles of total sesquiterpene mixing ratios were higher in the dry-to-wet transition season, followed by the dry season and the wet season (bottom panel of Fig. 3a). Taking mixing ratios of the dry-to-wet transition season as a reference, total sesquiterpene mixing ratios increased up to 30% from the dry season to the dry-to-wet transition season and decreased by up to 55% from the dry-to-wet transition season to the wet season. During the dry season and the dry-to-wet transition season, the maximum total sesquiterpene mixing ratios were observed near the ground. During the wet season, the maximum mixing ratio was at 17 m (sub-canopy). According to Jardine et al. (2011), during the daytime many sesquiterpenes (46%–61% by mass) are rapidly oxidized by ozone as they undergo within-canopy ozonolysis and contribute to the scarcity of total sesquiterpenes above and near the top of the canopy. Considering that higher insolation and also higher ozone concentrations were observed during the dry season (ozone daily average of ~ 23 ppbv and ~ 10 ppbv at 40 m in the dry and wet seasons, respectively), an important fraction of the sesquiterpenes emitted by vegetation could be rapidly oxidized by ozone, leading to significantly lower mixing ratios of total sesquiterpene during the dry season (Jardine et al., 2011), which creates a need to account for sesquiterpene oxidation within the canopy when calculating emission rates.

Another potential reason for higher mixing ratios of total sesquiterpenes near the ground is that emission could come from surface sources including litter, roots and soil microbes and fungi. Silva (2010) presented surface BVOC emissions at this site, and the results suggested that the litter decomposition could be an important source of sesquiterpenes to the atmosphere. Litter production is higher during the dry than during the wet season

(Luizão et al., 1989), which could lead to higher amounts of litter at the end of the dry season. Rain starting to increase in the dry-to-wet transition could contribute to more decomposition of the litter storage, which can potentially increase sesquiterpene emissions during the processes of decomposition of dead organic matter. Although the ecological functional role of these sesquiterpenes is not known, abiotic emissions from the litter have a specific signature that can be similar to the concentration profile in the green leaf content (Austin et al., 2014) and in sufficient concentration BVOCs can have the capacity of attracting and repelling soil organisms to a specific location (Austin et al., 2014). Therefore, higher sesquiterpene emissions from the litter could be a signal to the fauna related to the decomposition process and represent an important step of the biogeochemical cycling.

In contrast to the mixing ratios, the source-sink distribution analysis made from the vertical profiles of total sesquiterpenes indicated that the main source of these compounds is the canopy (24 m) (Fig. 4 g), and the integration of sources and sinks showed that the highest total sesquiterpene emission rates going into the atmosphere was during the dry-to-wet transition season (0.77 ± 0.1 mg m^{-2} h^{-1}), followed by the dry season (0.38 ± 0.2 mg m^{-2} h^{-1}), and the wet season (0.34 ± 0.2 mg m^{-2} h^{-1}) (Fig. 4 h). However, although Nemitz et al. (2000) have suggested that limitations on the σ_w/u^* parameterization close to the ground do not affect the net flux above the canopy, here we strongly suggest future studies focus on better characterizing the turbulence and oxidation processes at this site, in order to verify the source-sink distribution of sesquiterpenes within the canopy and the emissions from the canopy to atmosphere. This should include speciated sesquiterpene measurements in order to account for their specific reactivity with ozone and other oxidants.

Relative emissions can be calculated as emissions normalized to standard conditions of above-canopy PAR of 1500 µmol m^{-2} s^{-1} and temperature of 30 °C. Based only on light, temperature and LAI variation, relative emissions estimated by MEGAN 2.1 were maximum during the dry season for isoprene, α-pinene, and β-caryophyllene (Fig. 4 c, f, i), when the highest light and temperature were observed. This prediction differs from the ILT flux estimates (Fig. 4 b, e, h), which showed similar emissions between the dry and the dry-to-wet season for isoprene and total monoterpenes and maximum emission during the dry-to-wet season for total sesquiterpenes. The overall uncertainties related to ILT flux was calculated as ± 36% and MEGAN estimates are considered to be in agreement with observations when they are within ~30%. However, more observation studies are needed in order to evaluate the degree of observation-modeling agreement and to improve model approaches, especially for total monoterpenes and total sesquiterpenes, which could present larger uncertainties due to the lack of information about atmospheric concentrations and reactivity of monoterpene and sesquiterpene chemical species in Amazonia.

To compare the seasonal variation of isoprenoid emissions with changes in environmental (light and temperature) and biological (LAI) factors in more detail, monthly fluxes of isoprenoids were compared to PAR at 51 m, air temperature at 51 m, and LAI (satellite observations - MODIS) (Fig. 5). The highest fluxes of isoprene and total monoterpene were observed when PAR was at its highest (October 2010) (Fig. 5 b, c), and when there is high abundance of healthy efficient leaves (Nelson et al., 2014). The similarity in the behavior of isoprene and monoterpene emissions is supported by the evidence of the photosynthetic origin of monoterpenes (Jardine et al., 2015; Loreto et al., 1996). Interestingly, in September 2010 total monoterpene emissions were higher than isoprene emissions. This could be related to the higher source of monoterpenes in the upper canopy compared to isoprene during this month. When there are more young leaves at the upper canopy during the first half of the dry season (Nelson et al., 2014), high emissions of monoterpenes can be expected. Total sesquiterpene fluxes tracked neither PAR nor air temperature, having the highest emission when PAR and air temperature were decreasing (November 2010) (Fig. 5 d).

Predictions from MEGAN 2.1 again differed from measured emissions (Fig. 5 b, c, d), showing a reduction in emissions from September 2010 to January 2011. Major quantitative differences between ILT and MEGAN estimates can be shown for isoprene in September, when ILT estimates represented only 4 % of the MEGAN estimates; for total monoterpenes in December, when ILT estimates accounted for 14 % of the MEGAN estimates; and for total sesquiterpenes in November, when ILT estimates were 232% of the MEGAN estimates”. These differences may be related to local effects, especially leaf phenology and changes in the atmospheric oxidative capacity over the seasons. In order to evaluate the potential effect of leaf phenology on emissions, leaf flushing, PAR, isoprene and total monoterpenes at canopy scale were compared in Fig. 6. They closely tracked each other during the 4 months of measurements. For the period of this study, the analysis of canopy images for every six days from October 2010 to January 2011 showed a decrease in leaf flushing from the end of the dry season to the wet season, which was similar to the decrease of isoprene and total monoterpene emissions and PAR. Results from 28 months (October 2010-January 2013) of canopy imaging have shown that the highest number of treetops with leaf flushing occurred during the wet-to-dry transition season (June-July), accounting for 35-50 % of treetops with leaf flushing, followed by a subsequent decrease until the end of the wet season (Tavares, 2013) (Fig. 6). Correspondingly, the results of the present study suggest that lowest emissions might be expected in the June-July time period. These results agree with those presented by Barkley et al. (2009) using remote sensing, suggesting that seasonal changes in isoprene emissions may be strongly affected by leaf phenology in the Amazonia.

In order to verify if the seasonal trend of the isoprene emissions observed in this study can also be observed in a 0.5° grid cell around TT34 tower, isoprene emissions estimated based on tower vertical profile concentrations are compared with estimates constrained by satellite measurements of HCHO in Fig. 7. The top-down estimates have a seasonal cycle that is similar to the bottom-up approach. Compared to the dry season, fluxes decrease by 40% during the wet and the wet-to-dry transition season from April to July (Stavrakou et al., 2015), in qualitative agreement with the conclusions drawn in Barkley et al. (2009). The inferred dry season isoprene flux is about twice that of the wet-to-dry season. It peaks in September and gradually drops from October to January (Fig. 7), as a result of decreasing temperature and solar radiation, affecting the oxidation of isoprene leading to HCHO formation. The ground-based estimates exhibit a much stronger month-to-month variation, with flux estimates of 5 times higher in October compared to September and December. The small increase of the flux between December and January is not observed by the satellite observations. Despite these differences, partly due to reduced representativeness when comparing local measurements with flux estimates from a 0.5° grid cell, this comparison shows that both large (satellite) and small (ground-based) scales agree that there are enhanced isoprene emissions during the dry season followed by a reduction towards the wet season.

The results reported here are associated with a small footprint area. This together with the huge biodiversity of tropical rainforests makes it impossible to generalize these results to the regional scale. Moreover, although some previous reports have suggested significant seasonal variations of BVOCs based on *in situ* measurements in different sub-regions of

Amazonia, when those investigations (summarized in Table 1) and this study were compared, high variability is apparent among values of mixing ratios and fluxes. This variability could be due to: (1) different methodologies, (2) sampling in different seasons, (3) sampling in different regions (e.g., south, north, west, eastern Amazonia), (4) sampling in different ecotones of the same region, (5) different statistical analyses, and (6) perhaps due to small data sets that are not statistically significant to characterize emissions of a specific site.

3.3 Comparison with model predictions of seasonal isoprenoid emissions in Amazonia

Although the canopy scale isoprenoid emission measurements presented here differed from those modeled by MEGAN 2.1 (Figs. 4 and 5), which assume that variations are driven primarily by light, temperature and leaf area, in terms of seasonal variation, MEGAN 2.1 estimates of isoprene emission agreed fairly well with the satellite-derived isoprene emission, which suggests that other factors at this site could influence isoprene emissions locally. As already mentioned, leaf phenology may cause important effects on local emissions. As MEGAN 2.1 was driven with local variations in PAR and air temperature, and with regional variations of LAI (satellite observations at 1-kilometer resolution), this regional variation in LAI may not represent the local effect of LAI variation on local emissions, since vegetation in Amazonia is phenologically distinct due to the huge biodiversity of this ecosystem (Silva et al., 2013). Furthermore, as the canopy structure might vary seasonally due to leaf phenology/demography, the pattern of light penetration/absorption and then leaf temperature may change as well; thus, this, together with the differences in emissions among species and among leaf ontogenetic stages, could have an important impact on seasonal changes of local emissions.

Besides the effects of light, temperature and leaf phenology/demography, some efforts have been made to include effects of CO_2 variation (Arneth et al., 2007; Guenther et al., 2012) as well as the link between photosynthesis and emission (Grote et al., 2014; Morfopoulos et al., 2013, 2014; Unger et al., 2013) into isoprene emission models at regional and global scales. However, the current regional and global BVOC emission models predict much smaller seasonal variations (Guenther et al., 2006, 2012; Muller et al., 2008; Unger et al., 2013) compared to the measurements in Amazonia (Table 1). Furthermore, satellite observations indicate that the current understanding of the processes controlling seasonal variations is insufficient, and models do not simulate the unexpected shutdown of isoprene emission in the Amazonia during the wet-to-dry transition season (Barkley et al., 2009).

Many recently published studies have used the MEGAN model and the majority have focused on improving our understanding of isoprene emissions. Although other models have been developed on the basis of known biochemical processes (Grote et al., 2014; Morfopoulos et al., 2014; Unger et al., 2013), the general framework and processes simulated are similar. The biochemical basis of isoprene production and release must be further understood to develop mechanistic explanations for variation in isoprene emission (Monson et al., 2012), which may reduce uncertainties associated with the responses to environmental factors.

Seasonal variation of isoprene emissions might be explained by the change in energy supply from photosynthesis throughout the seasons (e.g. Grote et al., 2014). This is supported by the generally strong correlation between isoprene emission and gross photosynthetic capacity reported for Amazonian tree species (Kuhn et al., 2004b), and by the fact that higher demography of healthy efficient leaves (Nelson et al., 2014) coincides with the period of most efficient landscape-scale photosynthesis and photosynthetic capacity (Restrepo-Coupe et al., 2013). However, more measurements are needed to examine this relationship which should follow PAR variation. Additionally, since canopy structure may explain some variation in biomass growth over tropical landscapes due to differences in the pattern of light penetration and absorption by the canopies (Stark et al., 2012), measurements of canopy structure may also help to explain some of the differences in isoprenoid emissions among the Amazonian sub-regions.

Therefore, at least for the Amazonian rainforest, models currently do not fully capture seasonal variations in isoprenoid emissions, especially for monoterpenes and sesquiterpenes, which are less investigated compared to isoprene. The scarcity of measurements in Amazonia prevents the development and evaluation of accurate model approaches. Thus, this study strongly encourages future *in situ* measurements in Amazonia, including at leaf level, in order to verify changes driven by seasonal variations in leaf area, leaf age, phenology and emission response to soil moisture, and the short-term and long-term temperature and light environment.

4. Summary and conclusions

In this study, we present the first in situ measurements that show a seasonal trend in isoprenoid emissions for a primary rainforest of central Amazonia. Isoprenoid emissions peak at the end of the dry season and at the dry-to-wet transition season. Under conditions of high insolation and high temperatures joined together with the high demography of photosynthetically efficient leaves (Caldararu et al., 2012; Myneni et al., 2007; Nelson et al., 2014; Samanta et al., 2012), isoprenoid metabolic pathways may experience more favorable conditions for synthesizing these compounds in the dry season and the dry-to-wet transition season. This is especially for the case of isoprene and monoterpenes, which are light- and temperature-dependent and are affected by the recent production of photosynthetic substrates.

Although some studies have suggested that there are no seasonal variations in canopy structure and greenness in Amazonia (e.g. Morton et al., 2014), results reported here present a seasonal variation of leaf flushing and suggest maximum leaf demography in the late dry season, which generally agrees with the assumption that a greenup during the dry season in Amazonia may drive increasing isoprene emissions as suggested by satellite retrievals (Barkley et al., 2009). Moreover, this study also suggests that seasonal changes in the atmospheric oxidative capacity could have an important impact on the seasonality of at least some isoprenoid concentrations and above canopy emissions, especially for sesquiterpenes. Their quantification is challenged by rapid atmospheric chemical reactions catalyzed by high insolation and higher ozone concentrations in the dry season.

MEGAN 2.1 estimates did not fully capture the behavior observed with the isoprenoid emissions based on in-situ PTR-MS measurements (inverse Lagrangian transport model). Model emissions of isoprene and total monoterpenes were overestimated, especially during September 2010 (dry season) and December 2010 (wet season), respectively. Total sesquiterpenes were underestimated during November 2010 (dry-to-wet transition season). This difference between MEGAN 2.1 flux estimates and fluxes estimated by the PTR-MS vertical mixing ratio profiles could be due to experimental errors or the influence of very local effects on the seasonal emissions measured in this site, because satellite-derived isoprene emissions agree fairly well with MEGAN 2.1 emission estimates and the ground observations do not agree with the satellite data or the model, principally in September.

Perhaps the isoprene pattern observed at the site is due to a very local effect of leaf flushing by isoprene emitting species around this tower, but this is not seen on the regional scale where there are different species distributions.

Generally, current models assume that seasonal variation of BVOC emissions in the Amazonian rainforest are primarily based on light and temperature variations. These model simulations capture only a part of the actual variation and have uncertainties associated with the insufficient understanding of mechanistic processes involved in the seasonality of these compounds. Nevertheless, because the number of measurements and sites is limited in Amazonia, there is a scarcity of information, which hinders further model improvements. In summary, our results demonstrate strong seasonality and suggest that important processes are taking place during the transition seasons. Also, results reveal the need for long-term and continuous BVOC observations from leaf level to ecosystem level, and also suggest that standardized measurement procedures are required in order to compare the different Amazonian sub-regions. This may advance understanding of the seasonality of BVOC exchanges between forest and atmosphere, providing the information needed to improve BVOC emission estimates for climate and air quality modelling studies.

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Table1: Isoprene and monoterpenes from different regions in the Amazonian rainforest: comparison of estimates and direct measurements of mixing ratios and fluxes.

Study	**Site**	**Technical approach**	**isoprene (ppbv)**	**isoprene (mg m^{-2} h^{-1})**	**sum of Mt[†] (ppbv)**	**sum of Mt[†] (mg m^{-2} h^{-1})**	**season**	**comments**
Central Amazonia								
Greenberg and Zimmerman, 1984	Manaus/Humaitá-Amazonas, Brazil	GC-FID, canister samples (near ground to 30m)	2.40 (1-5.24)[a]		2.86		Dry (Aug-Sep 1980)	mean - daytime range is not reported
Greenberg and Zimmerman, 1984	Manaus/Humaitá-Amazonas, Brazil	GC-FID, canister samples (flights from treetop to 2 km)	2.27 (0.38-4.08)[a]		5.47		Dry (Aug-Sep 1980)	mean - daytime range is not reported
Greenberg and Zimmerman, 1984	Manaus/Humaitá-Amazonas, Brazil	GC-FID canister samples (flights from 2km to Tropopause)	0.19 (0.14-0.22)[a]		1.91		Dry (Aug-Sep 1980)	mean - daytime range is not reported
Jacob and Wofsy, 1988*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	Inverse modeling approach using Zimmerman et al. 1988 data		1.58			Dry (July-Aug 1985)	mean average of 24 hours
Zimmerman et al., 1988*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	GC-FID, teflon bag on tethered balloon (30m)	2.65 [1.39-3.38] [b]		0.27 [0.15-0.54] [b]		Dry (July-Aug 1985)	median and interquartile range (24h)
Zimmerman et al., 1988*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	GC-FID, teflon bag on tethered balloon (305m)	1.73 [1.03-2.15] [b]		0.15 [0.04-0.33] [b]		Dry (July-Aug 1985)	median and interquartile range (24h)
Zimmerman et al., 1988*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	GC-FID, teflon bag on tethered balloon (up to 305m)		3.1		0.23	Dry (July-Aug 1985)	mean daytime (08:00-16:00, LT)
Rasmussen and Khalil, 1988	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	GC-FID, canister samples (near ground level)	2.77 (±0.4)				Dry (July-Aug 1985)	mean daytime (11:00-15:00, LT)
Rasmussen and Khalil, 1988	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	GC-FID, canister samples (aircraft flights from 150m to 5000m)	1.5 (±0.75)				Dry (July-Aug 1985)	daytime
Davis et al., 1994*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	Mixed Layer Gradient approach using Zimmerman et al. 1988 data		3.63 (±1.4)			Dry (July-Aug 1985)	mean daytime (08:00-18:00, LT)
Kesselmeier et al., 2000	Balbina - ~100 km north of Manaus-Amazonas, Brazil	GC-MS, cartridge samples (outside forest)	6.55 (±1.26)		0.63 (±0.19)		Wet (Apr 1988)	mean daytime (09:30-15:00, LT)
		GC-MS, cartridge samples (inside Canopy)	3.55 (±0.07)		0.24 (±0.04)		Wet (Apr 1988)	mean daytime (09:30-15:00, LT)
		GC-MS, cartridge on tethered balloon (200-500m)	~3		~0.2		Wet (Apr 1988)	mean of 24h

Cont. **Table1:** Isoprene and monoterpenes from different regions in the Amazonian rainforest: comparison of estimates and direct measurements of mixing ratios and fluxes.

Study	**Site**	**Technical approach**	**isoprene (ppbv)**	**isoprene (mg m^{-2} h^{-1})**	**sum of Mt[†] (ppbv)**	**sum of Mt[†] (mg m^{-2} h^{-1})**	**season**	**comments**
Central Amazonia								
Kesselmeier et al., 2000	Cuieiras Biological Reserve (C14-ZF2) - Manaus-Amazonas, Brazil	GC-MS, cartridge samples (inside and above canopy)	6.7 ±1.07		0.73 ±0.24		Wet (Apr 1988)	daytime
Stefani et al. 2000	Cuieiras Biological Reserve (K34-ZF2) - Manaus-Amazonas, Brazil	GC-MS, cartridge on Relaxed Eddy Accumulation (~53m)		3.6 -5.4		0.72 – 0.9	Aug 1999 and Jan 2000	range of daytime average normalized fluxes for the whole period of measurements
Andreae et al., 2002	Cuieiras Biological Reserve (K34-ZF2) - Manaus-Amazonas, Brazil	GC-MS, cartridge on Relaxed Eddy Accumulation (~53m)		2.88		0.36	Dry-Wet (Nov 1999-Jan 2000)	midday values
Ciccioli et al., 2003	Cuieiras Biological Reserve (K34-ZF2) - Manaus-Amazonas, Brazil	GC-MS, cartridge on Relaxed Eddy Accumulation (~51m)		5.11 max.		1.36 max.	Dry (July 2001)	midday values
Greenberg et al., 2004	Balbina - ~100 km north of Manaus-Amazonas, Brazil	GC-MS, cartridge on tethered balloon (200-1000m)	2.86 [2.25-3.64] [b]		0.21 [0.17-0.31] [b]		Wet (March 1998)	median and interquartiles - daytime (12:00-15:00, LT)
Greenberg et al., 2004	Balbina - ~100 km north of Manaus-Amazonas, Brazil	Box model		5.3		0.23	Wet (March 1998)	maximum midday emission fluxes estimated for the ecoregion
Karl et al., 2007[††]	Cuieiras Biological Reserve (C14-ZF2) - Manaus-Amazonas, Brazil	PTR-MS, Disjunct Eddy Covariance (~ 54 m)	7.8 ±3.7	8.3 ±3.1	0.87 ±0.3	1.7 ±1.3	Dry (Sep 2004)	mean daytime (12:00-14:00, LT)
Karl et al., 2007[††]	Cuieiras Biological Reserve (C14-ZF2) - Manaus-Amazonas, Brazil	PTR-MS, Mixed Layer Gradient (up to ~1200 m)	5.5 ±2.6	12.1 ±4.0	0.52 ±0.2	3.5 ±1.2	Dry (Sep 2004)	mean daytime (10:00-11:30, LT)
Kuhn et al., 2007**	Cuieiras Biological Reserve (K34-ZF2)- Manaus-Amazonas, Brazil	GC-FID, cartridge on Relaxed Eddy Accumulation (~51m)		2.4 ±1.8 (max. 6.1)		0.44 ±0.49 (max. 1.9)	Dry (July 2001)	mean daytime (10:00-15:00, LT)
Kuhn et al., 2007**	Cuieiras Biological Reserve (K34-ZF2) - Manaus-Amazonas, Brazil	GC-FID, cartridge on Surface Layer Gradient (28, 35.5, 42.5, 51m)		3.9 ±4.1 (max. 12.8)		0.43 ±0.65 (max. 2.1)	Dry (July 2001)	mean daytime (10:00-15:00, LT)
Kuhn et al., 2007**	Cuieiras Biological Reserve (K34-ZF2) - Manaus-Amazonas, Brazil	GC-FID, cartridge samples, Mixed Layer Gradient (50-3000m)		4.2 ±5.9 (max. 15.7)			Dry (July 2001)	mean daytime (10:00-18:00, LT)
Karl et al., 2009	Cuieiras Biological Reserve (TT34-ZF2) - Manaus-Amazonas, Brazil	PTR-MS, Gradient flux (2, 10.9, 16.7, 23.9, 30.3 and 39.8 m)		0.7 ±0.2			Wet (Feb 2008)	mean daytime (11:00-17:00, LT); flux at 35 m
Rizzo et al., 2010[††]	Cuieiras Biological Reserve (C14-ZF2)- Manaus-Amazonas,	PTR-MS, Disjunct Eddy Covariance (54 m)	7.8	 8.4	0.29	 0.93	Dry (Sep 2004) Dry (Sep 2004)	max. at early afternoon max. at noon

Cont. **Table1:** Isoprene and monoterpenes from different regions in the Amazonian rainforest: comparison of estimates and direct measurements of mixing ratios and fluxes.

Study	**Site**	**Technical approach**	**isoprene (ppbv)**	**isoprene ($mg\ m^{-2}\ h^{-1}$)**	**sum of Mt[†] (ppbv)**	**sum of Mt[†] ($mg\ m^{-2}\ h^{-1}$)**	**season**	**comments**
Central Amazonia								
Silva, 2010	Cuieiras Biological Reserve (K34-ZF2)- Manaus-Amazonas, Brazil	GC-MSFID cartridge samples at 1m	3.2 ±0.9		0.28 ±0.13		Wet (May 2009)	mean daytime (07:00-17:00, LT)
		GC-MSFID cartridge samples at 10m	4.6 ±0.94		1.09 ±0.35		Wet (May 2009)	mean daytime (07:00-17:00, LT)
		GC-MSFID cartridge samples at 20m	6.17 ±1.03		0.75 ±0.17		Wet (May 2009)	mean daytime (07:00-17:00, LT)
Jardine et al., 2011[‡]	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (2, 11, 17, 24, 30 and 40 m)			~ 0.78		Dry-Wet (Sep-Dec 2010)	mean daytime 10:00-16:00, LT) at 40 m
Jardine et al., 2011[‡]	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (2, 11, 17, 24, 30 and 40 m)				~ 1.47	Dry-Wet (Sep-Dec 2010)	mean daytime 10:00-16:00, LT) at 35 m
Jardine et al., 2012[‡]	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (2, 11, 17, 24, 30 and 40 m) and Gradient flux		~1.43			Dry-Wet (Sep-Dec 2010)	mean daytime (10:00-16:00, LT); flux at 40 m
Yáñez-Serrano et al., 2015	ATTO site - Manaus Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (0.05, 0.5, 4, 24, 38, 53 and 79 m)	5.22 ±1.5		0.75 ±0.18		Dry (Sep 2013)	Isoprene, daytime median (12-15:00, LT). Mt, daytime median (15-18:00, LT)
Yáñez-Serrano et al., 2015	ATTO site - Manaus Manaus-Amazonas, Brazil		1.5 ±0.78		< 0.23		Wet (Feb-Mar 2013)	Isoprene, daytime median (12-15:00, LT). Mt, daytime median (15-18:00, LT)
This study[‡]	Cuieiras Biological Reserve (TT34-ZF2) - Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (2, 11, 17, 24, 30 and 40 m) and Gradient flux	2.68 ±0.9	1.37 ±0.7	0.67 ±0.3	1.47 ±0.06	Dry (Sep-Oct 2010)	mean daytime (10:00-14:00, LT) at 40m
This study[‡]	Cuieiras Biological Reserve (TT34-ZF2) - Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (2, 11, 17, 24, 30 and 40 m) and Gradient flux	2.65 ±1.33	1.41 ±0.1	0.85 ±0.4	1.29 ±0.2	DWT[¥] (Nov 2010)	mean daytime (10:00-14:00, LT) at 40m
This study[‡]	Cuieiras Biological Reserve (TT34-ZF2) - Manaus-Amazonas, Brazil	PTR-MS, Gradient profile (2, 11, 17, 24, 30 and 40 m) and Gradient flux	1.66 ±0.9	0.52 ±0.1	0.47 ±0.2	0.36 ±0.05	Wet (Dec 2010 -Jan 2011)	mean daytime (10:00-14:00, LT) at 40m
Eastern central Amazonia								
Rinne et al., 2002	Tapajós National Forest - Santarém-Pará, Brazil	GC-MS cartridge on Disjunct Eddy Accumulation (~ 45m)	5 max.	2.4			Dry (July 2000)	Afternoon values 30 ºC and 1000 µmol $m^{-2}\ s^{-1}$
Greenberg et al., 2004	Tapajós National Forest - Santarém-Pará, Brazil	GC-MS, cartridge on tethered balloon (200-1000m)	0.74 [0.6-1] [b]		0.08 [0.03-0.06] [b]		Wet (Jan-Feb 2000)	median and interquartiles - daytime (12:00-15:00, LT)
Greenberg et al., 2004	Tapajós National Forest - Santarém-Pará, Brazil	Box model		2.2		0.18	Wet (Jan-Feb 2000)	maximum midday emission fluxes estimated for the ecoregion

Cont. **Table1:** Isoprene and monoterpenes from different regions in the Amazonian rainforest: comparison of estimates and direct measurements of mixing ratios and fluxes.

Study	**Site**	**Technical approach**	**isoprene (ppbv)**	**isoprene ($mg\ m^{-2}\ h^{-1}$)**	**sum of $Mt^{\dagger}$ (ppbv)**	**sum of $Mt^{\dagger}$ ($mg\ m^{-2}\ h^{-1}$)**	**season**	**comments**
Eastern central Amazonia								
Trostdorf et al., 2004	Tapajós National Forest - Santarém-Pará, Brazil	GC-FID, canister samples (54, 64 m)	1.9 ±1.2; 1.3 ±0.8				Wet (Jan- May 2002)	mean daytime (11:00-14:00, LT)
Trostdorf et al., 2004	Tapajós National Forest - Santarém-Pará, Brazil	GC-FID, canister samples (54, 64 m)	1.4 ±0.5; 1.0 ±0.4				WDT$^{¥¥}$ (June-July 2002)	mean daytime (11:00-14:00, LT)
Trostdorf et al., 2004	Tapajós National Forest - Santarém-Pará, Brazil	GC-FID, canister samples (54, 64 m)	2.8 ±0.9; 2.5 ±0.8				Dry (Aug-Nov 2002)	mean daytime (11:00-14:00, LT)
Western Amazonia								
Helmig et al., 1998	Peru - 500 km west of Iquitos	GC-MS, cartridge on tethered balloon (up to 1600 m)	3.31, 1.39, 0.16		0.21, 0.06, 0.015		July 1996	Median daytime (ground, mixed layer and above mixed layer)
Helmig et al., 1998	Peru - 500 km west of Iquitos	GC-MS, cartridge samples, Mixed Layer Gradient		7.4		0.42		mean daytime
Helmig et al., 1998	Peru - 500 km west of Iquitos	GC-MS, cartridge samples, Mixed Layer Budget		8.1		0.41		mean daytime
Southern Amazonia								
Kesselmeier et al., 2002	Jaru Biological Reserve, Rondônia, Brazil	GC-FID, cartridge samples (8-52m)	~4		~0.8		WDT$^{¥¥}$ (May 1999)	mean daytime (11:00-18:00, LT)
Kesselmeier et al., 2002	Jaru Biological Reserve, Rondônia, Brazil	GC-FID, cartridge samples (8-52m)	~12		~0.8		DWT$^{¥}$ (Sep-Out 1999)	mean daytime (11:00-18:00, LT)
Greenberg et al., 2004	Jaru Biological Reserve, Jaru-Rondônia, Brazil	GC-MS, cartridge on tethered balloon (200-1000m)	6.89 [2.78-7.73] ^{b}		0.83 [0.56-2.65] ^{b}		Wet (Feb 1999)	median and interquartiles - daytime (12:00-15:00, LT)
Greenberg et al., 2004	Jaru Biological Reserve, Jaru-Rondônia, Brazil	Box model		9.8		6.1	Wet (Feb 1999)	maximum midday emission fluxes estimated for the ecoregion
Simon et al., 2005	Jaru Biological Reserve, Rondônia, Brazil	Lagrangian transport sub-model.		~5.9			WDT$^{¥¥}$ (May 1999)	midday values
Simon et al., 2005	Jaru Biological Reserve, Rondônia, Brazil	Modeling using data of Kesselmeier et al., 2002		~8.2			DWT$^{¥}$ (Sep-Out 1999)	midday values

Cont. **Table1:** Isoprene and monoterpenes from different regions in the Amazonian rainforest: comparison of estimates and direct measurements of mixing ratios and fluxes.

Study	**Site**	**Technical approach**	**isoprene (ppbv)**	**isoprene (mg m^{-2} h^{-1})**	**sum of Mt† (ppbv)**	**sum of Mt† (mg m^{-2} h^{-1})**	**season**	**comments**
Southern Amazonia								
Aquino, 2006	Jaru Biological Reserve, Rondônia, Brazil	GC-FID, canister samples (50, 60 m)	4.5 ±0.9; 4.0 ±1.2				Wet (Feb-May 2002)	mean daytime (11:00-16:00, LT)
Aquino, 2006	Jaru Biological Reserve, Rondônia, Brazil	GC-FID, canister samples (50, 60 m)	2.1 ±2.0; 1.8 ±1.8				WDT[¥¥] (Jun 2002)	mean daytime (11:00-16:00, LT)
Aquino, 2006	Jaru Biological Reserve, Rondônia, Brazil	GC-FID, canister samples (50, 60 m)	4.6 ±2.7; 4.0 ±2.5				Dry (Jul-Sep 2002)	mean daytime (11:00-16:00, LT)
Aquino, 2006	Jaru Biological Reserve, Rondônia, Brazil	GC-FID, canister samples (50, 60 m)	3.4 ±1.2; 3.0 ±0.5				DWT[¥] (Out-Nov 2002)	mean daytime (11:00-16:00, LT)

Note: Seasons follow determination of each study. For some studies the exact times of sample collection are not available and then not reported. Statistics differed among studies. The most of studies showed mean values but others presented median values and/or just a range of all values measured.

†Mt - monoterpenes;

[a]- range of variation;

[b] - interquartile ranges based on median "[]";

*, ** studies derived from the same observational data base;

[‡],[††] studies derived from part of the same observational data base;

[¥]DWT - dry-to-wet transition season;

[¥¥]WDT - wet-to-dry transition season.

Figures

Figure 1: Precipitation, PAR and air temperature measured at K34 tower (~2 km far of TT34 tower); a) relative frequency (%) of monthly cumulative precipitation from 1999 to 2012, b) monthly cumulative precipitation from July 2010 to June 2011 (measured in 30 minute intervals for 24 hours) (bars), and average of monthly cumulative precipitation from 1999 to 2012 (red line); c) relative frequency of monthly PAR from 1999 to 2012 (measured every 30 min during 06:00-18:00, LT), d) monthly average PAR from July 2010 to June 2011 (measured every 30 min during 06:00-18:00, LT); e) relative frequency of monthly air temperature from 1999 to 2012, f) monthly average air temperature from July 2010 to June 2011 (measured in 30 minute intervals for 24 hours). Figures on the right side cover the period of this study; grey areas represent the period of dry season; and blue line at (b) represents 100 mm month^{-1}. Error bars represent one standard deviation.

Figure 2: Daytime (10:00-16:00, LT) and nighttime (22:00-04:00, LT) average vertical profiles of isoprene (a, b, c), total monoterpenes (d, e, f), total sesquiterpenes (g, h, i), and air temperature (j, k, l) of the dry season (DS), the dry-to-wet transition season (DWT) and the wet season (WS). Error bars represent one standard deviation.

Figure 3: Daytime (10:00-16:00, LT) vertical profiles of mixing ratios of isoprene, total monoterpenes and total sesquiterpenes from the dry season to the wet season; and estimated surface area density of the canopy at this study site (ground-based measurements carried out in March/2004 using LIDAR - Light Detection And Ranging) (Parker and Fitzjarrald, 2004) (a). Vertical profile of photosynthetic photon flux density (PPFD) penetration and absorption by the canopy from the dry season to the wet season modeled by MEGAN 2.1 (b). Daytime (10:00-16:00, LT) air temperature profiles from dry season to wet season measured at K34 tower (c). In fig. 1a the top and the bottom x axis represent isoprenoid mixing ratios and estimated surface area density of the canopy, respectively. Error bars represent one standard deviation.

Figure 4: Daytime (10:00-14:00, LT) source-sink distribution inside and above the canopy, cumulative flux estimation, and relative emission modeled by MEGAN 2.1 of isoprene (a, b, c), total monoterpenes (TMt) (d, e, f) and total sesquiterpenes (TSt) (g, h, i) from the dry season to the wet season. Error bars represent one standard deviation.

Figure 5: Monthly averages of air temperature and PAR (measured at K34 tower during 10:00-14:00, LT), and LAI (MODIS, 8-day observations) (a). Monthly averages of fluxes of isoprene (b), total monoterpenes (TMt) (c) and total sesquiterpenes (TSt) (d). Flux based on in-situ PTR-MS measurements (inverse Lagrangian transport model - estimates for 10:00-14:00, LT, at TT34 tower) are represented by solid squares and one standard deviation; fluxes modeled by MEGAN 2.1 (estimates for 10:00-14:00, LT) are shown by solid lines and filled areas that represent one standard deviation. Isoprene flux modeled by MEGAN 2.1 in (b) were divided by five. Error bars represent one standard deviation.

Figure 6: Estimated monthly leaf flushing (light green line) (Tavares, 2013), and monthly average of PAR measured from October 2010 to January 2013 at K34 tower (06:00-18:00, LT) (black line). For the period of this study, leaf flushing is also represented by the analysis

of canopy images for every six days from October 2010 to January 2011 (red circles). Monthly averages of fluxes of isoprene (dark green line) and total monoterpenes (blue line) (estimated for 10:00-14:00, LT, at TT34 tower). Grey areas represent the period of the dry season.

Figure 7: Comparison of monthly isoprene emissions based on in-situ PTR-MS measurements (inverse Lagrangian transport model) and satellite-derived estimates and MEGAN 2.1 estimates. Satellite-derived estimates are from January 2010 to January 2011, and ground-based estimates are from September 2010 to January 2011. Satellite-derived and MEGAN 2.1 estimates were divided by 2.5 and 5, respectively. Grey area represents the period of the dry season. Error bars represent one standard deviation.