MUDANÇAS SAZONAIS NA EMISSÃO DE ISOPRENÓIDES EM UMA FLORESTA PRIMÁRIA NA AMAZÔNIA CENTRAL

ELIANE GOMES ALVES

Manaus, Amazonas
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ORIENTADOR: DR. JULIO TÓTA DA SILVA

Tese apresentada ao Instituto Nacional de Pesquisas da Amazônia e a Universidade do Estado do Amazonas como parte dos requisitos para obtenção do título de Doutor em Clima e Ambiente.

Manaus, Amazonas
Janeiro, 2015

RELAÇÃO DA BANCA JULGADORA

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Sinopse:
Estudou-se a sazonalidade de emissão de Compostos Orgânicos Voláteis, do grupo dos isoprenóides, em uma floresta primária de terra-firme localizada ao noroeste de Manaus, Amazonas. Aspectos como a influência da sazonalidade da luz, temperatura e fenologia foliar foram avaliados.

Palavras-chave: Interação biosfera-atmosfera, isopreno, monoterpenos, sesquiterpenos.

Dedico aos meus pais, Sebastião Alves Sobrinho e Cecília Gomes Alves, por terem me guiado até este momento.

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E aquilo que nesse momento se revelará aos povos
Surpreenderá a todos não por ser exótico
Mas pelo fato de poder ter sempre estado oculto
Quando terá sido óbvio

Um Índio (Caetano Veloso)

RESUMO

As florestas tropicais são a maior fonte de isoprenóides para a atmosfera global. Considerando a representatividade da floresta Amazônica frente as demais florestas tropicais no globo, é possível destacar a necessidade de medidas de isoprenóides neste ecossistema. No entanto, poucos estudos com medidas *in situ* estão apenas começando a investigar as variações sazonais nas emissões de isoprenóides e outros Compostos Orgânicos Voláteis (COVs) na floresta Amazônica. Por isso, neste estudo, perfis verticais de razão de mistura de isopreno, monoterpenos totais (TMt) e sesquiterpenos totais (TSt) foram quantificados dentro e acima do dossel em uma floresta primária na Amazônia central, usando um Reação por Transferência de Prótons - Espectrômetro de Massas (PTR-MS). Os fluxos do dossel para a atmosfera foram estimados pelo modelo inverso de transporte Lagrangiano, e as medidas ocorreram da estação seca (Setembro/2010) a estação chuvosa (Janeiro/2011), continuamente. Além disso, medidas de fluxo de isopreno usando um sistema de Acumulação de Vórtices Relaxados (REA) foram realizadas em campanhas intensivas de Junho/2013 a Dezembro/2013, caracterizando as estações: transição de chuvosa para seca, seca, transição de seca para chuvosa e começo da chuvosa. Os resultados apresentaram uma tendência de sazonalidade para as emissões de isoprenóides, sendo as máximas emissões encontradas durante a estação seca e a estação de transição de seca para chuvosa. Para isopreno, menores valores de emissões foram observados durante a estação de transição chuvosa para seca, sugerindo que isto poderia estar relacionado com as variações de demografia foliar e estimativas de fenologia foliar. Uma comparação entre emissão de isopreno derivada de observações por satélite e medidas em superfície demonstrou que ambos apresentaram a mesma tendência de sazonalidade. As estimativas reproduzidas pelo MEGAN 2.1 não concordaram com as medidas de emissão de isoprenóides, entretanto isto poderia ser relacionado ao fato de que apenas variações sazonais de luz e temperatura foram consideradas para executar o modelo, o que pode não reproduzir os efeitos simultâneos de outros fatores ambientais e biológicos, como a fenologia foliar. Os resultados aqui apresentados sugerem que, além das mudanças sazonais na luz e temperatura, a variação sazonal das emissões de isoprenóides podem ser dirigidas também por mudanças sazonais na demografia foliar e na ontogenia das folhas.

Palavras-chave: isopreno, monoterpenos totais, sesquiterpenos totais, fenologia foliar, mudanças sazonais.

ABSTRACT

Tropical forest are the largest source of isoprenoids to the global atmosphere. Accounting for the representativeness of the Amazonian rainforest in relation to the all tropical forests in the globe, it is possible to highlight the need of isoprenoid measurements in this ecosystem. Yet, a few studies of seasonal variation with *in situ* measurements are just starting to investigate isoprenoid and other Volatile Organic Compound (VOC) emissions in the Amazonian rainforest. In this study, vertical mixing ratio profiles of isoprene, total monoterpenes (TMt) and total sesquiterpenes (TSt) were quantified, 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 by the inverse Lagrangian transport model, and measurements were carried out from the dry season (September/2010) to the wet season (January/2011), continuously . Also, measurements of isoprene fluxes using a Relaxed Eddy Accumulation system (REA) were carried out in intensive campaigns from June/2013 to December/2013, characterizing four seasons: the wet-to-dry transition season, the dry season, the dry-to-wet transition season and the beginning of the wet season. Results showed a seasonal trend for the isoprenoid emissions, being maximum isoprenoid emissions found during the dry season and the dry-to-wet transition season. For isoprene, low emissions were observed during the wet-to-dry transition season, suggesting that this low emission could be related to variations in leaf demography and estimates of leaf phenology. A comparison of satellite-derived isoprene emission and ground-based isoprene emission have shown that both presented the same trend of seasonality. MEGAN 2.1 did not show good agreement with isoprenoid emission measurements, however this could be related to the fact that only seasonal changes in light and temperature were considered to run this model, which may not reproduce simultaneous effects of other environmental and biological factors, as leaf phenology. Results here shown suggest thta, besides seasonal changes in light and temperarure, the seasonal variation in isoprenoid emissions could also be driven by seasonal changes in leaf demography and leaf ontogeny.

Key-words: isoprene, total monoterpenes, total sesquiterpenes, leaf phenology, seasonal changes

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INTRODUÇÃO GERAL

Os Compostos Orgânicos Voláteis (COV) são compostos com pressão de vapor maior que 10 Pa a 25ºC, apresentam ponto de ebulição de até 260ºC à pressão atmosférica, e possuem em sua constituição 15 ou menos átomos de carbono (Williams & Koppmann, 2007). Estes compostos podem ser classificados como os de origem antropogênica (COVA) e os de origem biogênica (COVB); sendo esta última a maior fonte destes compostos orgânicos para a atmosfera em escala global (Guenther et al., 1995, 2006, 2012).

A vegetação emite uma grande diversidade de espécies químicas de COVBs para a atmosfera com a finalidade de exercer importantes funções ecológicas e ecofisiológicas; dentre estas funções destacam-se: proteção da planta contra situações de estresse (termo-tolerância, tolerância ao estresse oxidativo e foto-proteção), defesa da planta (defesa direta e/ou indireta contra herbívoros e defesa direta contra patógenos), reprodução da planta (polinização e dispersão de frutos e sementes), e interação entre plantas (comunicação e alelopatia) (Penuelas et al., 2010). Uma vez na atmosfera, os COVBs podem interagir em complexas reações químicas, o que gera efeito sobre a capacidade oxidativa da troposfera, e influencia a taxa de oxidação, formação e concentração de outros gases traço (Pacifico et al., 2009). Ademais, os COVBs podem ser ativos na formação e crescimento de aerossóis orgânicos secundários (AOS), o que afeta o processo de desenvolvimento de nuvens (Andreae and Crutzen, 1997; Carslaw et al., 2010; Martin et al., 2010; Poschl et al., 2010) e interage com o balanço de radiação à superfície (Forkel et al., 2012). De uma maneira geral, as emissões de COVBs pela biosfera terrestre promovem uma forte conexão entre a biosfera e a atmosfera.

De acordo com Guenther et al. (2012), as emissões de isoprenóides - isopreno, monoterpenos e sesquiterpenos - são predominantes em relação aos outros COVBs, e são de particular interesse pois estimativas apresentam que aproximadamente 80% do total global de emissões de isoprenóides provêm de florestas tropicais. Deste modo, ao destacar a abrangência territorial da Floresta Amazônica frente as demais florestas tropicais existentes, percebe-se a importância das emissões deste ecossistema para a atmosfera em escala global.

Ainda neste contexto, vale ressaltar que, embora muito importantes e necessárias, medidas de isoprenóides na Floresta Amazônia ainda são escassas devido às dificuldades logísticas e estruturais para desenvolver pesquisa nesta área. Isto apresenta-se como uma limitação para o

aprimoramento de modelos que realizam estimativas de emissões de isoprenóides em um escalonamento da superfície para a atmosfera, e contribui para as incertezas das estimativas. O que já foi feito até hoje, com base em medidas *in situ* e estimativas por satélite, demonstrou o potencial de variações sazonais nas emissões de isoprenóides pela floresta Amazônica. Entretanto, o entendimento destas variações e o refinamento de modelos para reproduzi-las não puderam ser bem explorados devido a baixa representatividade temporal e espacial das medidas realizadas até o presente. Deste modo, este estudo objetivou investigar a variação sazonal da emissão de isoprenóides por uma floresta primária de terra-firme na Amazônia central, relacionando-a com fatores ambientais (luz e temperatura) e com fatores de resposta biológica (fenologia foliar e troca líquida de CO_2 pelo ecossistema - NEE), que apresentam ou podem apresentar sazonalidade.

Para apresentar os resultados, este estudo foi dividido em dois capítulos. O primeiro capítulo intitulado "Sazonalidade de perfis verticais atmosféricos de isoprenóides dentro de uma floresta primária na Amazônia central" tem por finalidade apresentar medidas contínuas (Setembro/2010 a Janeiro/2011) de razão de mistura e estimativa de fluxo (modelo inverso de transporte Lagrangiano) de isopreno, monoterpenos totais e sesquiterpenos totais, relacionando-as com medidas contínuas de temperatura e radiação solar e com uma estimativa de fenologia foliar. Este capítulo objetivou demonstrar como os perfis de isoprenóides se comportam dentro da floresta e como o fluxo emitido para a atmosfera pode mudar sazonalmente.

O segundo capítulo - " Mudanças sazonais nas emissões de isopreno inferidas por um sistema de Acumulação de Vórtices Relaxados em uma floresta primária na Amazônia central" - objetivou apresentar mudanças sazonais na emissão de isopreno, o composto dominante nas emissões das florestas tropicais, com medidas de fluxo realizadas mensalmente de Junho/2013 a Dezembro/2013, e relacionar as emissões com a sazonalidade de temperatura e radiação solar e com NEE.

Ao final, dispõe-se uma síntese dos resultados obtidos em ambos capítulos, e também apresentam-se perspectivas para pesquisas que enveredam esta temática.

OBJETIVOS

Objetivo Geral

Investigar as variações sazonais de emissão de isoprenóides - isopreno, monoterpenos totais e sesquiterpenos totais - em um floresta primária de terra-firme na Amazônia central

Objetivos específicos

- Avaliar como as variações sazonais de isopreno, monoterpenos totais e sesquiterpenos totais se assemelham à sazonalidade de fatores ambientais - radiação solar e temperatura;

- Analisar o potencial de relação entre variações sazonais de emissões de isopreno e monoterpenos totais e fenologia foliar;

- Verificar o potencial de correlação entre variações sazonais de isopreno e NEE.

Capítulo I

Alves, E.G.; Jardine, K.; Tóta, J.; Jardine, A.; Yãnez-Serrano, A. M.; Karl, T.; Tavares, J. V.; Nelson, B.; Gu, Dasa.; Stavrakou, T.; Guenther, A. Seasonality of isoprenoid atmospheric vertical profiles within and above a primary rainforest in central Amazonia. Manuscrito em preparação para *Atmospheric Chemistry and Physics*

Seasonality of isoprenoid atmospheric vertical profiles within and above a primary rainforest in central Amazonia

Abstract

A few studies of seasonal variation with *in situ* measurements are just starting to investigate isoprenoid and other VOC emissions in the Amazonian rainforest. In this study, vertical mixing ratio profiles of isoprene, total monoterpenes (TMt) and total sesquiterpenes (TSt) were quantified, 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 also estimated by the inverse Lagrangian transport model. Measurements were carried out from the dry season (September 2010) to the wet season (January 2011), continuously. All compound mixing ratios were higher during the dry season than during the wet season; the same behavior was observed for ambient air temperature and photosynthetically active radiation (PAR). Isoprene and TMt mixing ratios were higher within the canopy as compared to near the ground and above the canopy. Daytime TSt mixing ratios were higher near the ground than within and above the canopy. Isoprene and TMt mixing ratios had a diurnal cycle similar to diurnal cycles of air temperature and PAR suggesting that the emission of these compounds are light dependent and stimulated by increasing temperature. However, this same behavior was not observed for TSt. This is probably due to the fact that these sesquiterpene emissions are not strongly light dependent; the ozonolysis of sesquiterpenes during daytime could reduce ambient sesquiterpene concentrations; and a less turbulent atmospheric boundary layer during nighttime could make the mixing ratio of sesquiterpenes higher near the surface at nighttime. Daytime flux estimates also revealed significant seasonal variation for the fluxes of all compounds. The maximums for isoprene and TMt were observed during the dry season, whereas the maximum for TSt were found during the dry-to-wet transition season. These flux estimates suggest that the canopy is the main source of those compounds for the atmosphere for all seasons. These results suggest that isoprenoid could be driven by changes in light, temperature and leaf phenology.

Key-words: Isoprene, total monoterpenes, total 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 and deposition of reaction products (Lelieveld et al., 2008). 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 may be involved in the atmosphere chemistry, biogeochemical cycling and climate at local, regional and global scales.

One example of BVOC biosphere-atmosphere interactions is the influence that these compounds can exert on the greenhouse gases, because, although non-methane BVOCs are not thought to be important global greenhouse gases, these compounds can contribute to the formation of ozone (O_3) and may also have an effect on the oxidative capacity of the troposphere and influence the rate of oxidation, formation and concentration of other trace gases (Pacifico et al., 2009), affecting on the residence times of greenhouse gases. Additionally, BVOCs can influence the formation and growth of secondary organic aerosols (SOAs), which can affect cloud development and precipitation (Andreae and Crutzen, 1997; Carslaw et al., 2010; Poschl et al., 2010) and the radiation budget of the Earth's surface (Forkel et al., 2012).

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 is likely owing to a relativity small number of compounds (Laothawornkitkul et al., 2009). The most emitted group is the isoprenoids. 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 is the dominant emitted compound 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). In a group of more than 1000 monoterpene compounds identified in plants, only a few (less than 20) monoterpenes represented the largest fraction of all monoterpene emissions into the atmosphere (Guenther, 2002). Compounds such as α-pinene, β-pinene, Δ^3- carene, d-limonene, camphene, myrcene,

sabinene, β-phellandrene and ρ-cymene dominate monoterpene emissions globally, however at regional scales other monoterpene compounds may also be important (Geron et al., 2000). 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 a considerable amount (Guenther, 2002). However, for sesquiterpene emissions, measurements and estimates are still a challenge due to their high reactivity and low vapor pressure (Laothawornkitkul et al., 2009), making the characterization of sesquiterpene emissions still an open question.

Global isoprenoid emissions from the biosphere into the atmosphere have been broadly investigated (Laothawornkitkul et al., 2009), but estimates of global annual emissions still show large uncertainties (Guenther et al., 2006). One approach to constrain 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 (Guenther et al., 2006). This approach has produced additional evidence that tropical rainforests are the largest source of isoprene to the global atmosphere, and also suggested seasonal patterns on emissions of this organic compound (Barkley et al., 2009).

Due to the large biodiversity, the quantification of isoprenoid emissions from the major tropical rainforest in the globe - Amazonian rainforest - is a very arduous task. On the other hand, there is a need for reliable estimates, since regional isoprenoid emission estimates from tropical forests to the atmosphere are needed. In this context, there have been about 20 campaigns to study isoprenoid mixing ratios and emissions from the Amazonian rainforest at canopy and ecosystem scales (Table 1); however, there is a lack of continuous measurements to characterize the regional seasonality of emissions.

Seasonal variations of isoprene emissions in the Amazonian rainforest are established based on some studies with intensive campaigns *in situ* (table 1) and on satellite retrieval with modeling (Barkley et al., 2008, 2009, 2013). The seasonality presented by satellite-derived isoprene emissions in this ecosystem (Barkley et al., 2009) indicated that emission variations should be strongly affected by leaf phenology, which is probably driven by seasonal changes in insolation (Jones et al., 2014), because water availability does not seem to be a constrain for the majority of the Amazon basin and solar radiance peaks out of phase with precipitation due to cloud cover seasonality (Restrepo-Coupe et al., 2013).

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

2. Material and methods

2.1 Site description

Isoprenoid vertical profiles were investigated at the 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. This reserve has an area of about 230 km² and belongs to the National Institute for Amazonian Research (INPA). Soils are well drained Oxisols and Ultisols on the plateau and slopes, respectively, and poorly drained Spodosols in the valleys (Luizao et al., 2004). The vegetation in this area is considered mature, *terra firme* rain forest, 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 (figure 1a), being the wetter period from December to May. Although severe droughts had impacted part of the Amazon basin in 2005 and in 2010, those droughts have not affected the central Amazonia (Marengo et al., 2008, 2011). However, despite the lack of severe droughts in central Amazonian rainforest, micrometeorological measurements from 1999 to 2012 showed that from August to September the monthly cumulative precipitation can be less than 100 mm per month (figure 1a), characterizing this period as dry season. Average air temperature ranges between 24 °C (in April) and 27 °C (in September) (figure 1e). Soil moisture near the surface shows a small reduction (~ 10%) of water availability during the dry season 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 (figure 1b), and when Photosynthetic Active Radiation (PAR) (figure 1d) and air temperature (figure 1f) show their peaks. As October 2010 showed 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 dry season vary from year-to-year (da Rocha et al., 2009).
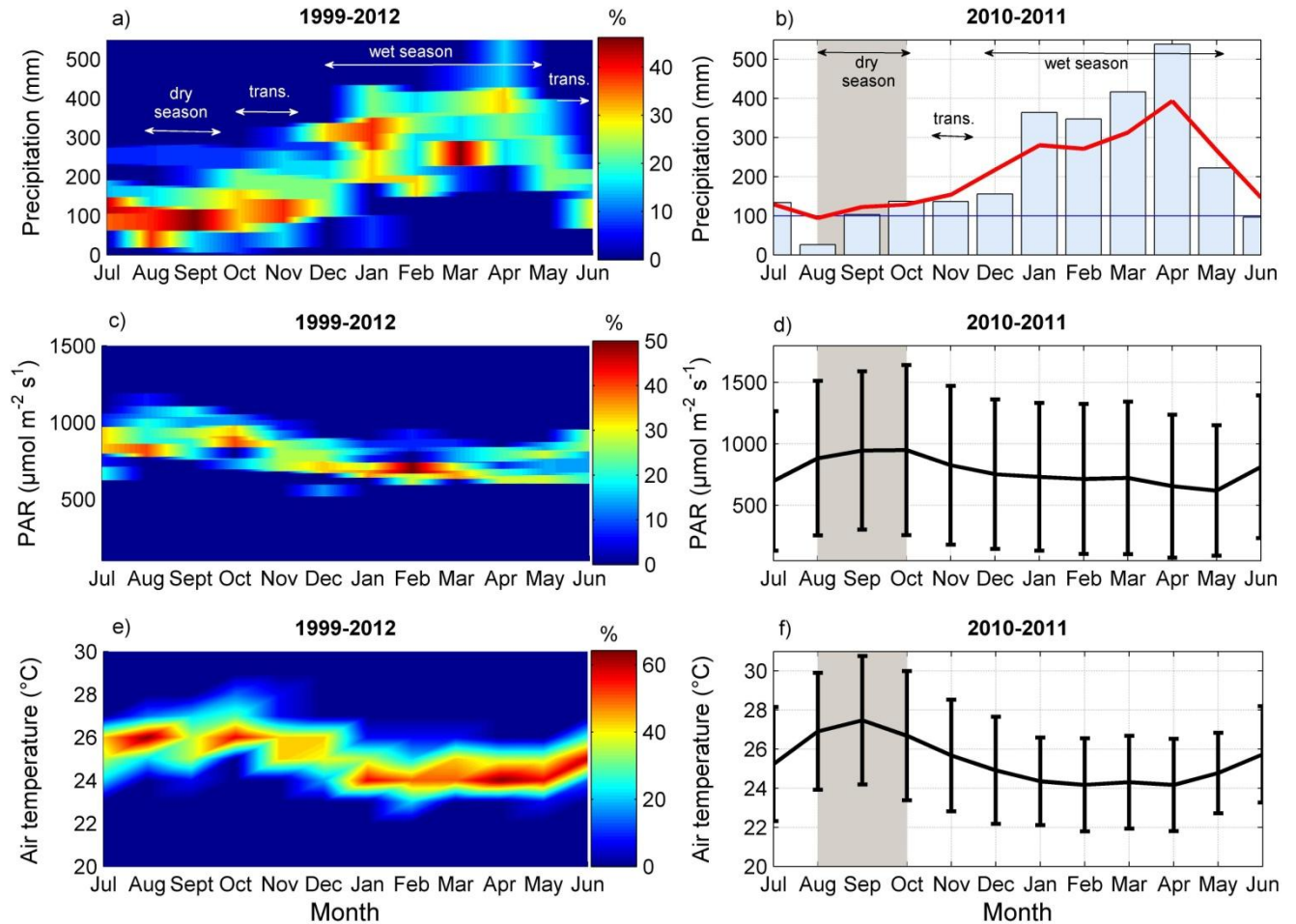
Figure 1: Precipitation, PAR and air temperature measured at K34 tower (~2 km far of TT34 tower); a) relative frequency (%) of monthly cumulative precipitation from 1999 to 2012, b) monthly cumulative precipitation from July 2010 to June 2011 (measured in 30 minute intervals of 24 hours) (bars), and 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 from 6h to 18h, local time), d) monthly average PAR from July 2010 to June 2011 (measured every 30 min from 6h to 18h, local time); 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 of 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) represent 100 mm month[-1].

2.2. Isoprenoid measurement and data analysis

Ambient mixing ratio measurements of isoprenoids - 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 mb (E/N, 136 Td). PTR-MS conditions showed high and sustained primary ion intensities (20-40 MHz H_3O^+) with low water cluster and O_2^+ formation (water cluster and $O_2^+ < 4\%$ H_3O^+). During each PTR-MS measurement cycle, the following mass to charge ratios (m/z) was monitored, 21 ($H_3^{18}O^+$), 32 (O_2^+), 37 (H_2O-H_3O^+) with a dwell time of 20 ms each, and 69 (isoprene-H^+), 137 (total monoterpenes-H^+) and 205 (total sesquiterpenes-H^+) with a dwell time of 5s each. Isoprenoids were quantified based on equation 1, where raw signals (counts per second, cps) were normalized by the adjusted primary ion signal (cps_{21}) and background subtracted from measurements of ultra high purity nitrogen to obtain normalized counts per second. The signal at m/z 21 ($H_3^{18}O^+$) was measured and multiplied by the oxygen isotopic ratio of a representative natural abundance water sample ($^{16}O/^{18}O=500$), which provided the adjusted primary ion signal (cps_{21}) (Jardine et al., 2011, 2012; Lindinger et al., 1998)

$$ncps = (\frac{cps}{cps_{21}})_{sample} - (\frac{cps}{cps_{21}})_{background} \qquad (1)$$

The PTR-MS was calibrated for isoprene, total monoterpenes and total sesquiterpenes twice in the field using the dynamic solution injection (Jardine et al., 2010). Solutions of 5 µL of isoprene, α-pinene and β-caryophylene standards (Merk) diluted in 100 mL of cyclohexane were injected into the mixing vial at 0.5, 1.0, 2.0, and 3.0 µL/min (30 min each flow rate) with a constant dillution flow of 1.0 slpm ultra high purity nitrogen passing through. Mixing ratios of isoprene, total monoterpenes and total sesquiterpenes were calculated by multiplying the calibration slope (ppbv/ncps) by ncps. More details about the determination of isoprene, total monoterpene and total sesquiterpene mixing ratios can be obtained in Jardine *et al.* (2011) and Jardine *et al.* (2012), where part of these data have been already published.

The isoprenoid vertical profile was installed with six ambient air inlets at different tower heights (2, 11, 17, 24, 30 and 40m) sequentially analyzed during 10 min at each of the six heights, resulting in one complete profile every hour. All Teflon gas inlets were continuously heated to ~ 50 °C, using self-regulating heating tape (Omega Engineering) in an insulated jacket, to minimize losses during sampling. All inlets had air sample tubing lengths equal to the inlet heights plus an additional 4 m each to reach the PTR-MS, which was located inside a container directly adjacent to the tower. An oil free diaphragm pump (KNF Neuberger) was used to draw the ambient air through all the inlets (¼ in O.D. Teflon PFA tubing). For each inlet, the sample airflow rates were set to ~4.0 slpm using needle valves downstream of the PTR-MS. The response time caused a delay time ranging from 6 s (2 m height inlet) to ~15 s (40 m height inlet), measured by spiking an VOC pulse at all six inlets of the tower (Jardine et al., 2011, 2012).

Background signals were obtained by running ultra high purity nitrogen directly into the inlet of the PTR-MS (bypassing the ambient inlets) for 2 h before of each vertical profile air measurement period. Limits of detection for isoprene, total monoterpenes and total sesquiterpenes were equal to 0.32 ppb, 0.15 ppb and 0.012 ppb, respectively. Vertical profiles were calculated by averaging the last 7 min of each 10 min measurement period of each inlet height. Mixing ratio averages were calculated for the daytime period (10:00 – 16:00 local time) and for the nighttime period (22:00 – 04:00 local time), and flux calculations were obtained of daytime concentration averages from 10:00 to 14:00h (local time) of the dry season, the dry-to-wet transition season and the wet season data.

2.3 Isoprenoid gradient flux

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

$$\vec{C} - C_{Ref} = \overleftrightarrow{D} . \vec{S} \tag{2}$$

where $\vec{C}$ is the concentration (g m^{-3}) vector for each level, C_{Ref} is the concentration (g m^{-3}) at reference height (40 m), $\overleftrightarrow{D}$(m) is a dispersion matrix and $\vec{S}$ (mg m^{-2} h^{-1}layer^{-1}) 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 $\overleftrightarrow{D}$: the Lagrangian timescale (Tl) was parameterized according to Raupach(1989); the vertical profile of the standard deviation of the vertical wind speed was scaled to measured friction velocity. The normalized turbulence profile was taken from turbulence measurements inside and above the canopy during the AMAZE (Amazonian Aerosol Characterization Experiment) 2008 experiment (Karl et al., 2009); the friction velocity was averaged for each season using daytime data (10:00-14:00h local time) of friction velocity measured at a tower (K34 tower - 2° 36' 32.67" S, 60° 12' 33.48" W) ~2 km far from the tower where isoprenoid profiles were measured (TT34 tower). The calculation of $\overleftrightarrow{D}$ was based on far- and near-field approach described by Raupach(1989). As some model inputs - 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 K34 tower has shown that u* along with other averaged turbulence data have similar quite daytime values between wet and dry seasons (Ahlm et al., 2010; Araujo et al., 2002).

2.4 Emission activity algorithms - Model of Emissions of Gases and Aerosols from Nature (MEGAN 2.1)

Isoprenoid emissions estimated by MEGAN are based on a simple mechanistic model that takes into account the main processes driving variations in emissions (Guenther et al., 2012). According to 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_{CO_2}) as

$$\gamma_i = C_{CE}LAI\ \gamma_P\ \gamma_T\ \gamma_A\ \gamma_{SM}\ \gamma_{CO_2} \tag{3}$$

where C_{CE} is the canopy environment coefficient, which sets $\gamma_i = 1$ for the standard conditions (PAR - 1000 μmol m^{-2} s^{-1} and T - 30 ºC) and is dependent on the canopy environment model being used. For this study, the Guenther et al. (2006) canopy environment model is used and it has a C_{CE} of 0.57.

Isoprene emissions are considered light-dependent, but emissions of monoterpenes and sesquiterpenes include a light-dependent fraction (LDF, see Table 4 of Guenther et al., 2012) and a light-independent fraction (LIF = 1-LDF) that is not influenced by light. Thus, the emission activity factor that considers the light response of emissions is estimated as:

$$\gamma_{P,i} = (1 - LDF_i) + LDF_{i\gamma P\_LDF} \tag{4}$$

where γ_{P_LDF} represents the light-dependent activity factor described for isoprene (Guenther et al., 2006):

$$\gamma_{P\_LDF} = C_P \left[\frac{(\alpha \times PPFD)}{((1 + \alpha^2 \times PPFD^2)^{0.5})}\right] \tag{5}$$

where $PPFD$ is the photosynthetic photon flux density (μmol m^{-2} s^{-1}) and C_P and α are estimated as:

$$\alpha = 0.004 - 0.005\ln(P_{240}) \tag{6}$$

$$C_P = 0.0468 \times \exp(0.0005 \times [P_{24} - P_S]) \times [P_{240}]^{0.6} \tag{7}$$

where P_S is the standard condition for PPFD averaged over the past 24 h and is set to 200 μmol m^{-2} s^{-1} for sun leaves and to 50 μmol m^{-2} s^{-1} for shade leaves; P_{24} is the average PPFD of the past 24 h and P_{240} is the average PPFD of the past 240 h.

The temperature activity factor also includes a light-dependent and light-independent fraction:

$$\gamma_{\text{T},i} = (1 - \text{LDF}_i)_{\gamma\text{T\_LIF},i} + \text{LDF}_{i\gamma\text{T}_{\text{LDF}},i} \tag{8}$$

The light-dependent fraction is calculated following Guenther *et al.*, (2006):

$$\gamma_{\text{T\_LDF},i} = E_{\text{opt}} \times \left[\frac{C_{\text{T2}} \times \exp(C_{\text{T1}} \times x)}{(C_{\text{T2}} - C_{\text{T1}} \times (1 - \exp(C_{\text{T2}} \times x)))}\right] \tag{9}$$

where $x = [(1/T_{opt}) - (1/T)]/0.00831$, T is leaf temperature (K), $C_{T1,i}$ (see Table 4 in Guenther et al., 2012) and C_{T2} (=230) are empirically determined coefficients,

$$T_{opt} = 313 + (0.6 \times (\text{T}_{240} - \text{T}_{\text{S}})) \tag{10}$$

$$E_{opt} = C_{eo} \times \exp\left(0.05 \times (T_{24} - T_S)\right) \times \exp(0.05 \times (T_{240} - T_S)) \tag{11}$$

where T_S is the standard condition for leaf temperature (= 297 K), $T24$ is the average leaf temperature of the past 24 h, $T240$ is the average leaf temperature of the past 240 h, and *Ceo* is an emission-isoprene dependent empirical coefficient (see table 4 of Guenther et al., 2012). The response of the light-independent fraction is based on the exponential temperature response function of Guenther et al.(1993):

$$\gamma_{T_{LIF},i} = \exp(\beta_i(T - T_S)) \tag{12}$$

where β_i is an empirical coefficient for each emission class (see table 4 of Guenther et al., 2012). The leaf age, soil moisture and CO_2 inhibition activity factors for isoprenoids were assigned a value of $\gamma_A = 1$, $\gamma_{\text{SM}} = 1$ $\gamma_{CO_2} = 1$, respectively, which assumes no variation in these parameters.

The inputs for the all model runs - PPFD and air temperature - were obtained from the K34 tower measurement time series (Program of Large Scale Biosphere-Atmosphere - LBA), of PPFD and air temperature measurements simultaneous to the PTR-MS measurements.

2.5 Canopy light penetration and leaf phenology

The MEGAN 2.1 standard canopy environment model, based on Guenther et al. (1999) was used to model light penetration by into the canopy (Guenther et al., 2006). Model inputs were: PAR measured (every 30 min) at ~ 50 m on the K34 tower for the whole period of isoprenoid measurements; and 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). In other words, the layers were distributed according to a Gaussian curve fit to the canopy surface area densities (from 0.5 m to 48 m); with the first layer (top canopy) and fifth layer (ground surface) represented by 12 % of the total canopy surface area density; second layer (upper canopy) and fourth layer (understory) represented by 23% of the total canopy surface area density, and the third layer (middle canopy) represented by 30% of the total canopy surface area density. Light absorption was calculated as the difference in light penetration between layers from the top to the bottom. This light absorption corresponded with light that passes through the canopy vertically while the remaining light is due to reflectance and/or scattering.

Leaf phenology was estimated based on the observation of leaf flushing events of upper crown surfaces of 63 living trees. For the monitoring, a system of data acquisition and storage - a Stardot (model Netcam XL 3MP) camera with a 1024 x 768 resolution CMOS sensor - was installed at 51 m in the K34 tower, at 15-20 m above the canopy. 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 seconds 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 area of sky in the image. The most distant trees in the image were located approximately at 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, an image was selected at every six days, and then grouped for each month of this study.

2.6 Satellite-derived isoprene emission estimates

The top-down isoprene emission estimates over the 0.5 degree region around TT34 tower were derived by using a grid-based source inversion scheme (Stavrakou et al., 2009) constrained by formaldehyde (HCHO) columns, which is an intermediate product of the isoprene degradation process (Stavrakou et al., 2014), measured by the Global Ozone Monitoring Experiment (GOME-2)/MetOp-A satellite between 2010 and 2012. The source inversion was created on the Intermediate Model of Annual and Global Evolution of Species (IMAGESv2) global chemistry-transport model run at a resolution of 2º × 2.5º and calculated in 40 vertical levels from the surface to the lower stratosphere (Stavrakou et al., 2014).

In summary, this was accomplished using the global model IMAGEV2 with a priori emission inventory from MEGAN 2.1 (with adjusted emission factors assigned to tropical forests) was constrained by satellite HCHO column to estimate the a posterior biogenic isoprene emission. Daily (24 hours) mean satellite-derived isoprene emissions were calculated from Jan 1st, 2010 to December 31st, 2012. More details about settings and corrections adopted for this retrieval can be found in Stavrakou et al. (2009a, 2014) and Bauwens *et al.* (2013).

3. Results

3.1 Vertical profiles of isoprenoids

Vertical profiles of isoprenoids were analyzed for daytime and nighttime for all the seasons considered in this study - dry season, dry-to-wet transition season and wet season. Both isoprene (Figure 2 a, b, c) and total monoterpenes (Figure 2 d, e, f) presented higher mixing ratios during daytime (10-16h, local time) than during nighttime (22-04h, local time) for all seasons,

showing that isoprene and total monoterpenes are light- and temperature-dependent. During daytime, isoprene showed maximum mixing ratios within the canopy; in contrast, at nighttime, vertical profiles of this compound showed maximum values above the canopy, with its vertical profiles similar to those of nighttime air temperature (Figure 2 j, k, l). Although the diurnal cycle of total monoterpenes indicates that they are light-dependent, the nighttime mixing ratios of these compounds revealed a small peak at the sub-canopy (17m) (Figure 2 d, e, f), which has lower light levels than the upper canopy. Total sesquiterpene mixing ratios have a different vertical profile compared to isoprene and total monoterpenes for all seasons. Total sesquiterpenes demonstrated higher mixing ratios near the ground and at the sub-canopy level (17 m) than above the canopy (Figure 2 g, h, i). Daytime and nighttime vertical profiles were similar, but total sesquiterpene mixing ratios were higher during the nighttime.
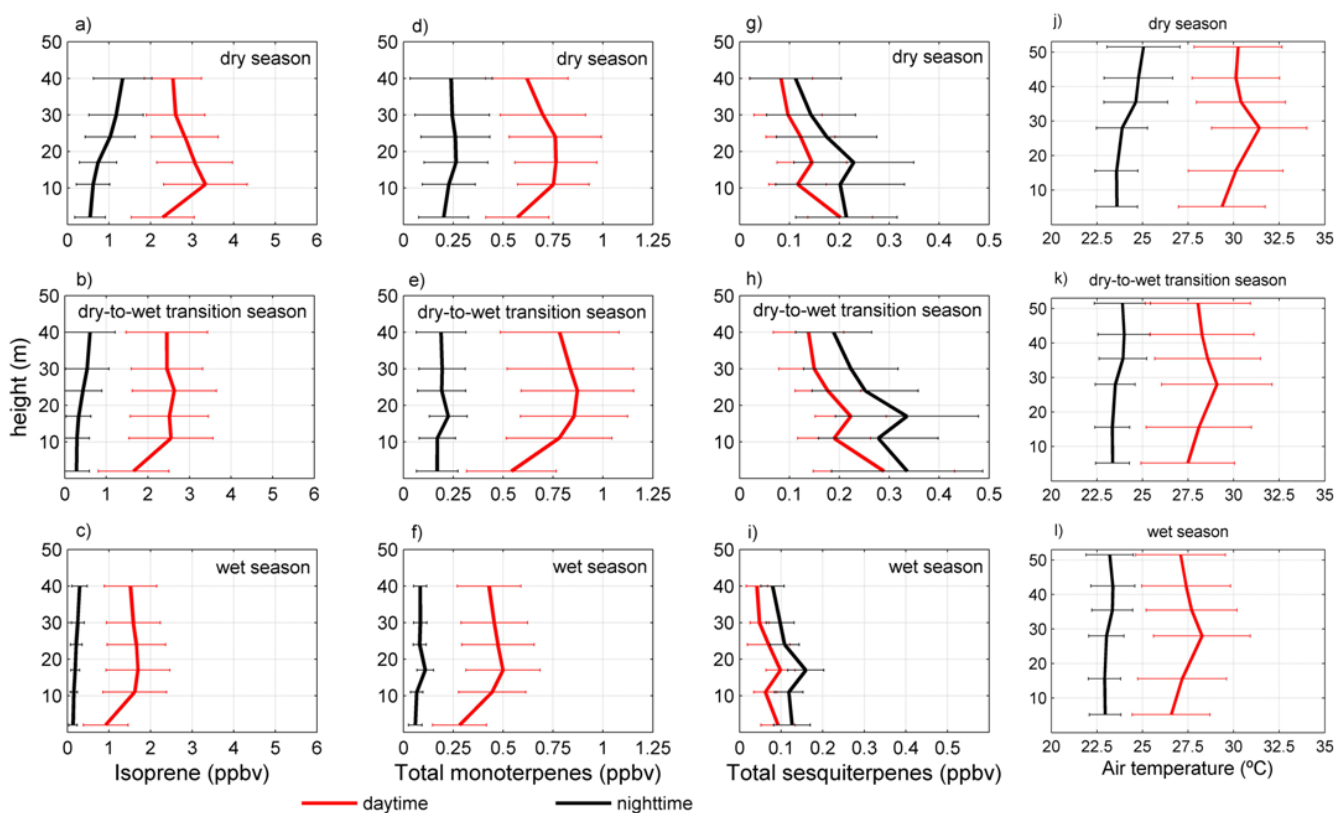
Figure 2: Daytime (10-16h, local time) and nighttime (22-04h, local time) average vertical profiles of isoprene (a, b, c), total monoterpenes (d, e, f) , total sesquiterpenes (g, h, i), and air temperature (j, k, l) from the dry season to the wet season.

Diurnal cycles of mixing ratios of isoprene and total monoterpenes presented a behavior similar to air temperature and PAR over the period of measurements (data not shown). In other

words, when PAR and air temperature increased, mixing ratios of isoprene and total monoterpenes also increased. However, the level of this dependency to light and temperature may be different between seasons, because both isoprene and total monoterpenes followed the PAR diurnal cycles more during the wet season (maximums at 12:00-13:00, local time) and, during the dry season, these compounds followed a pattern similar to the air temperature (maximums at 14:00-15:00, local time). All mixing ratios of these compounds as well as PAR decreased during the days when rainfall was observed, which could indicate that lower emissions of isoprene and total monoterpenes during the wet season is due to the more frequent precipitation and lower values of PAR. However, isoprene and total monoterpene mixing ratios of only sunny days of all seasons were compared and results still presented seasonal variation (figure 3 a), suggesting that long-term variations in environmental conditions may also influence isoprene and total monoterpene emissions.

Vertical profiles of isoprene showed higher mean mixing ratios in dry season, followed by the dry-to-wet transition season and wet season (top panel of Figure 3 a). The reduction of isoprene mixing ratios from the dry season to dry-to-wet transition season was up to ~ 23% and from dry season to wet season was up to ~ 67%. Although daytime isoprene mixing ratios were lower near the ground and above the canopy compared to within the canopy for all seasons, the shapes of vertical profiles were different among seasons. During the dry season, the maximum isoprene mixing ratio was located at 11 m (sub-canopy), where the maximum estimated surface area density of the canopy (top panel of Figure 3 a) was also observed. During the dry-to-wet transition season, isoprene mixing ratios showed a peak at 11m, but the maximum isoprene mixing ratio was observed at 24 m in the upper canopy. During the wet season, isoprene mixing ratios had a constant shape from 11 m to 24 m, and showed a small decrease from 24m to 40 m.

Daytime total monoterpenes showed higher mean mixing ratios in the dry-to-wet transition season, followed by the dry season and the wet season (middle panel of Figure 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 ~ 19% from the dry season to the dry-to-wet transition season, and a decrease of up to ~ 49% from the dry-to-wet transition season to the wet season. For all seasons, total monoterpene mixing ratios were lower near the ground and above the canopy compared to within the canopy. The shape of vertical profiles was similar between the dry season and the dry-to-wet transition season, with the maximum total monoterpene mixing ratio at 24 m

(upper canopy). However, during wet season, the maximum total monoterpene mixing ratio was observed at 17 m, with a small decrease from 17 m to 40 m.
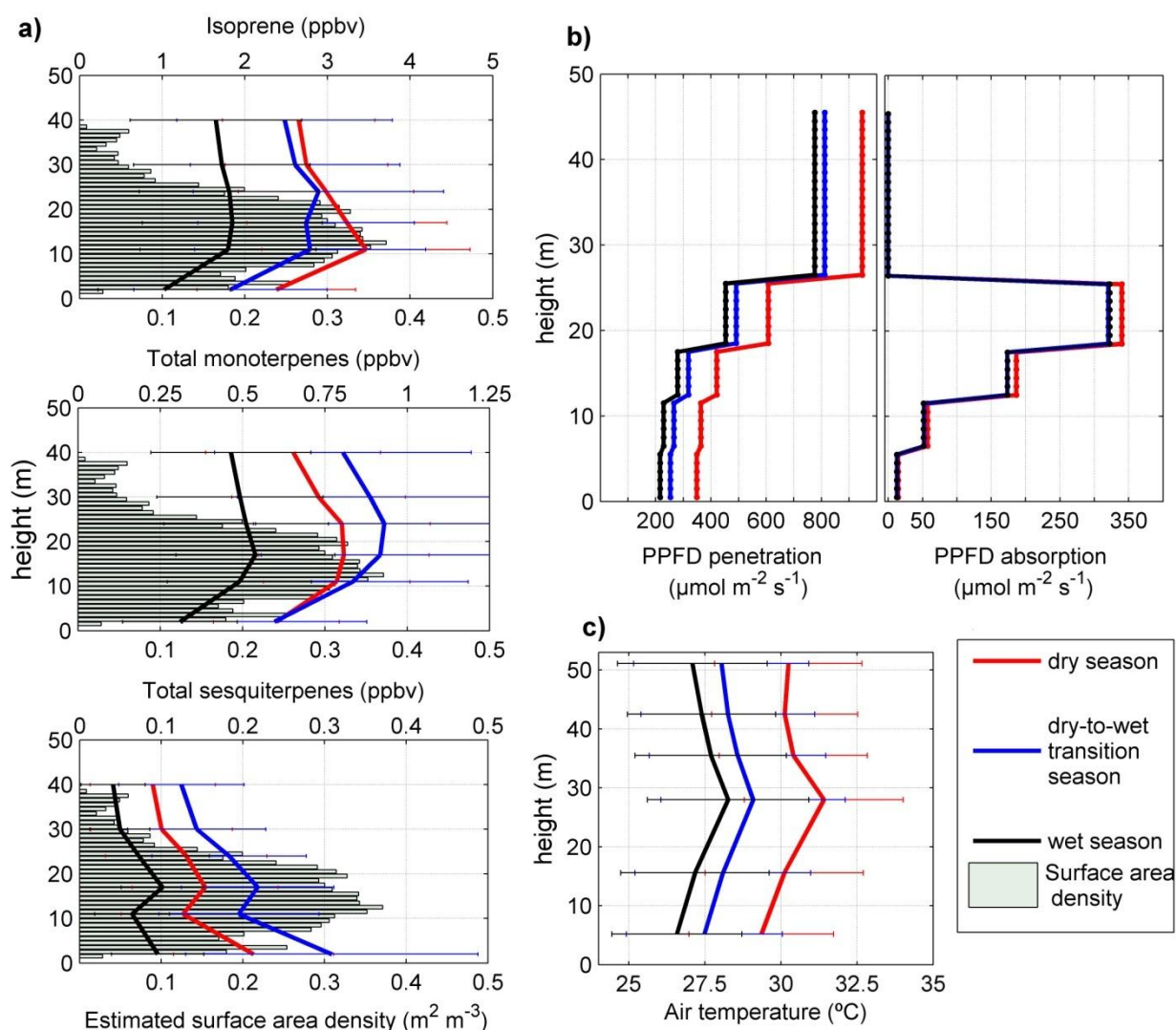
Figure 3: Daytime (10-16h, local time) vertical profiles of mixing ratios of isoprene, total monoterpenes and total sesquiterpenes from the dry season to the wet season; and estimated surface area density of the canopy in the plateau of this site of study (ground-based measurements carried out in March/2004 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 (10-16h, local time) air temperature profiles from dry season to wet season measured at K34 tower (c). In figure (a) top and bottom x axis represent isoprenoid mixing ratios and estimated surface area density of the canopy, respectively.

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 Figure 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 reduced up to 54% from the dry-to-wet transition season to the wet season. For the whole period of measurements, total sesquiterpene mixing ratios had similar vertical profiles, with mixing ratios higher near the ground and at 17 m (sub-canopy) than above the canopy. However, during the dry season and the dry-to-wet transition season, the maximum total sesquiterpene mixing ratios were observed near the ground and during wet season the maximum mixing ratio was observed at 17 m (sub-canopy) (bottom panel of Figure 3a).

The vertical profile of photosynthetic photon flux density (PPFD) absorbed by the canopy was higher during the dry season; followed by the dry-to-wet transition season and wet season (Figure 3 b), and the maximum absorption of PPFD occurred right above the maximum of estimated surface area density of the canopy. This maximum PPFD absorption at the upper canopy agrees with the maximum of isoprene mixing ratios during the dry-to-wet transition season (top panel of Figure 3 a), but differs when compared to peaks of isoprene mixing ratios during the dry season and the wet season.

Total monoterpenes seemed to be light-dependent and stimulated by increasing temperature, since peaks of these compounds were found where there was more PPFD penetration and absorption by the canopy and where the highest air temperature was observed (Figure 3 c). The relativity small difference of mixing ratios between the dry-to-wet transition season and the dry season (up to ~ 19%) could be related to some biotic (e.g. leaf phenology) or abiotic factors other than PAR and air temperature, because these environmental factors were higher during the dry season than during the dry-to-wet transition season. Nevertheless, when total monoterpene fluxes were computed (see section 3.2), this difference was much smaller and total monoterpene fluxes were somewhat higher during the dry season (Figure 4 e).

3.2 Seasonal isoprenoid fluxes

Isoprene emission rates inferred from concentrations were estimated to be highest at the sub-canopy (~16 m) during the dry season, and highest at the upper canopy (28 m) during the dry-to-wet transition season and the wet season (Figure 4 a). However, even with differences in the highest layer source 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 experiencing higher isoprene emissions than the wet season (0.52 ± 0.1 mg m^{-2} h^{-1}) (Figure 4 b).

The upper canopy (22-28 m) seemed to be the main source of total monoterpenes for all seasons (Figure 4 d). In the dry season, emissions of these compounds were slightly higher (1.47 ± 0.06 mg m^{-2} h^{-1}) than during the dry-to-wet transition season (1.29 ± 0.2 mg m^{-2} h^{-1}), and higher than during the wet season (0.36 ± 0.05 mg m^{-2} h^{-1}) (Figure 4 e). For total sesquiterpenes, the canopy (22 m) was the major source of emissions during all seasons (Figure 4 g). The highest total sesquiterpene emission rates were found at 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}) (Figure 4 h).

Based only on light and temperature variation, relative emissions (emission normalized to standard conditions - PAR at 1000 µmol m^{-2} s^{-1} and temperature at 30ºC) estimated by MEGAN 2.1 showed the maximum normalized emission during the dry season for all compounds (Figure 4 c, f, i), in contrast to those calculated based on the vertical profile concentrations (Figure 4 b, e, h), which showed similar emission values 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.

To compare the seasonal variation of isoprenoid emissions with changes in environmental factors in more details, monthly fluxes of isoprene, total monoterpenes and total sesquiterpenes were compared to PAR (at ~ 51 m) and air temperature (at ~ 51 m) (Figure 5). Isoprene and total monoterpene fluxes seemed to be more related to PAR than to air temperature, since the highest fluxes of these compounds were observed when PAR also showed its highest value (October 2010). Total sesquiterpene fluxes did not show behavior similar to PAR or air temperature, having the highest emission when PAR and air temperature were decreasing (November 2010) (Figure 5 b). Again, MEGAN 2.1 estimates (Figure 5 c) differed of emissions based on vertical profiles (Figure 5 b), showing a behavior similar to air temperature variation for all compounds.
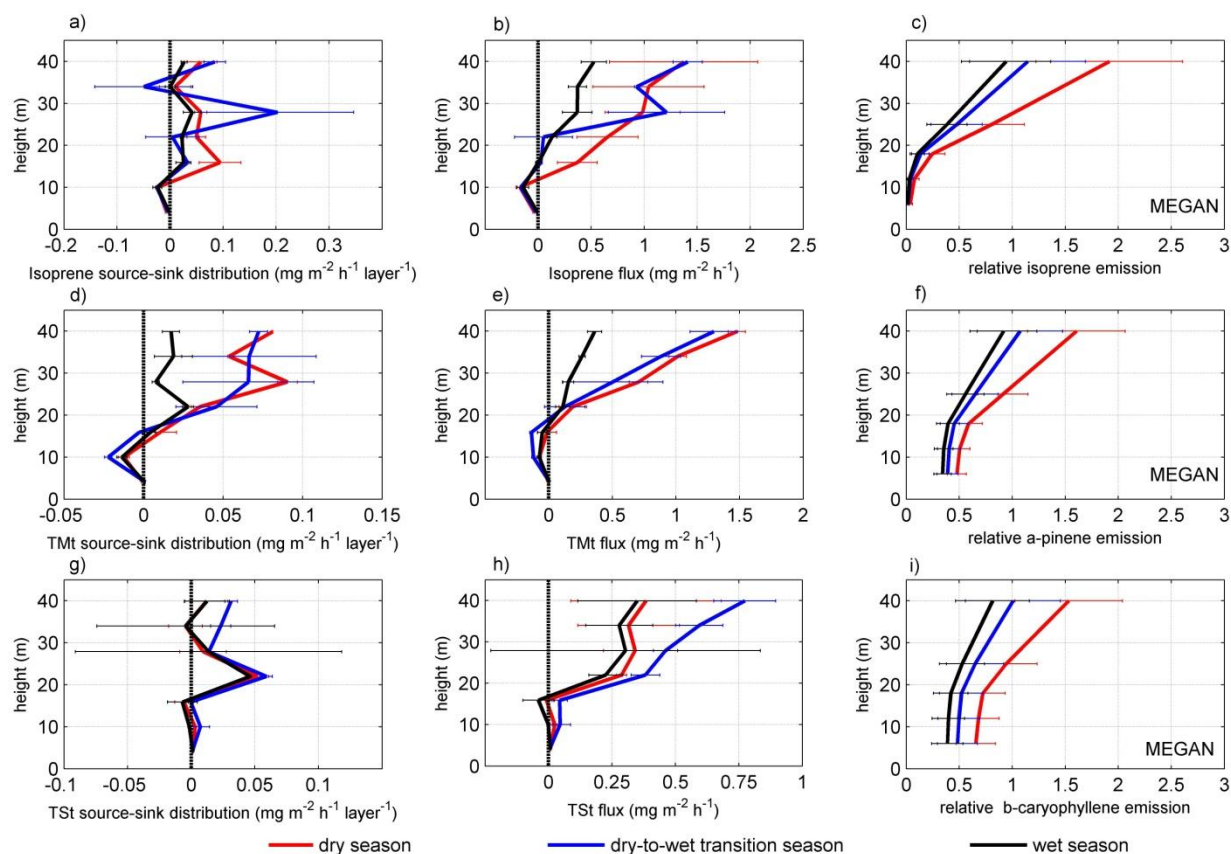
Figure 4: Daytime (10-14h, local time) source-sink distribution inside and above the canopy, flux estimation, and relative emission modeled by MEGAN 2.1 of isoprene (a, b, c), total monoterpenes (TMt) (d, e, f) and total sesquiterpenes (TSt) (g, h, i) from the dry season to the wet season.

From October 2010 to December 2010, a decrease only on the emissions of isoprene and total monoterpenes was observed, which was expected due to decreasing light and temperature. However, from December 2010 to January 2011 increasing emissions of these compounds was observed. This was only a small variability or may indicate that emissions start increasing at the beginning of wet season. It is interesting that the strong decrease on emissions of isoprene and of total monoterpenes in December 2010 resulted in values comparable to and even lower than total sesquiterpene emissions, respectively (Figure 5 b).
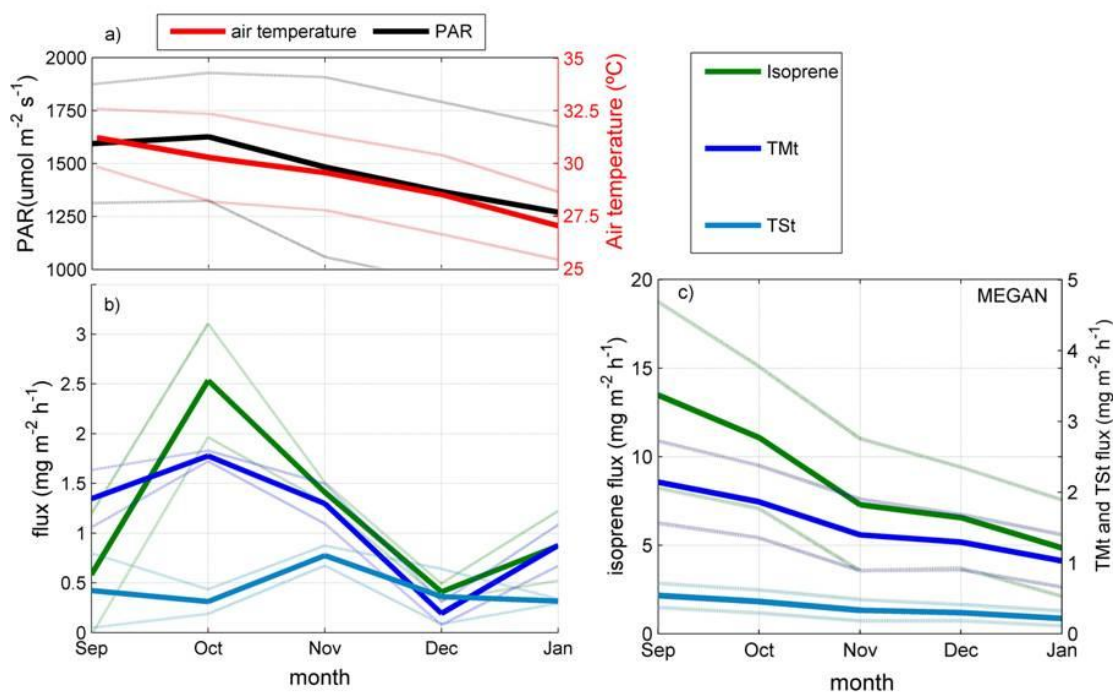
Figure 5: Monthly averages of air temperature (red line) and PAR (black line) (measured at K34 tower during 10-14h, local time,) (a). Monthly averages of emissions of isoprene (green line), total monoterpenes (TMt) (dark blue line) and total sesquiterpenes (TSt) (light blue line) (estimated for 10-14h, local time, at TT34 tower) (b). Monthly emissions of isoprene (green line), total monoterpenes (TMt) (dark blue line) and total sesquiterpenes (TSt) (light blue line) modeled by MEGAN 2.1 (estimated for 10-14h, local time) (c). Solid lines are averages and hashed lines represent one standard deviation.

Leaf phenology seemed to be an important driver of isoprene and total monoterpene emissions. When leaf flushing, PAR, isoprene and total monoterpenes were compared, it was observed that all of these factors have a similar behavior (Figure 6). For the period of this study, the analysis of images of 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 (Figure 6), being similar to the decrease of isoprene and total monoterpene emissions and PAR. However, 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 63 trees) of treetops with leaf flushing (Tavares, 2013), and presented a subsequent decrease until the end of the wet season (Figure 6). These results suggested that isoprene and total monoterpene emissions reached their peaks out of phase with the peak of leaf flushing, but emissions were synchronous to PAR variation. However, it is known that emission of isoprene and monoterpenes is species specific and so the relationship to

leaf flushing will depend on which season the emitting species are flushing so it is difficult to extrapolate beyond period studied.
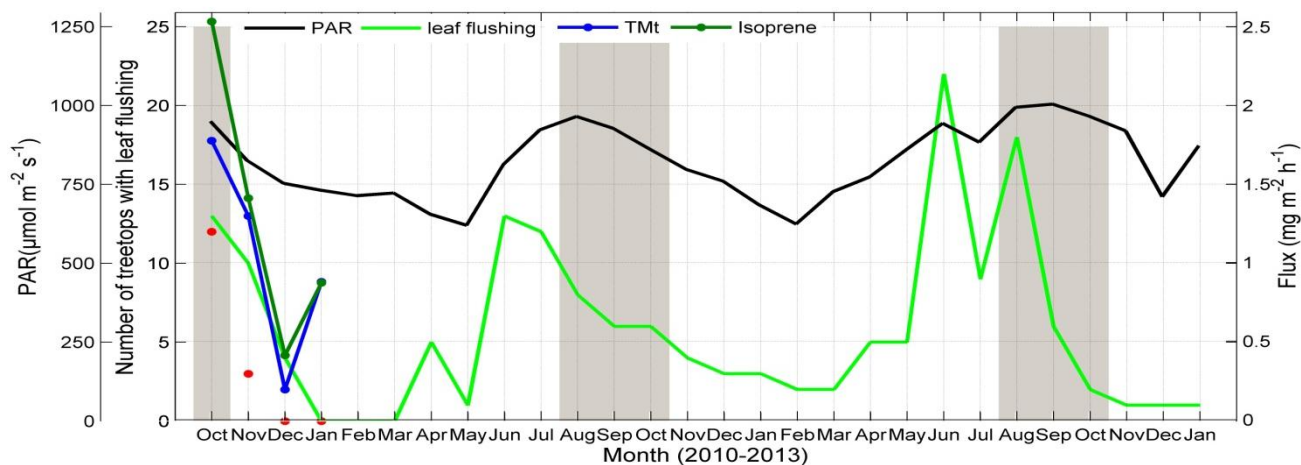
Figure 6: Estimated monthly leaf flushing (light green line) (Tavares 2013),and monthly average of PAR measured from October 2010 to January 2013 at K34 tower (06-18h, local time) (black line). For the period of this study, leaf flushing is also represented by the analysis of images of every six days from October 2010 to January 2011 (red circles). Monthly averages of fluxes of isoprene (dark green line) and total monoterpenes (blue line) (estimated for 10-14h, local time, at TT34 tower). Grey areas represent the period of the dry season.

3.3 Ground-based *versus* satellite-derived isoprene emissions

Isoprene emissions estimated based on vertical profile concentrations and satellite-derived isoprene emissions were compared in order to investigate if large-scale estimates made from satellite observations could represent well the seasonal pattern observed *in situ* in central Amazonia. Although the satellite-derived isoprene emissions being presented as monthly averages of daily values (24 hours, mg m^{-2} day^{-1}) and ground-based isoprene emissions being shown as monthly averages of hourly means (mg m^{-2} h^{-1}) (Figure 7), this comparison attempts to demonstrate that both large (satellite) and small (ground-based) scales have higher isoprene emissions during the dry season followed by a reduction during the dry-to-wet transition and the wet season.
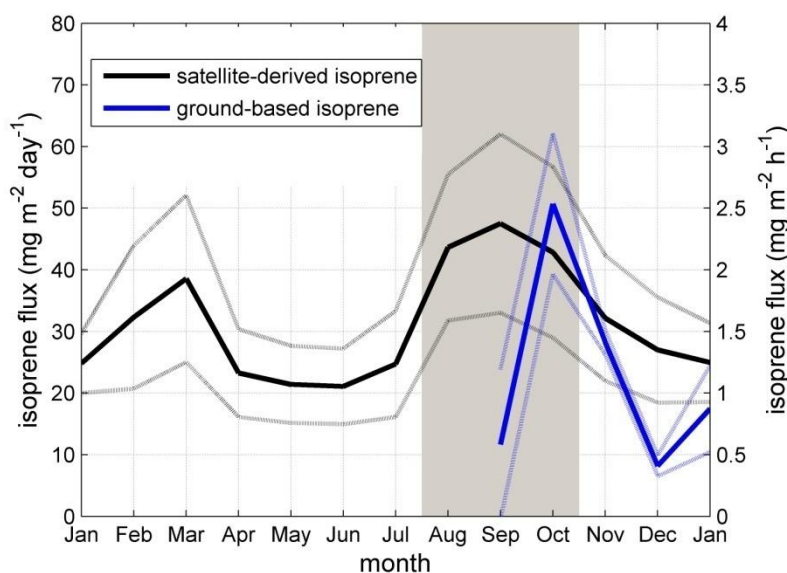
Figure 7: Comparison of monthly isoprene emissions of ground-based estimates (inverse Lagrangian transport model, mg m^{-2} h^{-1}) and satellite-derived estimates (mg m^{-2} day^{-1}). Satellite-derived estimates are from January 2010 to January 2011, and ground-based estimates are from September 2010 to January2011.

4. Discussion

4.1 Diurnal variation on isoprenoid mixing ratios

Isoprene and total monoterpene mixing ratios have a diurnal cycle similar to PAR and air temperature, 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) of Amazonian plant species are light-dependent and stimulated by increasing temperature. However, this same behavior was not observed for total sesquiterpenes. Although sesquiterpene emissions have been suggested as 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 diurnal 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 essential oils 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), are probably dominated by emissions that occur with no storage (e.g. Loreto et al., 1996), similar to isoprene emission processes.

Another reason for the higher total sesquiterpene mixing ratios at nighttime is related to the fact that the ozonolysis of sesquitepenes during daytime can reduce ambient sesquiterpene concentrations (Jardine et al., 2011). Furthermore, sesquiterpene concentrations can buildup in the shallow nighttime atmospheric boundary layer, because during nighttime the storage in the forest dominates (80-90%) and is significantly larger compared to turbulent flux (Karl et al., 2004).

At nighttime, the maximum abundance of mixing ratio of isoprene was observed above the canopy with a decrease towards the ground. As isoprene is not emitted at night, this maximum nighttime abundance of isoprene above the canopy is due to the daytime residual concentrations and likely related to the inversion of the stable boundary layer observed in the air temperature vertical profiles. In addition, as isoprene lifetime increases during nighttime owing to the decrease of OH (hydroxyl radical) concentrations and to the low NO_3 (nitrate) concentrations in the Amazonia, similar results found at another site in central Amazonia suggested that low isoprene concentrations near the ground are due to the fact that after sunset isoprene is deposited onto surfaces (Yañez-Serrano et al., 2014). Isoprene up-take in the soil has been suggested previously in central Amazonia (Silva, 2010), being it most likely due to isoprene microbial consumption (Cleveland and Yavitt, 1997; Gray et al., 2014). Total monoterpenes had nighttime vertical profiles similar to isoprene, with higher mixing ratios above the canopy compared to near the ground, however a small peak at the sub-canopy (17m) was observed, indicating that a fraction of monoterpene emissions could be a result of other factors, such as herbivory, as suggested in another tropical rainforest by Karl et al. (2004).

4.2 Seasonal variation on isoprenoid emissions

The seasonal variation of isoprene and monoterpene emissions presented in this study agree with previous report of with *in situ* measurements in the southern Amazonia (Kesselmeier et al., 2002b; Kuhn et al., 2004a), and more recently in the central Amazonia (Yañez-Serrano et al., 2014). Although methodologies are not standardized, a rough comparison of different studies

with intensive campaigns in different seasons (Table 1) suggests seasonal variation of emissions in the Amazon Basin. During the dry season, the higher concentrations and emissions, specifically of isoprene, have been attributed to the higher insolation and higher temperatures compared to the wet season and, for this reason, it may be expected to have more isoprene concentrations at the top of the canopy. Nevertheless, different from Yañez-Serrano et al. (2014), which found 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.

One reason for this could be in-plant isoprene oxidation especially at the top of the canopy . During the dry season a small source of methyl vinyl ketone and methacrolein (MVK+MAC) was observed at the top of the canopy (Jardine et al., 2012), and the ratio of MVK+MAC and isoprene were higher compared to the dry-to-wet transition and the wet season (data not shown). Under conditions of high abiotic stress; i.e., exposure to high values of temperature, light availability and ozone deposition (Loreto and Velikova, 2001), as probably found at the upper canopy during the dry season - elevated isoprene oxidation rates in plants can be observed and isoprene oxidation products could be emitted by plants (Jardine et al., 2012), which in theory could reduce the plant isoprene emission at the top canopy during the dry season.

Another important factor might be leaf phenology and/or leaf demography. As more leaf flushing is observed at the canopy top surface during the wet-to-dry transition and early dry season, this causes 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 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). The strong relationship between photosynthesis and isoprene emission have been shown for Amazonian tree species at leaf level (Alves et al., 2014) and at branch level (Kuhn et al., 2004b), and, similarly to photosynthesis, they also presented variation in isoprene emission based on leaf age. Here, results show maximum isoprene emission at the upper canopy during the dry-to-wet transition season that also coincides with the period of high abundance of healthy efficient leaves at the canopy top (Nelson *et al.*, 2014) and with the maximum isoprene emission shown in young mature leaves in the dry-to-wet transition season (Alves et al., 2014). Moreover, higher isoprene emissions during

the late dry season have also been related to the increase of active biomass in southern Amazonia (Kesselmeier et al., 2002b; Kuhn et al., 2004a, 2004b).

Total monoterpenes also showed a strong seasonal variation with maximum mixing ratios during the dry-to-wet season, but with fluxes slightly higher during the dry season compared to the dry-to-wet season. 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. However, this differs from previous results presented for the southern Amazonia, where monoterpene mixing ratios were higher during the wet season than during the dry season (Kesselmeier et al., 2002b). Nevertheless, 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). In spite of only a few studies have been carried out with the objective of showing monoterpene seasonal variations, it has been suggested that more factors other than light and temperature might influence monoterpene emissions by vegetation, which can be the oxidative capacity of the atmosphere and leaf phenology (Kesselmeier et al., 2002b; Kuhn et al., 2004a).

Monthly total monoterpene fluxes presented a maximum emission during the month when the highest insolation and high abundance of healthy efficient leaves (Nelson *et al.*, 2014) were observed (end of dry season). This similarity to isoprene emissions is supported by the evidence of the photosynthetic origin of monoterpenes (Loreto et al., 1996). However, in September 2010 total monoterepene emissions were higher than isoprene emissions. This is probably related to the fact that the upper canopy showed a higher source of monoterpenes than isoprene. 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 would be expected. In addition, these results only show the total monoterpenes, in other words, the sum of monoterpenes, preventing us from verifying seasonal changes in the monoterpene chemical composition as previously described (Andreae et al., 2002; Kesselmeier et al., 2002b; Kuhn et al., 2004a).

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 & Zimmerman, 1984	Manaus/Humaitá-Amazonas, Brazil	GC cartridge samples (near ground to 30m)	2.40 (1-5.24)[a]		2.86		Dry - Aug-Sep 1980	mean - daytime range is not reported
		GC cartridge samples (flights from treetop to 2 km)	2.27 (0.38-4.08)[a]		5.47			mean - daytime range is not reported
		GC cartridge samples (flights from 2km to Tropopause)	0.19 (0.14-0.22)[a]		1.91			mean - daytime range is not reported
Jacob & Wofsy, 1988*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	vegetation isoprene emission modeled on basis of midday isoprene concentrations		1.58				mean average of 24 hours
Zimmerman *et al.*, 1988*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	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)
		Tethered balloon (305m)	1.73[1.03-2.15][b]		0.15 [0.04-0.33][b]			median and interquartile range (24h)
		Tethered balloon (up to 305m)		3.1		0.23		mean daytime (08:00-16:00h LT)
Rasmussen & Khalil, 1988	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	GC canister samples (near ground level)	~ 2.77 (±0.4)				Dry - July-Aug 1985	mean daytime (11:00-15:00h LT)
		GC canister samples (flights from 150m to 5000m)	~1.5 (±0.75)					daytime
Davis *et al.*, 1994*	ABLE - Adolfo Ducke Forest Reserve - Manaus-Amazonas, Brazil	Mixed Layer Gradient (tethered balloon (up to 300m))		3.63(±1.4)			Dry - July-Aug 1985	mean daytime (08:00-18:00h LT)

Reference	Location	Method					Season	Notes
Kesselmeier et al., 2000	Balbina - ~100 km north of Manaus-Amazonas, Brazil	GC cartridge samples (outside forest)	~6.55 (±1.26)		~0.63(±0.19)		Wet - April 1988	mean daytime (09:30-15:00h LT)
		GC cartridge samples (inside canopy)	~3.55 (±0.07)		~0.24(±0.04)			mean daytime (09:30-15:00h LT)
		Tethered balloon (200-500m)	~3		~0.2			mean of 24h
	Cuieiras Biological Reserve (C14-ZF2)-Manaus-Amazonas, Brazil	GC cartridge samples (insideand above canopy)	~6.7 (±1.07)		~0.73(±0.24)			daytime
Stefani et al. 2000	Cuieiras Biological Reserve (K34-ZF2)-Manaus-Amazonas, Brazil	Relaxed Eddy Accumulation (~53m)	3.6 -5.4		0.72 – 0.9		Aug/1999 - 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	Relaxed Eddy Accumulation (~53m)	2.88		0.36		from Dry season (Nov1999) to Wet season (Dec 1999/Jan 2000)	midday values
Cicioli et al., 2003	Cuieiras Biological Reserve (K34-ZF2)-Manaus-Amazonas, Brazil	Relaxed Eddy Accumulation (~51m)	5.11max.		1.36max.		Dry - July 2001	midday values
Greenberg et al., 2004	Balbina - ~100 km north of Manaus-Amazonas, Brazil	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 (12:00-15:00h LT)
		Box model	5.3		0.23			maximum midday emission fluxes estimated for the ecoregion
Karl et al., 2007[††]	Cuieiras Biological Reserve (C14-ZF2)-Manaus-Amazonas, Brazil	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 (12:00-14:00h LT)
		Mixed Layer Gradient (up to ~1200 m)	5.5±2.6	12.1 ±4.0	0.52±0.2	3.5 ±1.2		mean daytime (10:00-11:30h LT)
Kuhn et al., 2007**	Cuieiras Biological Reserve (K34-ZF2)-	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)

Reference	Site	Measurement					Season	Notes
	Manaus-Amazonas, Brazil							
Kuhn et al., 2007**		Surface Layer Gradient (28, 35.5, 42.5, 51m)		3.9±4.1 (max. 12.8)		0.43±0.65 (max. 2.1)		mean daytime (10:00-15:00 LT)
		Mixed Layer Gradient (50-3000m)		4.2±5.9 (max. 15.7)				mean daytime (10:00-18:00 LT)
Karl et al., 2009	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	Gradient flux (2, 10.9, 16.7, 23.9, 30.3 and 39.8 m)		~0.7 (±0.2)			Wet - Feb 2008	mean daytime (11:00-17:00h LT); flux at 35 m
Rizzo et al., 2010[††]	Cuieiras Biological Reserve (C14-ZF2)- Manaus-Amazonas,	Disjunct Eddy Covariance (54 m)	7.8 8.4		0.29	0.93	Dry - Sep 2004	max. at early afternoon max. at noon
Silva, 2010	Cuieiras Biological Reserve (K34-ZF2)- Manaus-Amazonas, Brazil	GC cartridge samples: 1m 10m 20m	3.2 ±0.9 4.6 ±0.94 6.17 ±1.03		0.28±0.13 1.09±0.35 0.75±0.17		Wet - May 2009	mean daytime (07:00-17:00h LT) mean daytime (07:00-17:00h LT) mean daytime (07:00-17:00h LT)
Jardine et al., 2011[‡]	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	Gradient profile (2, 11, 17, 24, 30 and 40 m)			~ 0.78	~ 1.47	Dry-Wet, Sep-Dec 2010	mean daytime 10:00-16:00h LT) at 40 m mean daytime 10:00-16:00h LT) at 35 m
Jardine et al., 2012[‡]	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	Gradient profile (2, 11, 17, 24, 30 and 40 m)		~1.43			Dry-Wet, Sep-Dec 2010	mean daytime (10:00-16:00h LT)
Yañez-Serrano et al., 2014	ATTO site - Manaus Manaus-Amazonas, Brazil	Gradient profile (0.05, 0.5, 4, 24, 38, 53 and 79 m)	5.22±1.5 1.5±0.78		0.75±0.18 < 0.23		Dry - Sep/2013 Wet - Feb-Mar/2013	Isoprene, daytime median (12-15:00h LT). Mt, daytime median (15-18:00h LT)
This study[‡]	Cuieiras Biological Reserve (TT34-ZF2)- Manaus-Amazonas, Brazil	Gradient profile (2, 11, 17, 24, 30 and 40 m)	2.68±0.9 2.65±1.33 1.66±0.9	1.37±0.7 1.41±0.1 0.52±0.1	0.67±0.3 0.85±0.4 0.47±0.2	1.47±0.06 1.29±0.2 0.36±0.05	Dry - Sep-Oct 2010 DWT[¥] - Nov 2010 Wet - Dec 2010 -Jan/ 2011	mean daytime (10:00-14:00h LT) at 40m mean daytime (10:00-14:00h LT) at 40m mean daytime (10:00-14:00h LT) at 40m

Eastern Central Amazonia						
Rinne *et al.*, 2002	Tapajós National Forest - Santarém-Pará, Brazil	Disjunct Eddy Accumlation (~45m)	max. 5 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	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 (12:00-15:00h LT)
		Box model	2.2	0.18		maximum midday emission fluxes estimated for the ecoregion
Trostdorf et al., 2004	Tapajós National Forest - Santarém-Pará, Brazil	GC canister samples (54, 64 m)	1.9 (±1.2); 1.3(±0.8)		Wet - Jan-May 2002	mean daytime (11:00-14:00 LT)
		GC canister samples (54, 64 m)	1.4 (±0.5); 1.0 ±0.4)		WDT[¥¥] - June-July 2002	mean daytime (11:00-14:00 LT)
		GC 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	Tethered baloon (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)
		Mixed Layer Gradient	7.4	0.42		mean daytime
		Mixed Layer Budget	8.1	0.41		mean daytime
Southern Amazonia						
Kesselmeier *et al.*, 2002	Jaru Biological Reserve, Jaru-Rondônia, Brazil	GC cartridge samples (8-52m)	~4	~0.8	WDT[¥¥] - May 1999	mean daytime (11:00-18:00 LT)
			~12	~0.8	DWT[¥] - Sep-Out 1999	mean daytime (11:00-18:00 LT)
Greenberg *et al.*, 2004	Jaru Biological Reserve, Jaru-Rondônia, Brazil	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 (12:00-15:00h LT)
		Box model	9.8	6.1		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
		Modeling using data of Kesselmeier et al., 2002	~8.2	DWT[¥] - Sep-Out 1999	midday values
Aquino, 2006	Jaru Biological Reserve, Jaru-Rondônia, Brazil	GC canister samples (50, 60 m)	4.5 (±0.9); 4.0(±1.2)	Wet - Feb-May 2002	mean daytime (11:00-16:00 LT)
		GC canister samples (50, 60 m)	2.1(±2.0); 1.8(±1.8)	WDT[¥¥] - Jun 2002	mean daytime (11:00-16:00 LT)
		GC canister samples (50, 60 m)	4.6(±2.7); 4.0(±2.5)	Dry - Jul-Sep 2002	mean daytime (11:00-16:00 LT)
		GC canister samples (50, 60 m)	3.4(±1.2); 3.0(±0.5)	DWT[¥] - Out-Nov 2002	mean daytime (11:00-16:00 LT)
Northern Amazonia					
Gregory et al., 1986	Tropical rainforest of Guyana	GC stainless steel can samples (flights from 150m to 3500 m)	~2.4-0.1	June 1984	daytime values from 150 to 3500 m
Warneke et al., 2001	Tropical rainforest of Surinam	PTR-MS measurements (mixed layer)	3.3	March 1998	daytime values
Williams et al., 2001	Tropical rainforest of Surinam	PTR-MS measurements (flights up to 12500m)	0.8	March 1998	daytime values (Planetary Boundary Layer)

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;

Seasonality of total sesquiterpene mixing ratios and fluxes into the atmosphere had different patterns compared to isoprene and total monoterpenes. For all seasons, vertical profiles showed peaks near the ground and at the sub-canopy (17 m), where light penetration is less and air temperatures are lower than at the upper canopy. Although sesquiterpenes might not be strongly light dependent, it would be expected that more sesquiterpenes are present during the season with higher insolation, which consequently is the period of higher temperatures, since emissions of these compounds are expected to be stimulated by increasing temperature (Duhl et al., 2008). However, total sesquiterpene presented maximum mixing ratios during the dry-to-wet transition season with mixing ratios considerably higher near the ground than at the sub-canopy (17 m). 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 contributes to the scarcity of total sesquiterpenes above and near the top of the canopy. Considering that higher insolation and also higher ozone concentrations (data not shown) were observed during the dry season, total sesquiterpenes emitted by vegetation could be rapidly oxidized by ozone, leading to significantly lower mixing ratios of total sesquiterpene during the dry season and creating a need to account for sesquiterpene oxidation within the canopy when calculating emission rates. This makes sesquiterpene emission quantification a challenge in this and other ecosystems.

Another potential reason for higher mixing ratios of total sesquiterpenes near the ground is that emission could come from surface sources including litterfall, roots and soil microbes and fungi. Silva (2010) has presented surface BVOC emissions in this site, and the results suggested that the litterfall decomposition could be an important source of sesquiterpenes to the atmosphere. It is already known that the litter production is higher during the dry season than during the wet season (Luizão et al., 1989), which probably leads to higher amounts of litter at the end of the dry season. With the beginning of the rainy season - dry-to-wet transition season - the water that comes from the rain could contribute to more decomposition of the litter storage, which potentially can increase sesquiterpene emissions during the processes of leaching, fragmentation and mineralization of dead organic matter. Although the ecological functional role of these sesquiterpenes is not known, abiotic emissions from the litterfall have a specific signature that can be in a similar to the concentration profile in the green leaf content (Austin et al., 2014) and, in sufficient concentrations, BVOC emissions should have the capacity of

attracting and repelling soil organisms to a specific location (Austin et al., 2014); therefore, higher sesquiterpene emissions from the litterfall could be a signal to the fauna related to the decomposition process and represent an important step of the biogeochemical cycling.

The highest total sesquiterpene fluxes into the atmosphere were observed during the dry-to-wet transition season, when they were a factor of 3 higher than the emission during the dry season. But, in contrast to the mixing ratios, the source-sink distribution analysis made from the vertical profiles indicated that the main source of these compounds is the canopy (~24 m) for all seasons. 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.

The results reported here are associated with a small footprint area. This together with the huge biodiversity of the Amazonian rainforest makes it impossible to generalize these results to the regional scale. Moreover, when previous investigations of BVOCs in Amazonia (summarized in Table 1) and this study were compared, it was observed that there is high variability 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 ecotypes of the same region, (5) different statistics applied, and (6) perhaps due to a small data set that is not statistically significant to characterize emissions of a specific site.

Albeit isoprene mixing ratios reported here generally agree with some previously reported values in central Amazonia for the dry season and the dry-to-wet transition season (Greenberg et al., 1984; Rasmussen and Khalil, 1988; Zimmerman et al., 1988) and for the wet season (Yañez-Serrano et al., 2014), these results also presented the lowest fluxes of isoprene to atmosphere for all measurement periods. However, this could be a particularity of the site of this study, such as relatively low fraction of isoprene emitting species, because isoprene fluxes measured previously in this same site during the wet season have shown similar values (Karl et al., 2009). 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; Yañez-Serrano et al., 2014). But, 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, potentially, the seasonal species-specific composition of monoterpenes in the Amazonia.

Results reported here clearly show a seasonal trend in isoprenoid emissions for a primary rainforest of central Amazonia. As water soil content does not seem to be a limitation throughout the year in central Amazonia (Restrepo-Coupe et al., 2013), 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 propitious conditions for synthesizing these compounds at the dry season and the dry-to-wet transition season, especially isoprene and monoterpenes, which are light- and temperature-dependent and are affected by the recent production of photosynthetic substrates.

4.3 What are models saying about seasonal isoprenoid emissions in Amazonian rainforest?

Isoprenoid emissions presented here differed from those modeled by MEGAN 2.1, being observed differences in the magnitude of emissions going out of the forest canopy (Lagrangian inverse model *versus* MEGAN 2.1 - isoprene: $r^2=0.07$; total monoterpenes: $r^2=0.54$; total sesquiterpenes: $r^2=0.01$). However, in terms of seasonal trend, MEGAN 2.1 estimates of isoprene emission agree fairly well with the satellite-derived isoprene emission, which suggests that other factors particularly of this site could influence isoprene emissions locally.

Another important thing is that considering that only variations in PAR and air temperature were used to drive MEGAN 2.1, predicted emissions presented their highest values during the dry season for all compounds, when both PAR and air temperature showed their maximum. Comparing modeled (MEGAN) and measured emissions, a study conducted nearby this site demonstrated that light and temperature variations account for most of the short-term variation on isoprene and monoterpene emission, suggesting the feasibility of this model for reproducing short-term variation in tropical emissions (Karl et al., 2007). However, when long-

term emissions are being reproduced by modeling, other factors may be also important (e.g. leaf phenology) (Kesselmeier et al., 2009).

At regional and global scales, there have been attempts to improve model predictions by taking into account leaf phenology and leaf demography derived by the LAI variation captured by the MODIS satellite (Guenther et al., 2012), and some efforts have been attempted to include effects of CO_2 variation (Arneth et al., 2007) and the link between photosynthesis and emission (Grote et al., 2014; Morfopoulos et al., 2013, 2014; Unger et al., 2013) into isoprene emission models. Yet, 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). In addition, satellite observations indicated that the current understanding of the processes controlling seasonal variations are insufficient, and 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 focus 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. It is crucial to better determine the basis of isoprene production and to develop mechanistic explanations for variation in isoprene emission (Monson et al., 2012), which may reduce uncertainties associated to the responses to environmental factors.

Because higher demography of healthy efficient leaves (Nelson *et al.*, 2014) is synchronous with the period when landscape-scale photosynthesis and photosynthetic capacity is more efficient (Restrepo-Coupe et al., 2013), and because of the generally strong correlations between isoprene emission and gross photosynthetic capacity of an Amazonian tree species has been reported (Kuhn et al., 2004b), it may be possible to explain the seasonal development of emissions by the change in energy supply from photosynthesis throughout the seasons (e.g. Grote et al., 2014). Additionally, as the knowledge of canopy structure can explain 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), this may also help to explain differences on 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. This is probably because there is a lack of information owing to the scarcity of measurements in Amazonia. 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.

5. Summary and conclusions

Seasonal variation in temperature and in light availability at the surface is observed in central Amazonia. During the dry season, higher insolation occurs because of the reduced cloudiness and rain events are less frequent compared to the wet season. Isoprenoid emissions reach their peaks at the end of the dry season and at the dry-to-wet transition season. This is the period with elevated light and temperature, and also the period with maximum leaf demography of healthy and photosynthetically efficient leaves (Nelson et al., 2014; Restrepo-Coupe et al., 2013). Although very recently, no seasonal variation on canopy structure and greenness has been suggested for the Amazonia (Morton et al., 2014), results reported here present a seasonal variation on leaf flushing and suggest maximum leaf demography at late dry season, which generally agree with the assumption that a greenup during the dry season in Amazonia may act on the increasing 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 emissions, especially for sesquiterpenes, and their quantification is challenged by rapid atmospheric chemical reactions catalyzed by high insolation and higher ozone concentrations in the dry season.

Seasonal variations in isoprenoid emissions reproduced by MEGAN 2.1 did not show good agreement with measured emissions. One reason for this could be the fact that leaf phenology was not considered in the simulations. Another reason could be the influence of very local effects on the seasonal emissions measured in this site, because, for isoprene, the satellite-

derived emissions agree fairly well with MEGAN 2.1 emission estimates and the ground observations do not agree with either (especially 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, model predictions have suggested that seasonal variation on 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 to the insufficient understanding of mechanistic processes involved in the seasonality of these compounds. Nevertheless, because the number of measurement plants 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, which 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.

Acknowledgements

Capítulo II

Seasonal changes in isoprene emissions inferred from a Relaxed Eddy Accumulation system in primary rainforest in central Amazonia

Abstract

Seasonal variations in isoprene fluxes were investigated in primary rainforest northwest of Manaus in the central Amazonia. Isoprene flux measurements using a Relaxed Eddy Accumulation system (REA) were carried out in intensive campaigns from June 2013 to December 2013, characterizing four seasons: the wet-to-dry transition season, the dry season, the dry-to-wet transition season and the beginning of the wet season. Flux measurements were compared to bottom-up model estimates (MEGAN 2.1) and top-down isoprene emission estimates derived from satellite formaldehyde observations in a resolution of 0.5° around the site of the REA isoprene measurements. Isoprene emissions captured from the REA measurements clearly showed a seasonal variation, the lowest emissions being during the wet-to-dry transition season and the highest emission during the late dry season. Taking into account only variations in photosynthetic active radiation and air temperature, MEGAN 2.1 estimates did not capture the behavior observed with the REA isoprene fluxes as the model emissions were overestimated during the wet-to-dry transition season. In part, this could be due to the fact that no seasonal variation in leaf phenology was assumed for the model estimates. Top-down estimates of isoprene emission averaged from 2010 to 2012 showed a similar trend compared to the seasonal variation of ground-based measurements (REA); however, in order to do a quantitative isoprene emission comparison between ground-based measurements and satellite based estimates, more observational studies are needed. In terms of carbon losses from the forest to the atmosphere in the form of isoprene (isoprene/NEE), it is proposed that a higher fraction of carbon is emitted as isoprene during the dry season. Therefore, this study encourages future observational research that takes into account the seasonal and spatial variation of isoprene emissions to better understand the seasonality of isoprene emission in the different sub-regions of the Amazonian rainforest in order to improve bottom-up isoprene model estimates.

Keywords: biosphere-atmosphere interactions, isoprene, flux, Net CO_2 Ecosystem Exchange, seasonality

1. Introduction

Global emissions of Biogenic Volatile Organic Compounds (BVOCs) from the biosphere into the atmosphere have been widely investigated, and because these compounds have a carbon constituent and are high reactive, their important role for the atmosphere chemical processes and for the biogeochemical cycles is widely recognized. Global annual BVOC emission range from 700 to 1000 Tg C (see Table 1 of Laothawornkitkul *et al.*, 2009) and, despite a large number of BVOC species have been identified within plants and in emissions from plants, isoprene is considered the dominant emission from many landscapes and has the 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).

Isoprene emissions from tropical forests contribute almost half of the estimated global annual isoprene emission, ranging from about 220 to 340 Tg according to the estimates of the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006). There are large uncertainties associated with these estimates, particularly because of differences in the model-driving variables (Guenther et al., 2006), and because detailed information from observational studies in remote tropical forests is still scarce. However, in order to reduce these uncertainties, remotely sensed concentrations of isoprene oxidation products in the atmosphere, inverted and modeled using an atmospheric chemistry transport model, are beginning to constrain these estimates (Guenther et al., 2006).

In agreement with the fact that the isoprene degradation process in the atmosphere generates formaldehyde (HCHO) as an intermediate product (Stavrakou et al., 2014), satellite observations over densely forested areas have shown important enhancements in HCHO columns owing to the combination of biomass burning and high isoprene emission fluxes (Stavrakou et al., 2009). Some studies have used HCHO column concentrations observed by satellites to constrain the isoprene fluxes and to possibly improve the bottom-up inventories of isoprene (Stavrakou et al., 2014). This approach has also been used to indicate the seasonal variation on isoprene emission over the South America (Barkley et al., 2008, 2013), and particularly over the Amazon rainforest (Barkley et al., 2009).

Isoprene seasonal variation estimates from remote sensing observations do exist, however, only a few *in situ* observational investigations have been used to verify this seasonality within the

Amazonian rainforest (Andreae et al., 2002; Kesselmeier et al., 2002b; Kuhn et al., 2004a; Yañez-Serrano et al., 2014). In addition, besides seasonal variations in environmental factors - such as precipitation, light, temperature - and soil moisture and in CO_2 fluxes have been generally explored in studies carried out in this region (de Araújo et al., 2010; von Randow et al., 2004, 2013; Restrepo-Coupe et al., 2013; da Rocha et al., 2009; Zeri et al., 2014), *in situ* measurements of these factors have not been compared to the seasonality of isoprene or other BVOC emissions.

Indeed, one large limitation on doing flux measurements of isoprene or other BVOC in densely forested areas, as the Amazonian rainforest, is the fact that complex and very sensitive sensors are needed; these sensors, in the most of cases, are very expensive and with large power requirements and an air-conditioned room to avoid high temperatures and high humidity. These requirements are very often difficult to meet given lack of power sources in remote areas as well as the high temperatures and humidity in tropical rainforest. Thus, in order to minimize these limitations, a portable system of sampling has been used to measure isoprene and other BVOCs in the field. This system, called Relaxed Eddy Accumulation (REA) (see more details in Bowling *et al.*, 1998), can be fed with small batteries and the air samples can be analyzed afterwards in a laboratory. Although this technique has some limitations with respect to further micrometeorological analysis that need fast response measurements (e.g. autocorrelation of w'c$_{isoprene}$'), this technique has shown good agreement with Eddy Covariance flux measurements (Bowling et al., 1998), and has been suggested when no fast response isoprene sensor is available.

Therefore, in order to better understand the seasonality of isoprene emission in a primary rainforest in the central Amazonia, this study aimed to investigate the seasonal isoprene fluxes measured above the canopy (REA), comparing these fluxes with environmental factors (light and temperature) and a biological factor (Net CO_2 Ecosystem Exchange - NEE).

2. Material and Methods

2.1 Site description

Isoprene fluxes were measured at the K34 tower (2°36' 32.67" S, 60° 12' 33.48" 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. The K34 tower has been widely utilized for over 10 years for a range of meteorological studies, including energy and trace gases fluxes (de Araújo et al., 2010; Tóta et al., 2012) and also tropospheric variables such as precipitable water vapor (Adams et al., 2011). This reserve has an area of about 230 km² and belongs to the National Institute for Amazonian Research (INPA). The topography is characterized by a maximum altitude of 120 m. The site is characterized by 31 % of plateau, 26 % slope and 43 % valley (Rennó et al., 2008). Soils are well-drained Oxisols and Ultisols on the plateau and slopes, respectively, and poorly drained Spodosols in the valleys (Luizao et al., 2004). The vegetation in this area is considered mature, *terra firme* rain forest, with a leaf area index of 4.7 (Malhi et al., 2009), and with typical canopy height of 30 m with variation (20-45 m) throughout the reserve. The diversity of tree species is greater than 200 species ha^{-1} (Oliveira et al., 2008). Annual precipitation is about 2500 mm and dominated by deep atmospheric convection and associated stratiform precipitation, with the wetter season from December to May and the drier season from August to September, when the monthly cumulative precipitation can be less than 100 mm per month (Adams et al., 2013; Machado et al., 2004) . Average air temperature ranges between 24 °C (in April) and 27 °C (in September) (see figure 1 of Alves et al*.,* in preparation [chapter I]). Soil moisture shows a small reduction (~ 10%) of water availability during the dry season compared to the wet season (Cuartas et al., 2012). The duration of this study was 6 months from June 2013 to December 2013. The period from June to July represents the wet-to-dry transition season, August to September the dry season and October through November the dry-to-wet transition season and December the beginning of wet season.

2.2 Isoprene flux – Relaxed Eddy Accumulation system

Measurements of isoprene fluxes were carried out using a Relaxed Eddy Accumulation system (REA) developed by the National Center for Atmospheric Research (NCAR) (REA, NCAR/BEACHON Cassette Sampler, S/N #:1001). This REA system was installed at a height of 48 m of the K34 tower (approximately 20 m above the mean canopy height). The fundamental basis of this technique is to segregate the sample flow according to the vertical wind velocity measured by the sonic anemometer over the flux-averaging period (30 min). The basic equation to derive isoprene fluxes (F) from the REA system over this period was:

$$F = \overline{w'c'} = b\sigma_w(\overline{c_{up}} - \overline{c_{down}}) \tag{1}$$

where b is an empirical proportionality coefficient (described below), σ_w is the standard deviation of w, and $\overline{c_{up}}$ and $\overline{c_{down}}$ are the average of the isoprene concentrations in the up and down reservoirs, respectively (Bowling et al., 1998). The b-coefficient was calculated from the sonic temperature and heat flux by re-arranging the same equation, assuming scalar similarity (Monin-Obukhov Similarity Theory):

$$b = \frac{\overline{w'T'}}{\sigma_w(T_{up} - T_{down})} \tag{2}$$

The REA requires two initial data points at the beginning of each flux averaging period to be able to segregate the sample flow: (1) a mean vertical wind velocity, $\overline{w}$ and (2)σ_w. The $\overline{w}$ is needed to determine the direction of the instantaneous vertical wind velocity ($w' = w(t) - \overline{w}$) and σ_w is required to calculate a "deadband". A deadband was a range of small w' values, centered around $\overline{w}$, over which the air was sampled through the "neutral" line. This concentration was not necessary for the flux calculation, but was analyzed for ambient concentration information. The deadband was $\pm 0.6\sigma_w$. The use of a deadband is advisable, because this increases the differences in the measured concentrations ($\overline{c_{up}} - \overline{c_{down}}$), which allows the sampling of only larger eddies (with larger concentration fluctuations) into the up/down

reservoirs, reducing restrictions on the analytical technique used. The *b*-coefficient was also computed (from eq. 2) using the same deadband. For this study, *b*-coefficient ranged 0.3-0.7.

In order to verify the effectiveness of using *b*-coefficient to estimate isoprene flux, a comparison of the heat flux measured by the REA sonic anemometer (at 48 m) and heat flux data measured simultaneously by an Eddy Covariance (EC) system (at 53.1 m) was made, and the regression is shown in figure 1. The EC system belongs to the Program of Large scale of Biosphere-Atmosphere interaction (LBA), the flux calculation being made by the Alteddy software. More details about how the Alteddy software calculates the flux are available at http://climatexchange.nl/projects/alteddy/index.htm.
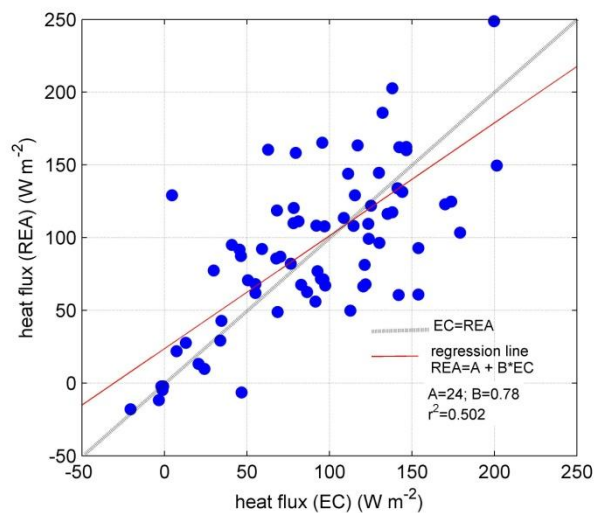
Figure 1: Comparison of heat fluxes determined by two systems installed at the K34 tower: Eddy Covariance (EC) (53.1 m) and Relaxed Eddy Accumulation (REA) (48 m).

The basic components of the REA are (1) the Main REA box containing the adsorbent cartridges (stainless steel tubes filled with Tenax TA and Carbograph5TD adsorbents) for reservoirs up/down/neutral, microcontroller, battery, data logger, selection valves and mass flow controller (200 ml min^{-1}) (MKS Instruments Inc., Model M100B01852CS1BV) and (2) a Sonic Anemometer(RM Young, Model 81000VRE) for fast wind velocity measurements (Figure 2).
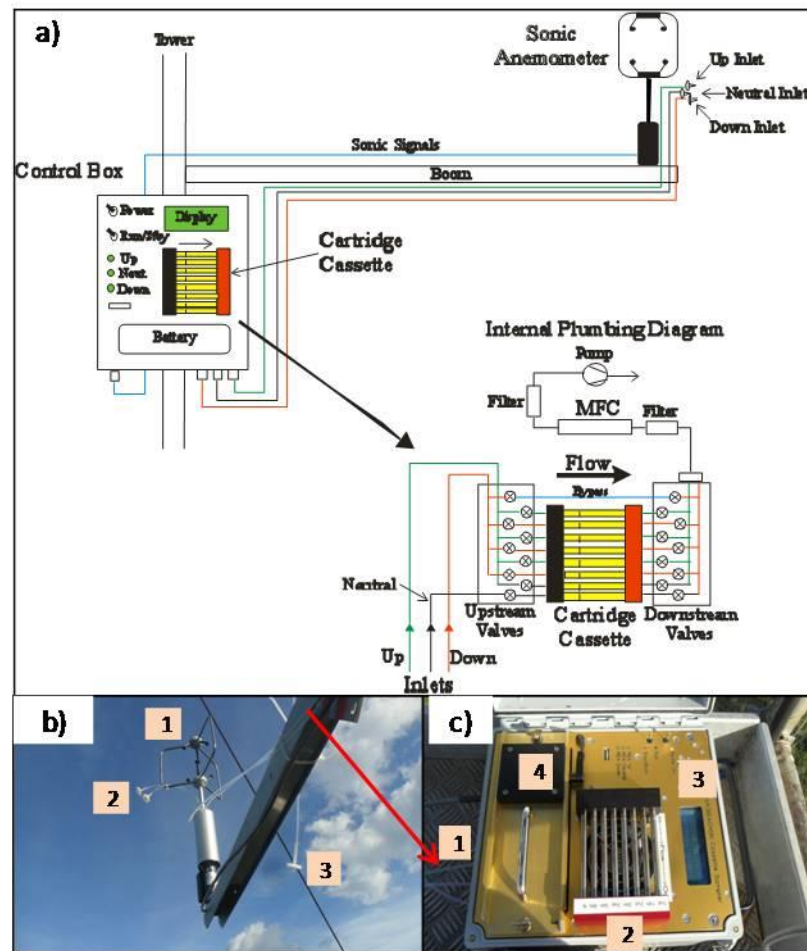
Figure 2: (a) Schematic of the PIC-REA Cassette Sampler designed by NCAR. Inset shows the flow path within the Main Control Box (adapted of PIC-REA Cassette Sampler manual). REA system in the field: (b) sonic anemometer (1), inlets for *up* and *down* reservoirs (2), inlet for neutral (3); (c) main box inlets for *up/down/neutral* (1); reservoirs (adsorbent cartridges) *up/down/neutral* (2), display(3), and battery(4).

The REA sampling was realized with two tubing lines for up (+w') and down (-w') and one tubing line for neutral sampling air ($\pm 0.6\sigma_w$ - deadband), each consisting of about 1.5 m long PTFE (Teflon) tubes. The inlets (up, down, and neutral) were installed at the sonic anemometer height (48 m) with a filter for particle matter (Pall Corporation, Glass Fiber Acrodisc), and then connected to the Main REA box containing the adsorbent cartridges for the respective reservoirs up/down/neutral. Air samples were drawn by a pump and controlled by a mass flow controller at a rate of 200 ml min^{-1}. Each inlet valve at the main REA box prevented air from entering the inactive tube (up- in case down sampling (-w') and down - in case up sampling (+w'), and both up and down in the case deadband) which otherwise would compromise the concentration differences between up and down reservoirs and, consequently, the flux calculation. The

sampling was carried out at 10 Hz by a Sonic Anemometer (RM Young, Model 81000VRE). A data logger recorded the anemometer data and a microcontroller accomplished the data acquisition and the valve triggering. The switching valve was based on the last flux-averaging period (30 min) of $\bar{w}$ and σ_w, the valves being activated according to the threshold condition ($\pm 0.6\sigma_w$, in the case of threshold condition, the valve of the neutral inlet, deadband, was activated). After 30 min of sampling, the data logger stored all the necessary wind and temperature information to compute the flux according to equation (1). The mass accumulated in the up/down reservoirs (adsorbent cartridges) was determined from laboratory analysis (section 2.3). The concentrations were then determined using the amount of volume that was passed through each respective reservoir. This volume was measured by integration of the mass flow meter signal and stored within the REA data.

All REA measurements were carried out during daytime from 9:00h to 16:30h, local time, in one intensive campaign per month. For each campaign, samples were collected during five consecutive days. All campaigns were carried out from June 2013 to December 2013.

2.3 Thermal desorption gas chromatography-flame ionization detection (TD-GC-FID)

Both up and down REA samples were collected by drawing 200 sccm of air through onto adsorbent tubes for 30 minutes (6.0 L). The adsorbent tubes were purchased commercially, filled with Tenax TA and Carbograph 5TD adsorbents (Markes International, UK). The tube samples were analyzed for isoprene with a thermal desorption system (TD) (Markes International, UK) interfaced to a gas chromatograph/flame ionization detector (GC-FID) (19091J-413 series, Agilent Technologies, USA). After loading a tube in the ULTRA Automatic Sampler (Model Ultra1, Markes International, UK), which was connected to the thermal desorption system, the collected samples were dried by purging for 5 minutes with 50 sccm of ultra-high purity helium (all flow vented out of the split vent) before being transferred (300ºC for 10 min with 50 sccm of helium) to the thermal desorption cold trap held at -10ºC (Unity Series1, Markes International, UK). During GC injection, the trap was heated to 300°C for 3 min while back-flushing with carrier gas (helium) at a flow of 6.0 sccm directed to the column (Agilent HP-5 5% Phenyl Methyl Siloxane Capillary 30.0 m X 320 μm X 0.25 μm). The oven ramp temperature was

programmed with an initial hold of 6 min at 27 °C followed by an increase to 85 °C at 6 °C min^{-1} followed by a hold at 200 °C for 6 min. The identification of isoprene from samples was confirmed by comparison of retention time with a solution of an authentic isoprene liquid standard in methanol (10 µg/ml in methanol, Sigma-Aldrich, USA). The GC-FID was calibrated to isoprene by injecting 0.0, 23, 35, and 47 nL of the gas standard onto separate tubes. The gas standard is 99.9% of 500 ppb of isoprene in nitrogen (Apel Gas Standard, USA) and was injected into separate tubes at 11 ml min^{-1}. The calibration curve (0.0, 23, 35, and 47 nL) was made thrice before the analysis of the sample tubes of each campaign, being the mean correlation coefficient equals to r²=0.98. In addition, two standard tubes (with 35 nL of isoprene) were run at every 20 sample tubes to check the system sensitivity. The limit of detection of isoprene was equal to 48.4 ppt.

All tube samples were analyzed as described above with the exception of tube samples from June 2013 and July 2013. These tube samples were analyzed in a TD/GC-MS-FID system from the Atmospheric Chemistry Division of the NCAR. For this system, thermal desorption was carried out via a two-stage process, where the adsorbent cartridge was initially desorbed at 275°C while passing a flow of ultra-high purity through using a commercial TD-autosampler (Model Ultra1, Markes International, UK). The sample was transferred via a heated line to a cold trap that was packed with Tenax-TA and cooled to 0°C via peltier (Unity Series1, Markes International, UK). Once the entire sample was transferred to this intermediate trap, it is rapidly heated to 300°C and injected onto the GC column (DB-5 column, Restek, 250 micron, etc.). The GC column was cryofocused to -30°C and then temperature programmed up to 275°C. After separation, the sample was split between the two detectors (FID and MS). This system is calibrated daily by filling adsorbent cartridges with a secondary standard consisting of isoprene and camphene. This isoprene/camphene standard was calibrated relative to a NIST-certified butane/benzene gas standard as well as a NIST-certified neohexane gas standard. The FID was used to quantitate isoprene.

All REA isoprene samples (tubes) were quantified in mg m^{-3}, then concentrations were subtracted from those found in the blank tubes that have been connected to the cartridge cassete (reservoirs) (figure 2) in the REA box during the sampling, but without flow passing through. Then, the resulted concentrations were used to calculate isoprene flux (equation 1) in mg m^{-2} h^{-1}.

2.4 Emission activity algorithms - Model of Emissions of Gases and Aerosols from Nature (MEGAN 2.1)

Isoprene emissions estimated by MEGAN are based on a simple mechanistic model that takes into account the major processes driving variations in emissions (Guenther et al., 2012). According to Guenther *et al.*, (2012), the isoprene activity factor (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_C) as

$$\gamma_i = C_{CE}LAI\gamma_P\gamma_T\gamma_A\gamma_{SM}\gamma_{CO_2} \tag{3}$$

where C_{CE} is the canopy environment coefficient, which results in $\gamma_i=1$ for standard conditions (Photosynthetic Active Radiation (PAR) - 1000 µmol m^{-2} s^{-1} and T - 30 ℃) and is dependent on the canopy environment model used here, which has a C_{CE} of 0.57 (Guenther et al., 2006).

Isoprene emissions are considered light-dependent, thus, the light-dependent activity factor described for isoprene (Guenther et al., 2006) follows:

$$\gamma_P = C_P \left[\frac{(\alpha \times PPFD)}{((1 + \alpha^2 \times PPFD^2)^{0.5})}\right] \tag{4}$$

where *PPFD* is the photosynthetic photon flux density (µmol m^{-2} s^{-1}) and C_P and α are estimated as:

$$\alpha = 0.004 - 0.005\ln(P_{240}) \tag{5}$$

$$C_P = 0.0468 \times \exp(0.0005 \times [P_{24} - P_S]) \times [P_{240}]^{0.6} \tag{6}$$

where P_S is the standard condition for PPFD averaged over the past 24 h and is equal to 200 µmol m^{-2} s^{-1} for sun leaves and equal to 50 µmol m^{-2} s^{-1} for shade leaves; P_{24} is the average PPFD of the past 24 h and P_{240} is the average PPFD of the past 240 h.

The temperature activity factor for isoprene is calculated following Guenther *et al.*, (2006):

$$\gamma_{\mathrm{T}} \;=\; E_{\mathrm{opt}} \;\times\; \left[\frac{C_{\mathrm{T2}} \times \exp\left(C_{\mathrm{T1}} \times x\right)}{\left(C_{\mathrm{T2}} - C_{\mathrm{T1}} \times \left(1 - \exp\left(C_{\mathrm{T2}} \times x\right)\right)\right)} \right] \tag{7}$$

where $x = [(1/T_{opt}) - (1/T)]/0.00831$, T is leaf temperature (K), C_{T1} (=95) and C_{T2} (=230) are empirically determined coefficients,

$$T_{opt} \;=\; 313 \,+\, (0.6 \times (\mathrm{T}_{240} - \mathrm{T}_{\mathrm{S}})) \tag{8}$$

$$E_{opt} \;=\; C_{eo} \,\times\, \exp\!\big(0.05 \times (T_{24} - T_S)\big) \times \exp(0.05 \times (T_{240} - T_S)) \tag{9}$$

where T_S is the standard condition for leaf temperature (= 297 K), T_{24} is the average leaf temperature of the past 24 h, T_{240} is the average leaf temperature of the past 240 h, and C_{eo} is an emission-isoprene dependent empirical coefficient (= 2).

The leaf age, soil moisture and CO_2 inhibition activity factors for isoprene were assigned a value of $\gamma_A = 1$, $\gamma_{SM} = 1$ $\gamma_{CO_2} = 1$, respectively, which assumes no variation in these parameters over all seasons.

The inputs for the all model runs - PPFD and air temperature - were obtained from the K34 tower measurement series (LBA), being considered for the model estimates the PPFD and air temperature measurements simultaneous to REA measurements, when data were available, and the whole series of PPFD and air temperature data from 2000 to 2012 were utilized.

2.5 Satellite-derived isoprene emission estimates

The top-down isoprene emission estimates over the 0.5 degree region around K34 tower (2° 36' 32.67" S, 60° 12' 33.48" W) were derived by using a grid-based source inversion scheme (Stavrakou et al., 2009) constrained by HCHO columns measured by the Global Ozone Monitoring Experiment (GOME-2)/MetOp-A satellite between 2010 and 2012. The source inversion was created on the Intermediate Model of Annual and Global Evolution of Species (IMAGESv2) global chemistry-transport model run at a resolution of 2° × 2.5° and calculated in 40 vertical levels from the surface to the lower stratosphere (Stavrakou et al., 2014). Basically,

the global model IMAGEV2 with a priori emission inventory from MEGAN 2.1 (with adjusted emission factors especially for tropical forests) was constrained by satellite HCHO column to estimate the a posterior biogenic isoprene emission.

Daily (24 hours) mean satellite-derived isoprene emissions were calculated from Jan 1st, 2010 to December 31st, 2012. More details about settings and corrections adopted for this retrieval can be found in Stavrakou et al. (2009, 2014) and Bauwens et al. (2013).

2.6 Net Ecosystem CO$_2$Exchange (NEE) *vs*. isoprene flux

The Net Ecosystem CO$_2$ exchange (NEE) was obtained from turbulent flux measurements by means of the eddy covariance plus the storage term (de Araújo et al., 2010; Cirino et al., 2014):

$$NEE \approx F_c + Stg \qquad (10)$$

where F_c is the CO$_2$ turbulent flux, calculated by eddy covariance at 53.1 m; *Stg* is the storage term, which is the CO$_2$ concentration (non-turbulent term) measured in a vertical profile at discrete levels z_i of Δz_i thickness, from close to soil surface to the height of eddy covariance measurements (53.1 m) (Cirino et al., 2014). The storage term was calculated according to Aubinet *et al.*, 2001 and de Araújo *et al.*, 2010:

$$Stg = \frac{P_a}{RT_a}\Sigma_0^z(\frac{\Delta C}{\Delta t}_{\Delta z}) \qquad (11)$$

where P_a is the atmospheric pressure (N m^{-2}), R is the molar gas constant (Nm mol^{-1}K^{-1}), T_a is the air temperature (K), C is the CO$_2$ concentration (µmol mol^{-1}), t is the time (s) and z is the maximum height (m) between the soil surface and canopy.

To calculate NEE, both vertical CO$_2$ concentration profile (storage term) and the CO$_2$ flux (turbulent term) data series were obtained from LBA, being the turbulent term was calculated from 30 min averages calculated by Alteddy software (more details about how the Alteddy software calculates the flux is available at http://climatexchange.nl/projects/alteddy/index.htm).

Since a comparison of carbon uptake by NEE and carbon emission in the form of isoprene was aimed, NEE in $\mu mol \ CO_2 \ m^{-2} \ s^{-1}$ was converted to $mg \ C \ m^{-2} \ h^{-1}$, following the same way of isoprene emission conversion ($mg \ C \ m^{-2} \ h^{-1}$). The conversion of both NEE and isoprene to the basis of carbon was made to get the ratio (%) of how much carbon absorbed by the ecosystem (NEE) was emitted into the atmosphere in the form of isoprene. Daytime (9:00-16:30h, local time) averages of NEE were calculated for the same time of REA measurements (when simultaneous data were available) and also calculated for the period from 2000 to 2012.

3. Results

Isoprene fluxes were measured in intensive campaigns for each month from June 2013 (wet-to-dry transition season) to December 2013 (wet season) to investigate the seasonality of this compound and relate it to seasonal changes in environmental factors – PAR and air temperature. Because precipitation data from K34 tower contained huge gaps and some problems, precipitation measured in Manaus city (Instituto Nacional de Meteorologia - INMET) was considered here in order to give an idea about how was the seasonal variation of precipitation during the year 2013 in this region. Although precipitation data have shown higher values during the wet season as expected, it is observed that precipitation was irregular from the wet-to-dry transition season to the early wet season, showing values below 100 mm per month during June, August, October and December 2013 (figure 3 a). PAR and air temperature measured at K34 tower (51 m) also presented seasonal variation with both showing higher values during the dry season and the dry-to-wet transition season compared to the wet season (figure 3 b). Considering only the days of isoprene flux measurements, PAR and air temperature reached a peak in August and October, respectively (figure 3 b).
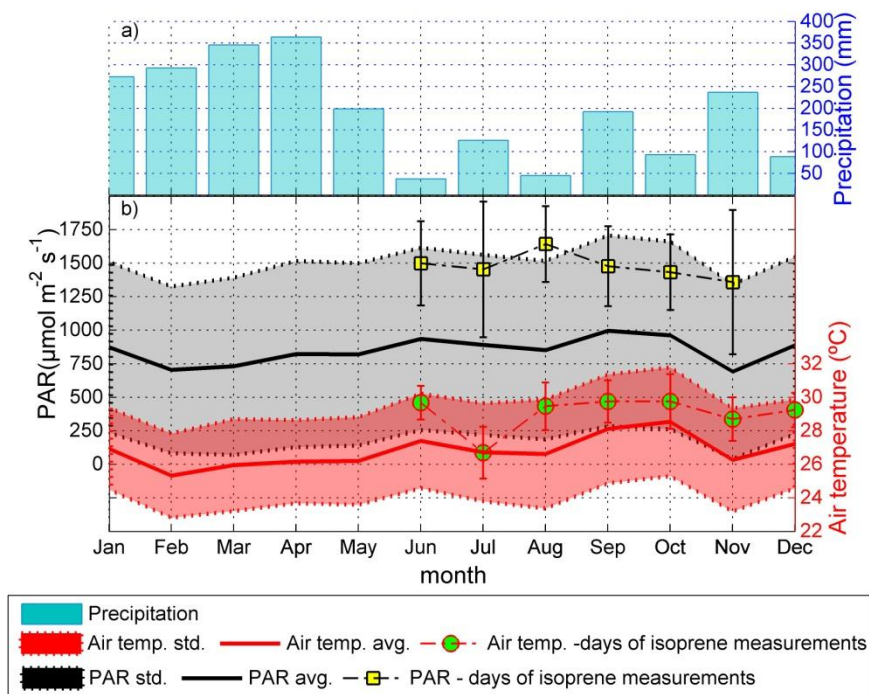
Figure 3: Seasonal variation of precipitation, PAR and air temperature - (a) monthly cumulative precipitation from January 2013 to December 2013 (measured in 60 minute intervals of 24 hours) (INMET data); (b) Monthly average of PAR from January 2013 to December 2013 (measured every 30 min from 6h to 18h, local time) (K34 tower) (black line), and average of PAR of the days of isoprene flux measurements (yellow square) (measured every 30 min from 6h to 18h, local time); monthly average of air temperature from January 2013 to December 2013 (measured every 30 min from 6h to 18h, local time) (K34 tower) (red line), and average of air temperature of the days of isoprene flux measurements (measured every 30 min from 6h to 18h, local time) (green circle).

Generally, high cloud cover and rain events were observed around noontime and at afternoon for the whole period of measurements described here. This indicated that part of the within month variability in isoprene emissions observed here (table 1) should be attributed to the rapid changes in weather conditions in the field of this study, because when cloudy and sunny periods were compared it was possible to verify that the short-term reduction in PAR can also reduce isoprene emission.

Table1: Mean monthly isoprene fluxes (mg m^{-2} h^{-1}) for three different daytime periods: morning (9:00-10:30h, local time), midday (12:00-13:30h), and afternoon (15:00-16:30h).

period of time	Jun	Jul	Aug	Sep	Oct	Nov	Dec
9:00-10:30h	7.07±10.6 (*n*=10)	-0.05±0.6 (*n*=11)	0.79±1.7 (*n*=12)	12.60±9.6 (*n*=8)	12.19±7.4 (*n*=12)	11.66±13.9 (*n*=5)	8.46±13.9 (*n*=11)
12:00-13:30h	3.67±4.0 (*n*=5)	-0.12±0.3 (*n*=6)	1.00±1.1 (*n*=11)	-2.02 (*n*=1)	11.66±10.7 (*n*=14)	9.68±7.1 (*n*=5)	20.60±13.8 (*n*=5)
15:00-16:30h	-0.08 (*n*=1)	-0.05 (*n*=1)	-0.33±1.3 (*n*=8)	17.93±10.2 (*n*=3)	1.75±9.6 (*n*=8)	3.86±7.9 (*n*=3)	9.12±6.7 (*n*=8)

Note: Means are followed by one standard deviation and by the number of samples (*n*).

Monthly averages of isoprene fluxes have shown lower values from June (wet-to-dry transition season) to August (early dry season) than from September (late dry season) to December (early wet season) (figure 4 b). It was observed that isoprene fluxes presented a slight reduction in October and November with a subsequent increase in December; this was also observed in both PAR and air temperature (figure 3 b). The very low isoprene flux observed in July could be related to the reduction of air temperature observed during the days of measurements (figure 3 b), which may be a result of the frequent events of rain. However, August also showed low isoprene flux and, during the days of measurements of this month, PAR and air temperature were high (figure 3 b) and rain events were not observed.

Generally, estimates of MEGAN 2.1, forced with variation in PPFD and air temperature of only days of REA sampling, did not show statistically significant agreement with isoprene flux measurements (r^2= 0.14). Comparing mean flux magnitudes, MEGAN 2.1 overestimated isoprene emission during the months of the wet-to-dry transition season and the early dry season. However, a model-measurement comparison of only dry season and dry-to-wet transition season has shown significant agreement (r^2= 0. 92).
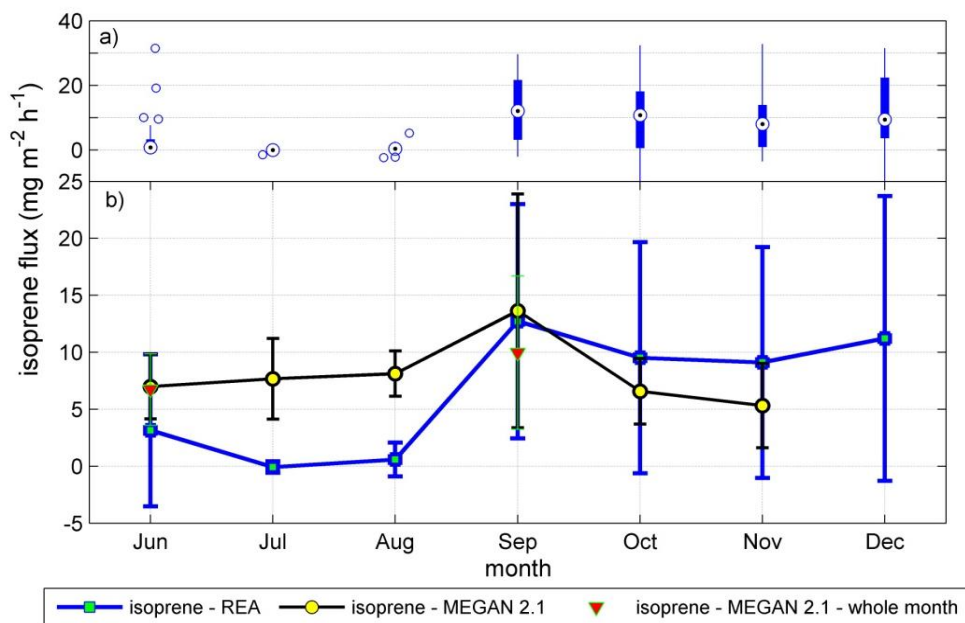
Figure 4: Variation of isoprene fluxes - (a) median (black dot) and interquartile range (25th - 75th quartiles) (blue box) of isoprene fluxes measured by REA at K34 tower (09:00-16:30h, local time); (b) mean (green squares) and one standard deviation of isoprene fluxes measured by REA at K34 tower (09:00-16:30h, local time), and mean (yellow circles) and one standard deviation of isoprene emission estimated by MEGAN 2.1 for the same time of REA samples, and mean (red triangles) and one standard deviation of isoprene emission estimated by MEGAN 2.1 taking into account air temperature and PAR data of the entire month (only June/2013 and September/2013).

Seasonal variation was shown in satellite-derived isoprene emission (figure 5 a). Results of satellite-derived isoprene emission were monthly averaged taking into account daily estimates from 2010 to 2012. Mean values have presented maximum emission from September to October, the dry and the dry-to-wet transition season, respectively; a second smaller peak was observed in March - the wet season. Monthly MEGAN 2.1 estimates averaged from 2010 to 2012 were compared to the satellite-derived isoprene emission, and this showed that the model could indicate a seasonal trend similar to the satellite-derived isoprene emission based only in PPFD and air temperature variations. However, in magnitude, MEGAN 2.1 overestimated isoprene emissions. Comparing both satellite-derived and modeled isoprene emission (2010-2012) to isoprene emission measured by REA (2013) (figure 5 b), it is observed that they all showed higher emissions during the late dry season and the dry-to-wet transition season as compared to the other seasons, suggesting good agreement in terms of seasonal trend.
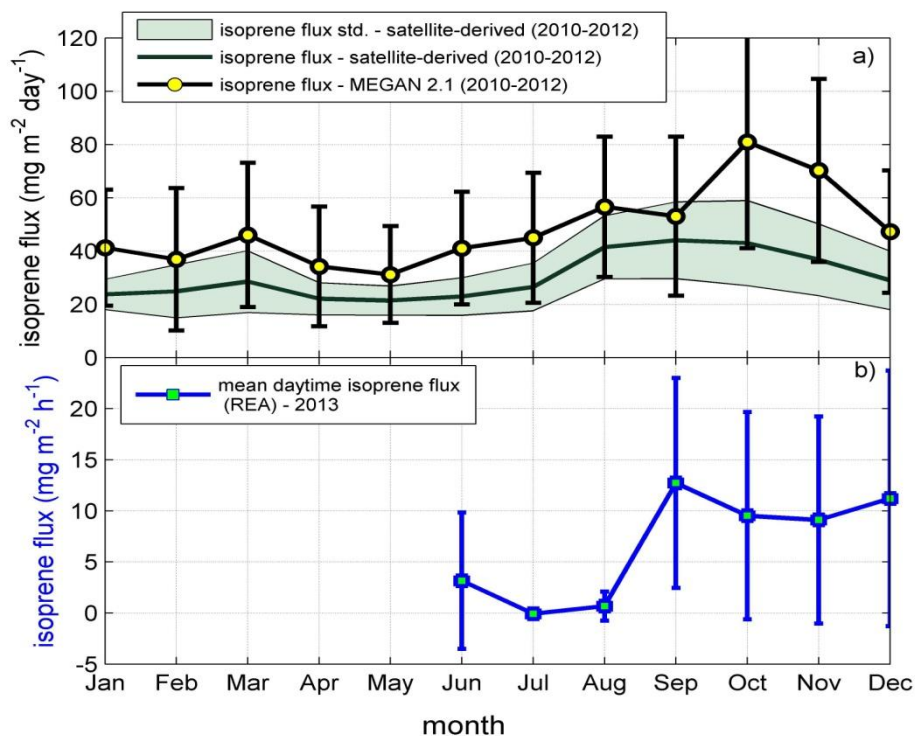
Figure 5: (a) Comparison of monthly average of daily isoprene flux (24 hours) from 2010 to 2012 derived from satellite HCHO column observations (mg m^{-2} day^{-1}) (green line); and average of daily isoprene flux (24 hours) from 2010 to 2012 estimated by MEGAN 2.1 (black line + yellow circles); and (b) monthly average of isoprene flux measured by REA (09:00-16:30h, local time) (blue line). REA fluxes are from June/2013 to December/2013.

Mean diurnal isoprene emission was compared to the Net CO_2 Ecosystem Exchange (NEE) during the dry-to-wet transition season (October and November) (figure 6). NEE showed maximum carbon uptake from 9:00 to 12:00 (local time), but maximum isoprene emission was a bit shifted slightly towards early afternoon (12:30-13:00, local time). One interesting thing is that isoprene fluxes proved to be very sensitive to PAR variation. For both months, October and November (figure 6 a, b), a reduction of PAR around noontime was mirrored in a reduction of isoprene flux with subsequent recovery after an increasing of PAR. Generally, the ratio of carbon up taken (NEE) and carbon emitted by the forest in the form of isoprene – isoprene (C) /NEE (C)– was up by approximately 3 %.
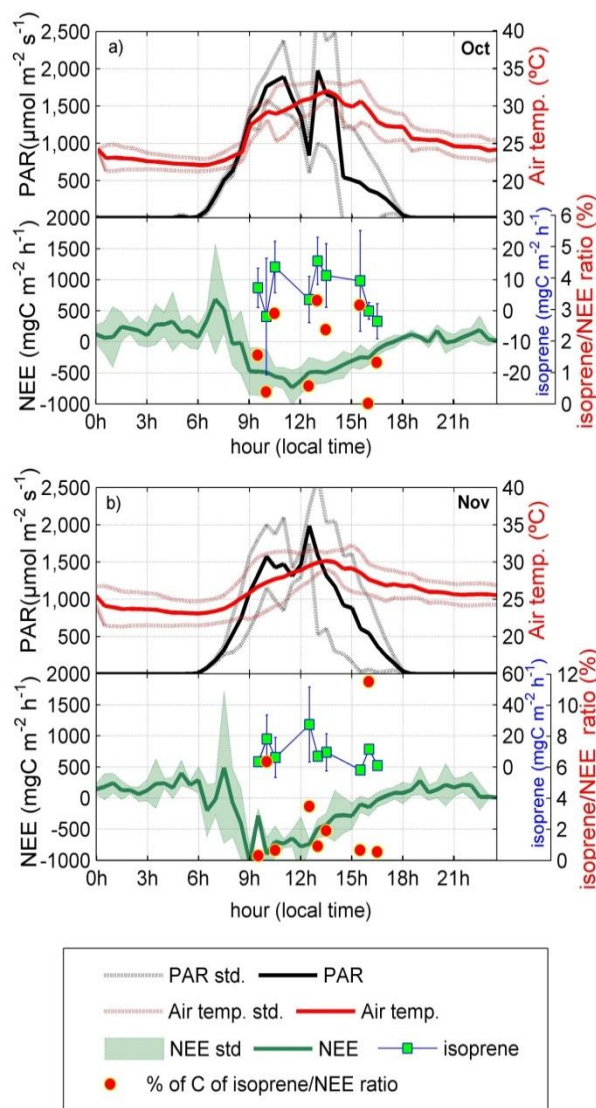
Figure 6: Mean diurnal cycle of PAR (black line), air temperature (red line), NEE (mg C m-2 h-1) (green line), isoprene flux (REA - mg C m-2 h-1) (green squares), and isoprene/NEE ratio (% of C) (red circles) for the days of REA samples of October/2013 (a) and November/2013 (b).

As data were not available to calculate NEE for almost whole year of 2013, monthly averages of daytime NEE (9:00-16:30, local time) from 2000 to 2012 were analyzed in order to verify the potential of seasonal variation in the carbon uptake by the forest and correlate it with the seasonal variation of isoprene emission in this study (figure 7 a). Annual averages of NEE presented high variability among the years. This variability resulted in low seasonal variation of the NEE averaged for all years (2000-2012), being the mean NEE difference between the wet season and the dry season up to approximately 90 mgC m^{-2} h^{-1}.
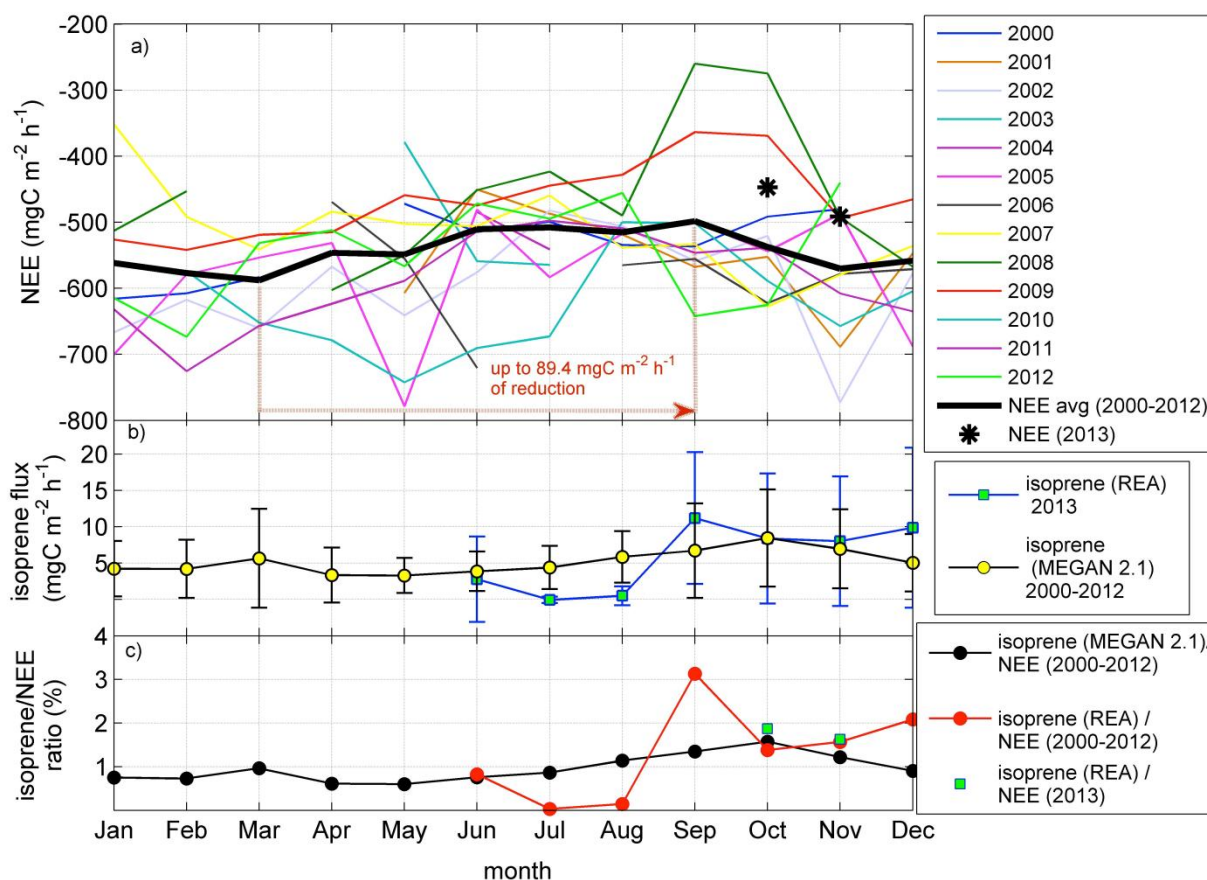
Figure 7: Monthly average of daytime NEE (09:00-16:30h, local time) from 2000 to 2012 and average of daytime NEE for the days of REA samples of October/2013 and November/2013 (black stars) (a). Monthly average of isoprene emission (09:00-16:30h, local time) estimated by MEGAN 2.1 from 2000 to 2012 (yellow circles), and monthly average of isoprene flux measured by REA (09:00-16:30h, local time) from June/2013 to December/2013 (green squares) (b). Monthly average of the ratio of isoprene emission estimated by MEGAN 2.1 and NEE, being both from 2000 to 2012 (black line); monthly average of the ratio of isoprene flux (REA - from Jun/2013 to Dec/2013) and NEE from 2000 to 2012 (red line); and ratio of isoprene flux (REA) and NEE, being both of the same days of October/2013 and November/2013 (green squares) (c).

On the basis of air temperature and PAR seasonal variation, MEGAN 2.1 estimated isoprene emission from 2000 to 2012 (figure 7b). Isoprene emission estimates have shown mean maximum values in October (dry-to-wet transition season) and a second smaller peak in March (wet season). The ratio of isoprene emission estimated by MEGAN 2.1 (2000-2012) and mean NEE (2000-2012) showed values approximately between 0.7 % (April) and 1.7 % (October) (figure 7 c). Assuming that isoprene flux measured in this study (figure 7b) is representative for this site and that the seasonality of isoprene emission from different years would be similar to this year of measurements, the ratio between isoprene emission (REA-2013) and mean NEE (2000-2012) were computed and showed that this ratio could be near zero during the wet-to-dry

transition season (July) and early dry season (August), and up to 3% in late dry season (September) (figure 7 c). The ratio of isoprene emission (REA-2013) and NEE (2013) were also computed for October and November, when NEE data were available in 2013. This ratio presented values of approximately 1.9 % and 1.7% during October and November, respectively.

4. Discussion

Isoprene flux measurements reported here have shown seasonal dependence. In many Amazonian forest sites, seasonal changes of environmental factors have been attributed to rainfall variation. When monthly cumulative precipitation is below 100 mm, this period is characterized as the dry season. The length of the dry season varies among the Amazonian sub-regions (Restrepo-Coupe et al., 2013) and, at the same region, the dry season also varies from year-to-year in length and intensity (da Rocha et al., 2009). Because there is a reduction of cumulus cloud cover during the dry season, an increase in solar radiation at the surface is observed in areas with low variation in top-of-atmosphere solar energy as the central Amazonia (Restrepo-Coupe et al., 2013). High temperatures consequently follow the high insolation during the dry season, which makes the forest environment different as compared to the wet season. As short-term and long-term variation of these both environmental factors – light and temperature – are suggested to primarily affect isoprene production and emission (Harley et al., 1999), studies with *in situ* measurements (Andreae et al., 2002; Kesselmeier et al., 2002b; Kuhn et al., 2004a, 2004b; Yañez-Serrano et al., 2014) and with satellite retrieval (Barkley et al., 2009) have suggested that seasonal changes in this environmental variables can exert important effects on isoprene emission into the atmosphere in the Amazonian rainforest.

Correspondingly, this study presented high isoprene emissions from the late dry season to the early wet season compared to the wet-to-dry transition season, this behavior being similar to PAR and air temperature variation. In addition, a general analysis of the isoprene emission investigated so far (see table 1 of Alves et al., in preparation [Chapter 1]) have shown that, although there is high variability among measurements, emissions of isoprene are considerably higher during the dry season and the dry-to-wet transition season compared to the wet season and the wet-to-dry transition season.

Emissions presented here have shown higher values than some isoprene flux measurements reported for the dry season (September) (Jardine et al., 2012; Karl et al., 2007; Rizzo et al., 2010) and the wet season (February) (Karl et al., 2009) near the site of this study, and for the dry-to-wet transition season (November) and the wet season (December-January) (Andreae et al., 2002) in the same site of this study. In the other hand, isoprene emissions for the wet-to-dry transition season (July) were lower than measurements reported for this same site (Kuhn et al., 2007; Ciccioli et al, 2003). However, a comparison of isoprene emissions of investigations reported in Amazonia may be a challenge, because methodologies are not standardized, the temporal and spatial representativeness of the amount of sampling varies widely, and means or medians account for different daytime period or potentially smooth seasonal changes when measurements of different seasons are averaged together (e.g. Andreae et al., 2002; Jardine et al., 2012; Stefani et al. 2000).

A comparison of isoprene emission among the months showed the lowest values of isoprene emission in July (wet-to-dry transition season). During the days of measurements of this month, precipitation was very often observed, which affected the environment with a reduction in PAR and air temperature. One could speculate that the low values of isoprene emission in July would be mostly related to the decreasing in PAR and air temperature. However, low values of isoprene emissions were also shown in August, when the days of measurements were sunny and rain was not observed. In addition, isoprene emission showed a small decreasing in November with a subsequent increasing in December, correspondingly to the behavior observed in PAR and air temperature during the days of measurements and for the whole month; but this decreasing were not comparable to the low values observed in July. This suggests that other factors might be simultaneously affecting the seasonal variation of isoprene emission, which could be seasonal changes in leaf biomass as previously suggested (Barkley et al., 2009; Kesselmeier et al., 2002b; Kuhn et al., 2004a).

In addition, differently from previous study (Karl et al., 2007), which indicated that for short-term variation in light and temperature MEGAN isoprene estimates have shown good agreement with measurements and suggested that light and temperature variations account for most of the isoprene emission variation, here with long-term variation in light and temperature, MEGAN 2.1 estimates did not capture the behavior observed with the REA isoprene fluxes, showing a large disagreement during the wet-to-dry transition season and early dry season. As

only PPFD and air temperature were used to run the MEGAN 2.1, other factors that may have an effect on isoprene emission are not being considered here; and a model-measurement comparison suggests that those different factors could be very important especially during the transition seasons.

It has been suggested that leaf biomass shows seasonal changes due to the seasonal variation of light at the surface in Amazonia (Huete et al., 2006; Myneni et al., 2007; Nelson et al. 2014; Samanta et al., 2012). Due to the high insolation during the dry season, forests in the central Amazonia would experience widespread leaf flushing (new leaf growth) during the wet-to-dry transition season in order to have more healthy photosynthetically active leaves at the period with high insolation (Jones et al., 2014; Restrepo-Coupe et al., 2013). According to Nelson et al. (2014), canopy imaging in this same site from December 2012 to November 2013 have shown that 40-50% of flushing crowns dropped all their leaves prior to adding new leaves, this leaf-off phase being brief and followed by the dry season leaf flushing. The period with low isoprene emission presented in this study – the wet-to-dry transition season and early dry season –corresponds to the period of high leaf flushing (leaf age from 0 to 2 months); and the period with high isoprene emission – late dry season and early wet season – corresponds to the period with more leaves in an age group between 3 and 8 months (Nelson et al. 2014). This suggests that canopy isoprene emission may be responsive to leaf demography and leaf phenology in central Amazonia, which has already been suggested by the satellite retrieval that showed simultaneous reduction of leaf biomass and atmospheric concentrations of HCHO – an isoprene oxidation product (Barkley et al., 2009).

Furthermore, the isoprene synthase activity depends on the leaf ontogenetic stage. Because isoprene synthase activity is absent in very young leaves, isoprene synthase activity increases gradually until full leaf maturation and decreases thereafter with the onset of leaf senescence (Schnitzler et al., 1997). This indicates that seasonal changes in leaf age might influence the seasonality of the emission factor activity of isoprene as suggested previously (Alves et al., 2014).

Indeed, some global isoprene models have demonstrated seasonal variation in emission in Amazonia (Guenther et al., 2006, 2012; Muller et al., 2008) and have attempted to reproduce the effect of leaf phenology on isoprene emission by using LAI variation derived by MODIS (Guenther et al., 2012); however, those estimates showed much smaller seasonal variations.

Satellite-derived isoprene emission is being used to reduce those uncertainties (Guenther et al., 2006). A comparison between isoprene emission measured in this study and satellite-derived isoprene emission (2010-2012) has shown that the seasonal trend observed in the field is similar to the satellite retrieval. However, more *in situ* measurements are needed in order to validate and reduce uncertainties associated to the satellite-derived isoprene emission, which could provide with better information to improve regional and global models of bottom-up isoprene estimates.

As in conditions without stress isoprene production/emission of tropical species seems to be mostly dependent of photosynthesis substrates (Jardine et al., 2014), a comparison of carbon uptake by the ecosystem and emitted as isoprene may give some information on how much carbon of emitted isoprene accounts for the ecosystem carbon losses to the atmosphere (Kesselmeier et al., 2002a). Here, it is shown that the ratio of carbon uptake and carbon emitted as isoprene might have diurnal and seasonal changes. However, a word of caution is needed in terms of state a seasonal pattern of this ratio, because, though mean NEE (2000-2012) presented a small seasonal variation, when mean NEE was compared between years, high variability was observed, limiting the interpretation of a potential pattern of seasonal changes in NEE (de Araújo et al., 2010; Araujo et al., 2002; Cirino et al., 2014). The unclear NEE seasonality for this site could be attributed to climate variability and to the uncertainties associated to the method of NEE estimative (de Araújo et al., 2010), which may be influenced by within canopy CO_2 advection in a such complex terrain (Tóta et al., 2012).

But, assuming the mean NEE (2000-2012) and mean isoprene emission measured (REA) and estimated by MEGAN 2.1 (2000-2012) in this study, it is suggested that carbon losses in the form of isoprene could be higher during the dry season compared to the wet season. Further research is needed to evaluate this suggestion, but if this is a pattern, this should be considered in regional and global models of carbon cycle.

5. Summary and conclusions

Isoprene emissions from a research site in central Amazonia using a REA system were investigated. This system permitted revealing seasonal variation over seven months of the year 2013. This period accounted for the wet-to-dry transition season, the dry season, the dry-to-wet

transition season and the beginning of the wet season. The results showed that high emission was found from the late dry season to the early wet season, and low isoprene emission was observed from wet-to-dry season to early dry season, being this seasonal trend similar to satellite-derived isoprene emission. MEGAN 2.1 estimates, based on variations only in light and temperature, were not satisfactory to reproduce the low isoprene emission measured by REA during the wet-to-dry transition season and early dry season. However, top-down estimates of isoprene emission averaged from 2010 to 2012 showed a similar trend compared to the seasonal variation of both ground-based measurements (REA) and MEGAN 2.1 estimates; however, in order to do a quantitative isoprene emission comparison between ground-based measurements and satellite based estimates, more observational studies are needed.

In terms of carbon losses from the forest to the atmosphere in the form of isoprene (isoprene/NEE), it is proposed that more carbon is emitted during the dry season, however, more investigations are needed to clarify this. Here it is suggested that, beyond seasonal variations in light and temperature, seasonal changes in leaf demography and leaf phenology may play important roles on isoprene emissions at canopy scale, especially during the wet-to-dry transition season. Because there are large uncertainties associated to satellite-derived leaf phenology (Jones et al., 2014) due to the heterogeneity mainly caused by the huge biodiversity in this ecosystem (Silva et al., 2013), more research is needed to better characterize the leaf phenology in the Amazonian sub-regions in order to improve isoprene emission models in terms of seasonality. Moreover, as the number of measurement sites and long-term measurements are limited in the Amazonian rainforest, only a rough distinction of a few forest types with measurements in short campaigns can be used to weight areal integrals, which potentially biases regional bottom-up emission model and estimates. Therefore, this study strongly encourages future research that aims long-term standardized measurements of isoprene and other BVOCs in different Amazonian forest sites, because this could reduce uncertain aspects of scaling biogenic emissions up to the regional and global system.

Acknowledgements

SÍNTESE E CONSIDERAÇÕES FINAIS

Ambos os capítulos deste estudo apresentaram uma tendência de mudanças sazonais na emissão de isoprenóides - isopreno, monoterpenos e sesquiterpenos. Esta sazonalidade foi relacionada a variações sazonais de radiação solar a superfície e de temperatura, como também, a mudanças nas fenofases de grande parte das folhas da copa das árvores localizadas próximas e no entorno da base experimental.

Houve uma tentativa de se reproduzir a sazonalidade da emissão de isoprenóides usando o modelo MEGAN 2.1. O modelo foi alimentado com valores de PPFD e temperatura que variam sazonalmente no sítio estudo. De acordo com a comparação entre as medidas e as estimativas do modelo, este último não foi satisfatório para reproduzir as emissões desta área de estudo, principalmente, para a transição entre as estações chuvosa e seca. Isto, provavelmente, é decorrente do efeito de outros fatores que influenciam as emissões, simultaneamente às variações de luz e temperatura. Entretanto, quando as emissões medidas e as emissões estimadas com base em observações por satélite foram comparadas, especificamente para isopreno, observou-se que há similaridade na tendência sazonal de ambos, o que demonstra que o uso de estimativas por satélite contribui positivamente para as estimativas do modelo MEGAN 2.1.

As relações feitas com os resultados apresentados aqui sugerem que outro fator importante para as emissões de isoprenóides poderia ser a fenologia foliar, e que tentativas para inserir e/ou aprimorar a parametrização dos efeitos causados pelas mudanças nas fenofases da vegetação são fortemente recomendadas para os modelos de emissão de COVBs.

Para realizar as medidas de perfis verticais de razão de mistura de isoprenóides em longo prazo na torre TT34 (Capítulo I), o PTR-MS se mostrou um equipamento eficiente, pois tem a capacidade de medir compostos em alta resolução, sem muitos custos com gases suplementares. No entanto, para os monoterpenos e sesquiterpenos esta técnica somente disponibiliza a soma total dos compostos de cada grupo, o que impede a identificação específica dos compostos químicos e também dificulta o aprofundamento do entendimento da reatividade e do papel dos diferentes compostos de monoterpenos e sesquiterpenos na atmosfera. Além disso, para estudos que visam o entendimento da sazonalidade das emissões dos isoprenóides na Amazônia, medidas de longo prazo são imprescindíveis, porém isto ainda é um desafio devido a dificuldades logísticas, estruturais e de orçamento para manter por longo prazo este equipamento em sítios experimentais na floresta Amazônica.

Por isso, com a finalidade de abranger as medidas para outras estações não investigadas no experimento com o PTR-MS, outra técnica foi utilizada para poder realizar medidas de fluxo de isopreno na torre K34 (capítulo II), um local de mais difícil acesso e menos perturbado comparado ao sítio da torre TT34. Esta técnica - *Relaxed Eddy Accumulation (REA)* - utiliza-se de baixo consumo de energia e é portátil, o que possibilitou a realização de medidas em um local remoto e em períodos variados. O uso desta técnica permitiu a verificação das baixas emissões de isopreno no período de transição entre as estações chuvosa e seca, o que corroborou as estimativas derivadas por satélite no que concerne a tendência de sazonalidade de isopreno.

Sumariamente, os resultados aqui apresentados sugerem sazonalidade para as emissões de isoprenóides e que estas variações não podem ser satisfatoriamente explicadas somente pela sazonalidade de luz e temperatura. Por isso, este estudo recomenda futuras pesquisas que visem integrar medidas em nível foliar com medidas em nível de dossel, com a finalidade de investigar como as possíveis mudanças nas taxas de transporte de elétrons, níveis de substratos e atividade enzimática, que são influenciadas por variações sazonais na área foliar, na idade da folha, na fenologia, na reposta a umidade do solo e na temperatura e luz, podem influenciar as emissões de isoprenóides, o que possibilitaria a inserção e/ou aprimoramento destes parâmetros para as estimativas de emissões de COVBs em modelos para o clima e qualidade do ar.

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