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# Within-Canopy Sesquiterpene Ozonolysis in Amazonia



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## *Abstract*

Sesquiterpenes are highly reactive terpenoids produced by vegetation and may serve many important biological functions such as acting as antioxidants and as semiochemicals (chemicals acting as messengers within or between species). Once emitted to the atmosphere, by reacting with oxidants like ozone and contributing to secondary organic aerosol formation, the emission of sesquiterpenes from vegetation may have significant impacts on radiation balance and precipitation dynamics. Although it is known that sesquiterpenes have short atmospheric lifetimes of a few minutes, analytical difficulties stemming from low concentrations, high reactivities, and high “stickiness” have so far prevented the detailed characterization of within-canopy sources and sinks. Therefore little is known about sesquiterpene emissions and chemistry within canopies. This study presents the first ambient air profile observations of rapid sesquiterpene ozonolysis reactions obtained during the BrazilianAir 2010 field campaign in Central Amazonia, from September 2010 to February 2011. Our results show that sesquiterpene concentrations followed a very different pattern compared to isoprene and monoterpenes, by peaking at night instead of during the day and peaking near the ground instead of within the canopy. Furthermore, their concentrations were inversely related with ozone, suggesting that sesquiterpene concentrations were more strongly determined by ozonolysis rather than by emissions, which is further corroborated by experiments done in Biosphere 2, Arizona, where no oxidation was taking place and sesquiterpenes followed the same diurnal pattern as isoprene and monoterpenes. These observations suggest rapid ozonolysis reactions within the canopy which strongly determine sesquiterpene concentrations in both time and space. Moreover, calculated sesquiterpene ozonolysis rates peaked during midday at a height of ca. 20m above ground, suggesting that they are mainly determined by the high ozone concentrations during the day. We conclude that ambient concentrations of sesquiterpenes are not necessarily low because of low plant emissions, but rather high ozonolysis rates which were unaccounted for in previous ambient air studies. Our findings should help to better understand the environmental and biological controls on the dynamics of chemical emission, loss, and transport of highly reactive species like sesquiterpenes within canopies and their potential biological and atmospheric impacts. In particular, our observations suggest that the fraction of emitted sesquiterpenes lost within the canopy to ozonolysis could be large and that this process reduces ozone concentrations thereby providing plants protection against exogenous reactive oxygen species.

Keywords: Sesquiterpenes, ozonolysis, ozone, Amazon, oxidation.

## *Popular summary*

### En mycket reaktiv spårgas i Amazonas

Växter släpper ut flyktiga organiska ämnen, som är mycket viktiga eftersom de släpps ut i stora mängder och påverkar tillverkningen av aerosoler, förändrar luftkvaliteten och fungerar som kommunikation mellan växter och herbivorer. Det här arbetet presenterar uppmätningar av sesquiterpener, vilka är flyktiga organiska partiklarna inom gruppen isoprenoider, de har de största utsläpps grupperna. Sesquiterpener är mycket reaktiva och finns därför i väldigt små koncentrationer, därför har det inte varit möjligt att mäta dem tidigare. Här presenteras de första mätningarna av sesquiterpener i ett flux torn i en central amazon region, detta låter oss se sesquiterpenernas roll i trädkronorna. För att få mätningarna användes en 'Proton Transfer Reaction Mass Spectrometer' som har inläpp på olika höjder från 2 till 40 meter. Vårt resultat tyder på att sesquiterpenerna är invert relaterade till ozon, eftersom sesquiterpenerna visar höga koncentrationer under natten, och ozon visar höga koncentrationer under dagen. Därför, i Amazonas, är sesquiterpenernas koncentration bestämda av ozon, vilket är deras sink, eftersom sesquiterpener försvinner från systemet som en följd av deras reaktion med ozonet. Detta medför att en serie av möjlig feedback mekanismer för klimatet förklaras, men det behövs många fler undersökningar för att man ska kunna bekräfta alla dessa processer.

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## *Introduction*

### 1.1. BVOC general information

BVOCs (Biogenic Volatile Organic Compounds) are organic atmospheric trace gases other than methane, CO and CO<sub>2</sub>, emitted from biogenic source such as vegetation or microorganisms (Kesselmeier and Staudt, 1999). These compounds have several roles depending on the scale that they are being looked at, such as an atmospheric role, ecosystem role, leaf surface and plant level role, or tissue level role. For instance, at the atmospheric level, BVOC are very important since they affect the climate system, the air quality and to some degree the carbon cycle due to the large quantities emitted. Their climate and air pollution effects act via the formation and growth of SOA (secondary organic aerosol) and formation from BVOC oxidation products. BVOC rapid atmospheric reactivity with OH leads to increase of methane lifetime in the atmosphere, and the production of pollutants such as tropospheric ozone (Laothawornkitkul et al., 2009). At the ecological level they serve as communication between plants, protection against biotic and abiotic stresses, wound sealing or protection against cellular damage. By mass, the most important single VOC (Volatile Organic Compounds), even when including anthropogenic sources, is isoprene, (C<sub>5</sub>H<sub>8</sub>, 2-methyl-1,3-butadiene). On a global scale, BVOC dominate the annual VOC budget with emissions estimated around 1000-2000 Tg y<sup>-1</sup> (Kesselmeier et al., 2000; Laothawornkitkul et al., 2009).

#### 1.1.1. BVOC ecological role

BVOC emitted by plants have different roles in addition to the chemical reactions that affect tropospheric aerosol and O<sub>3</sub> loads. BVOC are used by plants as a means of signalling, and hence plant-plant interactions. In this case, plants emit BVOC in order to allocate the energy within the plant and to trigger the growth of plants. For instance, jasmonates (a type of BVOC) induce the formation of fruit ripening-related BVOC, such as ethylene which is associated with germination and ripening plants responses (Kondo et al., 2007). Another role is for plant reproduction; in this case BVOC (such as flower scent) are emitted in order to attract pollinators and facilitate pollination. Furthermore, BVOC also are part of biotic stress responses: plants may be emitting BVOC to repel pathogens protecting the plant in this way, or as a mean of wound sealing, as well as protection against cellular damage at plant tissue level (Laothawornkitkul et al., 2009; Vickers et al., 2009).

#### 1.1.2. BVOC atmospheric role

##### 1.1.2.1. Climate role

BVOCs have very different roles in the atmosphere associated with their diverse chemical reactions. Once a VOC (either from biological or anthropogenic sources) is emitted, it can be oxidized with either OH (during the day), O<sub>3</sub> (during day and night) or NO<sub>3</sub> (mostly at night) (Vizuete et al., 2004). Many of the oxidation products are condensable vapours that can undergo gas-to-particle conversion, forming SOA. BVOC may contribute to SOA formation in different pathways. They could follow

heterogeneous particle nucleation with help from sulphuric acid present in the background particulate concentration, they can condense onto the surface of pre-existing aerosol load or they can be kept in their gas-phase if saturation is not reached (Rizzo, 2006; Hobbs, 2000). Once condensation takes place and the aerosol is formed, SOA can have different optical properties depending on the height at which they are formed due to the light and temperature dependence of such reactions (Winterhalter et al., 2009; Tsigaridis and Kanakidou, 2003). Due to their relatively low volatility, some BVOC with high molecular weight compounds, are particularly good precursors for growth of SOA, condensing with more ease than other BVOC to form aerosols (Helmig et al., 2007; Sakulyanontvittaya et al., 2008; Bouvier-Brown et al., 2009a).

Secondary organic aerosols are important for our understanding of radiative forcing and climate change. Aerosols have a strong direct climate effect by the scattering or absorbance of solar radiation, which is dependent upon the chemical structure of the aerosol in question. Some aerosols absorb light, such as black carbon, while others reflect radiation, such as the SOA or sulphate aerosols (Artaxo et al., 2006). The aerosols formed depend on the oxidation product precursors, for instance, VOC of biogenic origin are estimated to yield 2.5 – 44.5 Tg of particulate organic matter per year, whereas anthropogenic VOCs lead to 0.05-2.69 Tg of organic matter per year (Sakulyanontvittaya et al., 2008; Guenther, 2008).

Furthermore, indirect effects associated with SOA in the atmosphere act via aerosol-induced changes in cloud properties and precipitation dynamics, since SOA can grow to size classes that make them relevant as cloud condensation nuclei (CCN). Once aerosols have reached a diameter of ca. 50 nm from the further condensation of more vapours they are typically considered a CCN (Boy et al., 2008). Depending on the aerosol and CCN yield, cloud droplets may or may not grow to the size where precipitation occurs. In a hypothetical low atmospheric VOC scenario, yields of aerosol and CCN number concentrations are low. In this case, cloud droplets are able to grow rapidly in size, resulting in rainfall from warm clouds (Rizzo, 2006). On the other hand, in a high VOC scenario the concentration of particles is relatively high (~ 2000 particles per cm<sup>3</sup> in average), especially when formed from fine mode aerosols coming directly from burning biomass or indirectly from the oxidation of biomass burning VOCs once in the atmosphere (Andreae et al., 2002). Therefore, the hygroscopic behaviour and amount of particle condensation is important to determine the cloud fate, since low particle concentration can lead to a low concentration of big cloud droplets, giving low clouds with higher rain efficiency, or, on the other hand, high particle concentration can give high concentration of small cloud droplets, forming deep clouds with lower precipitation efficiency (Rizzo, 2006; Varutbangkul et al., 2006).

Furthermore, BVOC affect the climate change by increasing the lifetime of methane, a very potent greenhouse gas. Methane, with a 25 times larger global warming potential than CO<sub>2</sub> (over 100 years' time horizon), is tropospherically removed by the hydroxyl radical OH, leading to the formation of water vapour and carbon dioxide. If the OH available for oxidation is used for BVOC oxidation, methane lifetime in the atmosphere could increase, thus inducing more positive forcing into the earth's radiative balance (Pacífico et al., 2009). Its lifetime could be increased 15% from 7.4 years as OH decreases, as NMHC (non-methane hydrocarbon) induced chemistry is simulated by Poisson et al., (2000).

### 1.1.2.2. Air Quality role

BVOC have also an important role in air quality since they fuel tropospheric chemistry (Atkinson, 2000). When  $\text{NO}_x$  are present in the atmosphere, such as from the emission of biomass or fossil fuel combustion, they act as catalysts. BVOCs are first oxidized by the OH radical forming oxygenated compounds (oBVOCs) which react with  $\text{NO}_x$  leading to the formation of aerosol precursors and  $\text{NO}_2$ . Such  $\text{NO}_2$  undergoes photolysis which leads to the formation of more ozone,  $\text{O}_3$  (Atkinson and Arey, 2003). Tropospheric ozone is considered a secondary pollutant leading to environmental problems through its detrimental impact on vegetation and human health. In the troposphere,  $\text{O}_3$  also is a strong greenhouse gas, adding to the climate role of BVOC (see 1.1.2.1). On the other hand, when ozone undergoes photolysis it leads to the formation of OH radical, which is considered the atmospheric detergent since it is responsible for the removal of many pollutants (Kesselmeier et al., 2009; Rummel et al., 2007).

## 1.2. Terpenoids General Information

There are many different types of BVOC (> 30000), with terpenoids having the highest fraction of emissions. Terpenoids or isoprenoids are compounds containing at least one isoprene unit ( $\text{C}_5\text{H}_8$ ) formed from photosynthetic and glycolytic intermediates. These isoprene units can assemble and modify in an extraordinary number of ways (Lichtenthaler et al., 1997). Volatile isoprenoids, such as isoprene, monoterpenes and sesquiterpene are emitted from terrestrial vegetation, mostly woody plants, at high rates, especially in tropical biomes where some species are known to re-emit up to 10% of their assimilated carbon as isoprene (Kesselmeier et al., 2002a). Even though the functions of volatile isoprenoids still remain a matter of intense debate, model estimates suggest that global BVOC emissions are dominated by volatile isoprenoid emissions from tropical forests due to high solar radiation and temperature (Guenther et al., 1995; Kesselmeier et al., 2009).

### 1.2.1. Antioxidant effect

Although the mechanisms remain unclear, there is a substantial amount of indirect evidence which suggests plants emit volatile isoprenoids to protect themselves from oxidative damage. A wide variety of biotic (microbes, nematodes, insects, etc.) and abiotic (thermal, radiative, drought, salt stress, etc.) plant stressors are associated with the accumulation of reactive oxygen species (ROS) including ozone, hydrogen peroxide, singlet oxygen, superoxide anion, and the hydroxyl radical (Vickers et al., 2009) within plants. These accumulations induce plant cell death, by causing oxidative damage to proteins, DNA and lipids (Apel and Hirt, 2004). Nevertheless, recently, it has been shown how exogenous isoprene can protect leaves against, short, acute exposure to ozone (300 ppb ;(Loreto et al., 2001)). Furthermore, the possibility has also been suggested of plants emitting volatile isoprenoids to oxidize ROS within the plant before any damage is caused to the plant cell (Jardine et al., submitted).

### 1.2.2. Terpenoid biosynthesis

In plant tissues, most BVOC are synthesized by three different biochemical routes, the isoprenoid, the lipoxygenase or the shikimic acid route (Laothawornkitkul et al., 2009). Although the formation of the routes is well understood, the exact biochemical regulations and functions are still a matter of debate, including crosstalk as biochemical pathways seem to interact with each other (Jardine et al., 2010b). Isoprenoids are synthesized by the condensation of five-carbon precursors: isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP). Today we know that two different pathways exist for their production (Lichtenthaler et al., 1997; Dudareva et al., 2005). Whereas in plant plastids, IPP is formed from pyruvate and glyceraldehyde 3-phosphate, via the methylerythritol phosphate (MEP or nonmevalonic) pathway; in the cytosol, IPP is derived from the mevalonate (mevalonic acid, MVA) pathway, which starts from the condensation of acetyl-CoA. The isoprenoid end-products formed are differing, depending on the pathway they derive from. Isoprene and monoterpenes (as well as other important compounds such as phytol and the carotenoids) are synthesized in the plastids, whereas di- tri and sesquiterpenes are exclusively synthesized in the cytosol (Kesselmeier and Staudt, 1999). This clear separation in biosynthesis underlies some observations such as the emission dependences on light and temperature for example. However, there is some crosstalk observed, i.e. exchange of IPP between plastids and cytosol (Dudareva et al., 2005).

### 1.2.3. Environmental controls of terpenoid production and emission

Terpenoids (or isoprenoids) are controlled by many different drivers, depending on composition and biochemical pathway of formation. Nevertheless, we know that the most important drivers are light and temperature. Production of isoprene and monoterpenes (MT) are mainly light dependant since light is needed for the activation of the isoprene synthase, taking place in the chloroplasts. Furthermore, temperature is also very important for enzymatic processes of the MEP pathway, having a very important role on the emissions of isoprenoids. Furthermore, temperature strongly affects emissions of those isoprenoids that are stored in pools after production (i.e., monoterpenes in many conifers); since it alters the vapour pressure of the pools, thus enhancing emissions by increasing the concentration of gas phase MT and other stored compounds inside the plant stomata. CO<sub>2</sub> also controls the emissions of isoprenoids in two different directions. One effect consists on the stimulation of plant growth by increasing CO<sub>2</sub> concentration and thus isoprenoid-producing biomass. On the other hand, elevated CO<sub>2</sub> has also been shown to reduce emissions, especially of isoprene, from leaves. This may be due to more phosphoenolpyruvic acid (PEP), which is a precursor for pyruvate, allocated for mitochondrial respiration (Rosenstiel et al., 2004). In addition, other environmental controls such as nitrogen, developmental stage, ozone, water content, heavy metals, etc. are also important for the production and emissions of isoprenoids, but they are dependent on each specific compound (Arneeth et al., 2007; Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009).

### 1.2.4. Sesquiterpenes in particular

Sesquiterpenes are larger isoprenoids consisting on three isoprene units and are highly reactive due to their double bonds. The most known SQT (and thus the most widely

studied) is  $\beta$ -Caryophyllene,  $C_{15}H_{24}$ , with a molecular weight of 204.35 amu (Figure 1) (Kesselmeier and Staudt, 1999; Varutbangkul et al., 2006; Duhl et al., 2008; Pollmann et al., 2005; Dudareva et al., 2005; Ormeno et al., 2007a).

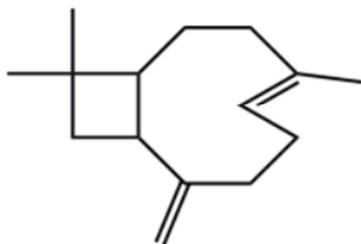


Figure 1: Chemical diagram of  $\beta$ -Caryophyllene.

At ecosystem level, the role of SQT in particular is to provide communication as semiochemicals in plant-insects interaction, as demonstrated by studies showing disturbances from insect herbivory, increasing SQT emissions to serve as a defensive agent (Duhl et al., 2008; Back et al., 2005; Helmig et al., 2004; Helmig et al., 2003). Furthermore, emissions of SQT are highly dependent upon the two major drivers temperature and light, although lately, other drivers have been found, such as soil moisture, air humidity, phenological state and plant water stress, as well as recent weather history and disturbances (Tarvainen et al., 2005; Arey et al., 1995). All these drivers, especially disturbances causing plant damage, will influence the amount of SQT emitted to the atmosphere (Duhl et al., 2008; Helmig et al., 2007; Ormeno et al., 2007b). However, over the course of the day, the driver that seems the most important determining SQT emissions is temperature, on which the vapour pressure of SQT stored in pools is dependant (Duhl et al., 2008; Helmig et al., 2007; Helmig et al., 2006). This further corroborates the cytosol location of SQT synthesis, where the PEP is coming from either mitochondrial respiration or fermentation (Vickers et al., 2009; Ormeno et al., 2007a; Kesselmeier and Staudt, 1999; Ormeno et al., 2007b). Due to the drivers controlling emissions of sesquiterpenes, distinct diurnal and seasonal patterns are expected to occur. Several emission experiments were carried out giving contrasting results in which some emissions peaked during the day whereas others peaked during the night. Ciccioli et al. (1999) detected  $\beta$ -Caryophyllene emission at night with no correlation with carbon assimilation, and De Moraes et al. (2001) found herbivore induced night time SQT emissions of tobacco plants, although there were high diurnal emissions as well.

#### 1.2.4.1. Atmospheric role

Sesquiterpenes have a distinct oxidation behaviour compared to isoprene or many monoterpenes. Reaction with ozone is the most likely, due to the high SQT reaction rate constant (Shu and Atkinson, 1994). SQT (for instance:  $\beta$ -Caryophyllene) atmospheric lifetime when oxidised with  $O_3$  is around 2 minutes, compared to 53 minutes if SQT were oxidized by OH, as theoretically calculated by Calogirou et al., 1997 (Calogirou et al., 1997). This lower lifetime towards ozone arises from the  $\beta$ -Caryophyllene endocyclic double bond in the molecule, which quickly reacts with ozone first resulting in a primary ozonide (POZ) (Winterhalter et al., 2009; Nguyen et al., 2009) followed by ring opening to generate Stabilized Criegee Intermediates (SCI). Ring closure of the SCI yields rearranged secondary ozonide (SOZ) products, or further reaction of SCIs

with hydroxylic or carbonyl compounds (such as  $\text{H}_2\text{O}$ ,  $\text{HCOOH}$  or  $\text{HCHO}$ ) yielding SOA (Figure 2).

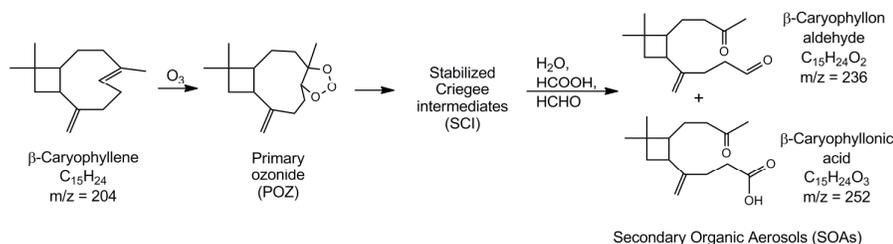


Figure 2: Sesquiterpene ozonolysis reaction shown with  $\beta$ -Caryophyllene as an example, having condensable vapours as SOA products, after the formation of Stabilized Criegee Intermediates. Adopted from Winterhalter et al., (2009).

#### 1.2.4.1.1. Climate and air quality

SQT have the highest aerosols yields of the BVOC terpenoid class, up to 100% in some cases, since yields are correlated with VOC molecular weight. This means they are very good SOA precursors since most of the compounds will go into the particle phase instead of the gas phase during gas-phase partitioning (Ormeno et al., 2007a; Vizuete et al., 2004; Bonn and Moortgat, 2003). Nevertheless, it seems that CCN activity of  $\beta$ -Caryophyllene is lower than for monoterpenes, since apparently the hydroscopic fraction of SOA formed from SQT is more volatile. (Winterhalter et al., 2009).

In figure 3, I provide an example for the tropical atmosphere which is considered a good photochemical reactor due to high UV light and air humidity content and because of the large amount of BVOC emitted (Kesselmeier et al., 2009). During the dry season, biomass burning from deforestation emits large amounts of VOCs together with  $\text{NO}_x$ . These VOCs together with large quantities of BVOCs emitted from live vegetation are oxidized by OH. In presence of the pyrogenic  $\text{NO}_x$  acting as a catalyst, tropospheric ozone is formed (Kesselmeier et al., 2009). Since ozonolysis rate is so rapid, SQT tend to be sinks for ozone especially in remote areas such as the Amazon (Hakola et al., 2006; Pollmann et al., 2005; Bonn and Moortgat, 2003; Kim et al., 2009), when other VOCs are inducing the formation of tropospheric ozone (Artaxo et al., 2006; Holzke et al., 2006; Hakola et al., 2006; Kuhn et al., 2010). Therefore figure 1 represents a relatively high ozone (>20 ppbv) scenario for a pristine atmosphere. In such case, sesquiterpenes emissions would rapidly be oxidized, already within the canopy, since the ozone concentration is relatively high (Shu and Atkinson, 1994).

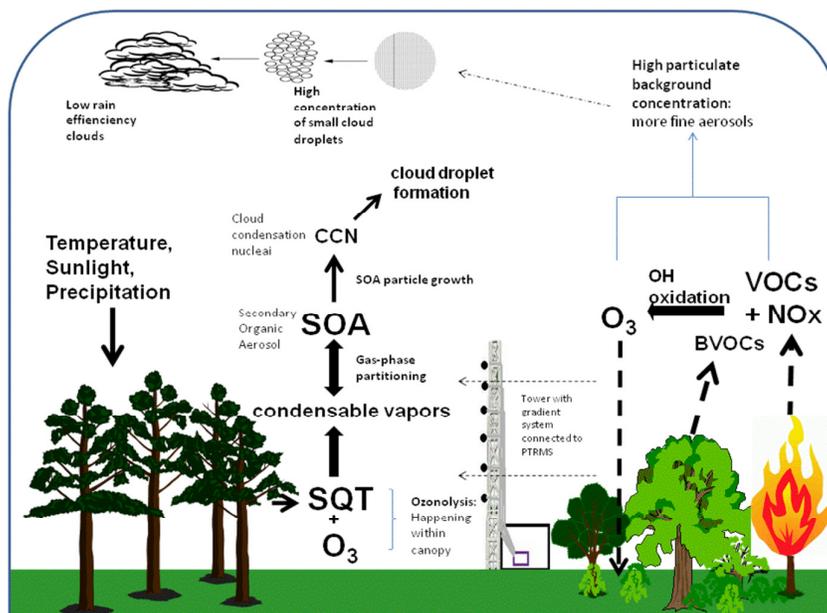


Figure 3: Diagram showing the behaviour of SQT reactivity in the atmosphere in a relatively high ozone scenario, in a rainforest ecosystem during the biomass burning season. During this season a large amount of VOCs are emitted to the atmosphere, leading to a high particulate background concentration proceeding to low rain efficiency clouds. At the same time, under these circumstances SQT are emitted by vegetation and get quickly oxidized by the tropospheric ozone formed after the oxidation of VOCs in the regional atmosphere. In addition, the tower with the gradient scheme connected to a proton-transfer reaction mass spectrometer (PTR-MS, see methods) is also shown as an example of the setup of the experiment explained in this thesis.

### 1.3. Amazon rainforest

The Amazon rainforest is thought to be a very suitable place for the study of interactions of BVOC emissions and the atmospheric environment. The region represents a pristine ecosystem with strong coupling to the atmosphere via the hydrological cycle and substantial recycling by in situ evapotranspiration of precipitation (Nepstad et al., 2008; Phillips et al., 2009). Furthermore, the Amazon rainforest has relatively low ozone mixing ratios ranging from 18-40 ppb as the typical background levels (during the dry season, with even lower values during wet season). The only sources of ozone are downward transport from the stratosphere, in situ photochemical production from BVOC oxidation, plus a fraction source from cities like Manaus (Kuhn et al., 2010). In addition, emissions of BVOC are high due to the high species richness, with the order of  $10^5$  different trees species, as well as due to warm temperatures and high irradiance (Kesselmeier et al., 2009; Martin et al., 2010b). Moreover the high UV light radiation and air relative humidity in the Amazon a “tropical reactor” (Andreae, 2001) greatly favours atmospheric chemical reactions, to the point that changes in the atmospheric chemical properties and processes in the Amazon could inflict climate impacts on a global scale (Kuhn et al., 2007; Kuhn et al., 2010; Karl et al., 2007). Furthermore, the biomass burning season allows for the study of regional BVOC gas-chemistry and aerosol formation due to the large amount of VOC emitted from fires (Longo et al., 2009) (see also Figure 3).

#### 1.4. Ambient Profile Measurements

Measurement of ambient air concentrations is an important component in this context, since emissions are plant species dependent (even individual dependent), as well as environmental and phenological state dependent. Thus, ambient air measurements integrate over whole canopy emissions and chemistry. To date, ambient air measurements of SQT with a PTR-MS were done by Boy et al., 2008 (alpine ecosystem), Bouvier-Brown et al., 2009 (ponderosa pine, alpine ecosystem), Kim et al., 2009 (transition to boreal ecosystem) (Kim et al., 2009; Bouvier-Brown et al., 2009a; Boy et al., 2008). These studies covered no more than a few weeks of measurements and with exception of the study by Kim et al., 2009, none used a tower for canopy profiling. Kim et al., 2009 applied a tower gradient scheme with 2 inlets. Their focus was on ion fragmentation; only the noon time average canopy scale flux, the mixing ratio and OH reactivity were reported. A more elaborate gradient scheme system can provide full canopy coverage of the concentration profile and by causing less disturbances than plant enclosures, avoids artificially high SQT emissions as wounding response (Duhl et al., 2008).

#### 1.5. Aim and hypothesis

The aim of this study was to investigate the atmospheric behaviour of sesquiterpene emissions at canopy scale, and their interactions with climate, atmospheric chemistry and air quality. It is the very first time tropical ambient air concentrations of SQT are measured over a long-term period, covering dry and wet season and without pre-concentration techniques (i.e. cartridges). It was hypothesized that there will be a rapid processing of sesquiterpene compounds in the atmosphere due to their high reactivity especially with ozone. Furthermore, it was also hypothesized that sesquiterpenes emissions might also be detectable at night reflecting emission patterns that are temperature and light dependant.

## 2. Methodology

### 2.1. Personal Contribution to the Project

This study was part of a joint US/Brazil research (University of Arizona and INPA, Brazilian National Institute for Amazonian research) and the education program on tropical forest functioning (Amazon PIRE, <http://www.amazonpire.org/>) and consisted of six month ecosystem-scale field study at the TT34 flux tower in central Amazonia, Brazil, spanning both the dry (started September 2010) and the wet season (finished February 2011). My contribution to the project was the supervision and maintenance of the PTR-MS (Proton Transfer Reaction Mass Spectrometer) while it was at the field site from November 1<sup>st</sup>, 2010 until February 20<sup>th</sup>, 2011. I provided the full maintenance of the instrument, providing quality check of the recorded data as well as providing the necessary weekly adjustment of software and data recording schemes.

For the purpose of this thesis, the data used was the one regarding sesquiterpenes. Even though I was not present in the first two months of measurements, the entire set of data was available to me. When handling data, iGOR software (Wavemetrics, Inc, USA) was used. In analysis of the data, I was responsible for time series analysis and profile averaging. Figures in the thesis were prepared applying software developed at Arizona University (based on iGOR) which allowed me to extract the graphs needed for the analysis of the data.

### 2.2. Study site

The study site was located in Central Amazonia, 60 km NNW of the city of Manaus, Brazil (Figure 4). The field site, called Reserva Biologica de Cueiras, has been run by INPA under the LBA (Large Scale Biosphere-Atmosphere Interactions in the Amazon) program. This site has a 40 m tower, called TT34, with coordinates, 02°35.657'S, 060°12.557'W, at 110m a.s.l. The tower footprint is considered relatively small, with typically 0.1-3 km<sup>2</sup> (Andreae et al., 2002). The vegetation in this area is considered to be undisturbed mature terra firme tropical rainforest, with a Leaf Area Index of 5-6 and an average canopy height of 30-35 m (Martin et al., 2010a). Many studies have been done to identify the tree species in the area that represent more than 48 families, with some of the most frequent species being *Eschweilera micrantha*, *Chrysophyllum sanguinolentum* and *Licania davillifolia* (Michiles and Gielow, 2008). Furthermore, despite difficulties to link BVOC emissions to Amazon forest tree species, Harley et al., 2004 found 44% of the screened taxa to emit isoprene (Harley et al., 2004). The climate at the site is characterized by large changes in precipitation, with an annual average rainfall of 2200mm but with a seasonal amplitude of  $\approx 70$  mm per month in the dry season and  $\approx 350$  mm per month in the wet season (Artaxo et al., 2006). Temperature and solar radiation remain relatively constant all year around. The dry season, from July to October, occurs when the Intertropical Convergence Zone (ITCZ) is at its northern extreme, whereas the wet season comprehends the period from November to May (Kuhn et al., 2007; Karl et al., 2007; Andreae et al., 2002).



Figure 4: Satellite map of South America showing the location of the study site with coordinates: 02°35.657'S, 060°12.557'W. Obtained from Google Maps, 2011.

### 2.3. PTR-MS

A Proton Transfer Reaction Mass Spectrometry (PTR-MS, IONICON, Austria) is an online gas analysis tool which uses low-energy chemical ionization to simultaneously monitor a range of volatile organic compounds in the air (Karl et al., 2007). It is based on protonating water molecules (primary ions;  $\text{H}_3\text{O}^+$ ) to the VOCs inserted into the instrument. This allows control in an electric field, since the compounds acquire a charge that is measurable by an ion beam. This ion beam makes it possible to separate the protonated VOCs and their fragments with respect to their mass-to-charge ratio, which is usually the molecular mass of the measured compound plus 1, its new charge. For the SQT measurements a mass to charge ( $m/z$ ) ratio of 205 (sesquiterpene- $\text{H}^+$ ) was used. This technique is very suitable since it is an online technique for ambient air measurements, giving a fast response time at a very high sensitivity (regarding compounds in low concentration) (Taipale et al., 2008). The PTR-MS does not require previous sample preparation, VOCs mixtures are simultaneously introduced into the instrument. The PTR-MS reports absolute concentrations calculated according to their reaction rate coefficients, reaction times and the ion counts rates of the primary and product ions (Ionicon, Austria). The PTR-MS can only measure compounds with proton affinities higher than water, thus air acts as a buffer, since its major component, nitrogen has a lower proton affinity. The airstream with a certain VOC concentration enters the PTR-MS through the instrument inlet and hydronium ions are formed at high density in the ion source with a hollow cathode (Figure 5). Then, the VOCs are protonated in the drift tube under the influence of an electric field, with the production of water clusters as a by-product as shown in equation 1. The protonated ions are then filtered and passed through the detector, a QMZ 422 quadruple mass spectrometer (Balzers, Switzerland) as

cps (counts per second) (Figure 5) (Kim et al., 2009; Hewitt et al., 2003; Rinne et al., 2005; Taipale et al., 2008; Maleknia et al., 2007; Lindinger and Hansel, 1997; de Gouw and Warneke, 2007). The PTR-MS used at the Amazon field site was operated at standard conditions of drift tube voltage to 600 V and the pressure of the drift tube to 2.0 mba. Optimization obtained a higher sensitivity and higher detection limit. The optimization consisted on setting the ion source voltage to 70 V, the flow rate of water to 5.0 sscm, and the pressure of the detector to  $10^5$  mbar. This optimization resulted in high primary ion ( $\text{H}_3\text{O}^+$ ) intensity ( $> 2.0 \times 10^7$  cps) with low water cluster and  $\text{O}_2^+$  formation ( $< 4\% \text{H}_3\text{O}^+$ ) (Jardine et al., submitted).

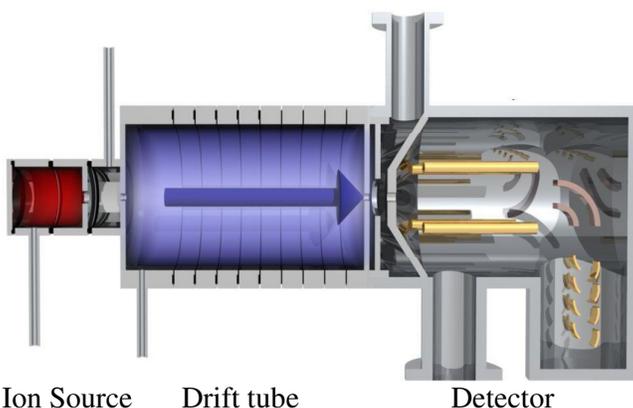


Figure 5: Diagram of the parts composing a PTR-MS as designed by Ionicon, Austria. It is composed by an ion source at the beginning of the system, following the drift tube or reaction chamber, where protonated VOC's are formed to finish with the detector, a quadruple mass spectrometer (Figure adopted from ionicon: <http://www.ptrms.com/>).

The BVOC of my concern, sesquiterpenes, were monitored during each PTR-MS measurement cycle with a dwell time of 5 seconds, in which  $\beta$ -Caryophyllene is the most abundant ion. Abundances are dependent upon collision energy in the drift tube, humidity and stereochemistry (Kim et al., 2009). Raw signals were normalized by the adjusted primary ion signal ( $\text{cps}_{21}$ ) and background subtracted from measurements of ultra-high purity nitrogen (Brazil) or zero air (Biosphere 2, Arizona) to obtain normalized counts per second (ncps, Equation 2). The adjusted primary ion signal ( $\text{cps}_{21}$ ) was obtained by measuring the signal at  $m/z$  21 ( $\text{H}_3^{18}\text{O}^+$ ) and multiplying it by the oxygen isotopic ratio of a representative natural abundance water sample ( $^{16}\text{O}/^{18}\text{O} = 500$ ).

Equation 2:  $\text{ncps} = (\text{cps}_{\text{VOC}}/\text{cps}_{21})_{\text{sample}} - (\text{cps}_{\text{VOC}}/\text{cps}_{21})_{\text{nitrogen}}$

The calibration slope (m, ppbv/ncps) for sesquiterpenes was obtained at Biosphere 2, Arizona, and in the field site using the dynamic solution injection (DSI) technique developed by (Jardine et al., 2010a). The calibration slope was  $4 \times 10^6$  ppbv/n cps at  $2.0 \times 10^7$  cps of hydronium ions, corresponding to a sensitivity of 4.93 cps/ppbv. The calibration

solution was prepared at the field site by diluting 5 microL of an authentic  $\beta$ -caryophyllene standard in 100 mL of cyclohexane. The  $\beta$ -caryophyllene solution was injected into the mixing vial at 0.5, 1.0, 2.0, and 3.0 microL/min (30 minutes each flow rate) with a constant dilution flow of 1.0 slpm ultra high purity nitrogen passing through. Sesquiterpene concentrations were calculated by multiplying the calibration slope by ncps (normalized counts per second) according to Equation 3. Furthermore, it is important to mention that  $\beta$ -caryophyllene was assumed to be one of SQT major contributor species to m/z 205+ ion counts.

Equation 3: 
$$\text{ppbv} = m \times \text{ncps}$$

#### 2.4. Experimental set up

Direct gas samples at different heights in the Amazon forest canopy were obtained through a gradient scheme based on a setup put in place during the AMAZE 2008 campaign (Karl et al., 2009). In our experiment we used six ambient air inlets at different tower heights, 2, 10.9, 16.7, 23.9, 30.3, and 39.8 m, connected to the PTR-MS (Figure 6 and 7), which were sequentially analysed for VOCs (for this study, SQT). For each inlet, 10 minutes sampling times was used, to obtain one complete canopy profile per hour. Ambient air (~0.1 m from the tower) was drawn through 1/4 inch outer diameter Teflon PFA tubing using an oil free diaphragm pump (KNF Neuberger) with a sample point to detector delay time of < 15 seconds, determined with a pulse of isoprene at the inlet. Since previous studies had shown problems with water condensation within the inlet, thus damaging the internal PTR-MS system, the tubing was heated to 50 °C by placing it in a 2 inches neoprene insulating jacket with a Teflon coated self-regulating heating tape (Omega Engineering), in order to prevent condensation and the loss of SQT to the tubing walls. In addition, an insect netting filter was placed in each inlet (created with a plastic funnel) to prevent insect and big particulate contamination. Furthermore, at the beginning of the dry season, prior to each vertical gradient ambient air measurement period (usually lasting 4-7 days), ultra high purity nitrogen was run for two hours to obtain background signals.



Figure 6: Set of pictures from the setup of the experiment. The one on the left shows the tower at approximately 17m, with the inlets made with plastic funnels on the left side of the tower. The picture in the middle shows how the tower is connected to a container, and the picture on the right shows the PTR-MS inside the container.



Figure 7: Shows the different vegetation pictures of the canopy layers (11, 17, 24, 30 and 40 m) analysed for sesquiterpene concentration.

## 2.5. Ozone

The ozone data were obtained from the LBA project in which measurements were done every 5 minutes at 40 m by thermoluminescence, with a Thermo Environment model 49i (Thermo Electron Corporation, USA) averaged every hour. For obtaining an estimate of ozone concentrations within the canopy, we assumed a similar gradient profile to that found by Karl et al. 2009 during the AMAZE 2008 campaign; we scaled the data at 40 m to match this pattern. Diurnal patterns in sesquiterpene ozonolysis rates ( $\text{molec cm}^{-3} \text{s}^{-1}$ ) at each height were calculated in the dry season using equation 4, where  $k = 1.16 \pm 0.43 \times 10^{-14} \text{ molec}^{-1} \text{ cm}^{-3} \text{ s}^{-1}$  (Shu and Atkinson, 1995) and  $[\text{O}_3]$  and  $[\text{sesquiterpenes}]$  are the hourly averaged dry season concentrations of ozone and sesquiterpenes ( $\text{molec cm}^{-3}$ ). The average ecosystem-scale sesquiterpene ozonolysis flux during the dry season was estimated by integrating the average ozonolysis rates over the height of the entire canopy, up to 40 m, using equation 4. In addition, the calculated flux was determined by layers, which the assumption of each layer being 6.7 m tall and using the Avogadro's number.

Equation 4:                   ozonolysis rates =  $k[O_3][\text{sesquiterpenes}]$

## 2.6. Data analysis

The data obtained by the PTR-MS was in count per seconds and was transformed to concentration units using the above calibrations applying iGOR software. Vertical gradients were calculated by averaging the last seven minutes of each ten minute measurement period. The rest of data was discarded due to stabilization issues. Furthermore, for the same reason, the first three hours of each measurement were also discarded, since oxygen contamination was always high at the beginning of the measurements. Average vertical gradients for daytime (10:00-16:00) and night time (22:00-4:00) were calculated for both the dry and wet season data.

## 2.7. Biosphere 2

For comparative purposes, data from Biosphere 2 was used. Biosphere 2 is a 2000 m<sup>2</sup> tropical rainforest mesocosm run by the University of Arizona. It encompasses 91 species of tropical plants under a flat-topped pyramidal glass enclosure operated in a semi-closed system. This glass avoids the entrance of UV-light therefore no oxidation takes place allowing the study the plant role in emissions. Temperature and photosynthetically active radiation (PAR) are continuously recorded. Further information on the VOC measurements taking place in this mesocosm are explained elsewhere (Jardine et al., 2010b). The data on MT, SQT, temperature and PAR was used as means of comparison with the data obtained in the Amazon to see if some differences could be observed.

### 3. Results

#### 3.1. Overall data

The data obtained in the study was extensive, spanning both the dry and the wet season and allowed for the first time the real-time observations of sesquiterpene concentration dynamics, without the use of adsorbent tubes or other long-term averaging or preconcentration techniques. Figure 8 shows the combination of all the sesquiterpene concentration data for inlets 1, 3 and 6 (selected for easier visibility) which represent the gradient from bottom to top of the canopy. The data were gathered between September 2010 and January 2011. Several gaps can be observed, which correspond to the time when other compound-ions were being measured by the PTR-MS. The range of sesquiterpene concentration observed during the whole study period varies from 0 to 0.8 ppbv, with some exceptionally high values peaking close to 1 ppbv. A small difference in average concentrations was found between values during the dry season (comprehending September, October and November) and the values from the wet season (comprehending December and January), especially towards the end of the dry season, when values were highest. Furthermore, lowest concentrations of sesquiterpenes were found at the top of the canopy, since the grey dots (inlet 6) are always at the bottom of the data points.

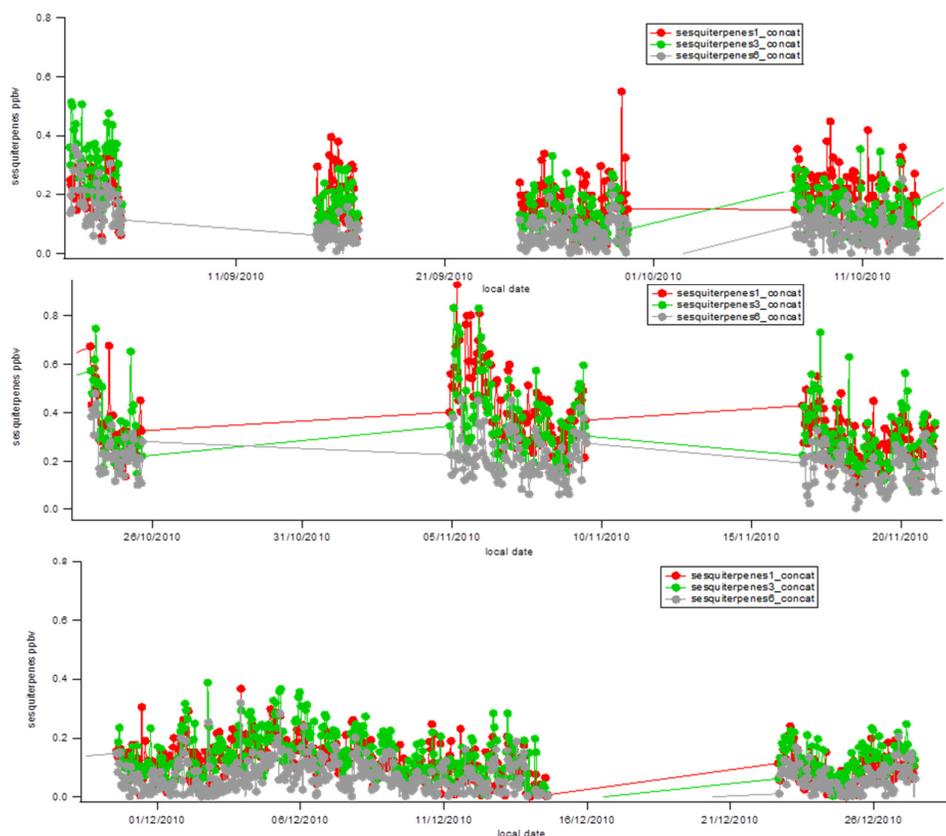


Figure 8: Sesquiterpene concentrations observed during the dry and wet season and both day and night for the six inlets. Inlet 1, at 2 m, is represented by red dots; inlet 3, at 17 m, is represented with green dots and inlet 6, at 40 m, is represented by grey dots. The x-axis shows the local time from the 2<sup>nd</sup> of September 2010 to the 27<sup>th</sup> of January 2011, separated into three different panels for easier visibility. Sesquiterpene concentration is expressed in the y-axis in ppbv.

### 3.2. Biosphere 2

The results for Biosphere 2 are courtesy of Kolby Jardine, and are included in this study in order to better understand the picture regarding SQT and MT that were observed in the Amazon. Figure 9 shows monoterpene and sesquiterpene emissions in the tropical mesocosm having strong diurnal patterns with maxima during midday. Both compounds seem to follow the same pattern as temperature and photosynthetically active radiation (PAR), peaking at 14:00pm and midday, respectively. In that pattern, MT were found to be more closely linked to the diurnal pattern of PAR with sharp maxima at 12:00 and becoming zero at night. For SQT maxima were measured later in the day, and emissions did not decline to zero during the night. It must be noted that SQT emissions are overall small compared to MT.

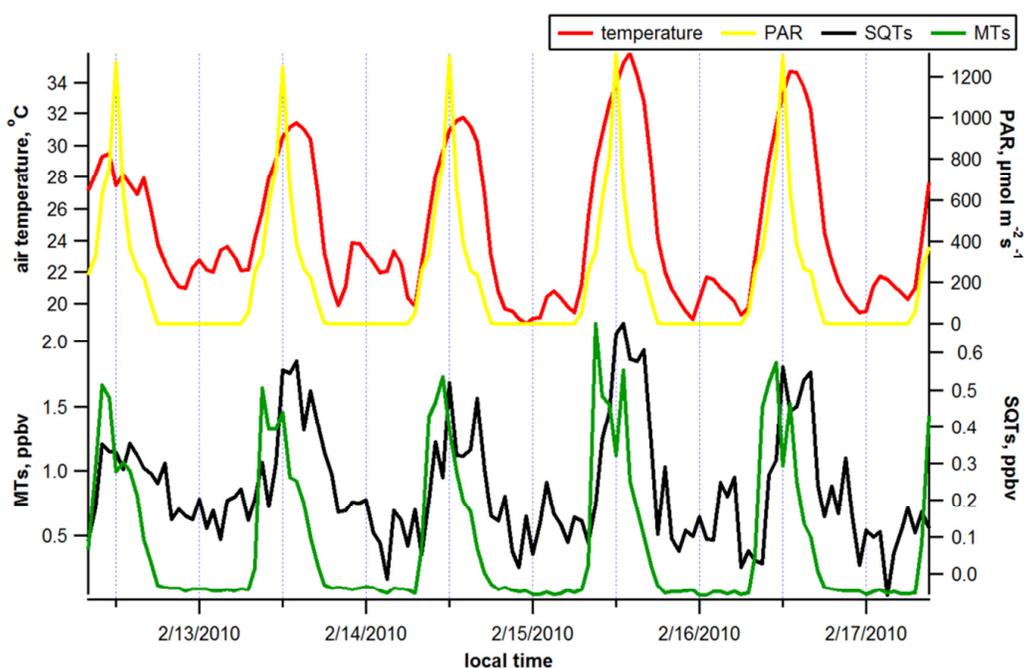


Figure 9 (courtesy of Kolby Jardine): Top panel shows the Photosynthetically Active Radiation (PAR) as the yellow line expressed in  $\mu\text{mol per m}^2$  per second and air temperature as the red line expressed in  $^{\circ}\text{C}$ . These parameters were measured at 20 m height inside the Biosphere 2 tropical mesocosm. The bottom panel shows the sesquiterpene (black line) and monoterpene (green line). The left y-axis represents MT concentrations, in ppbv and the right-y axis represents the SQT concentration also in ppbv. The x-axis represents the local time from 12 pm on the 13<sup>th</sup> of February 2010 to 12am on the 17<sup>th</sup> of February of 2010.

In order to further investigate the relationship between temperature and PAR, and MT and SQT, correlations were investigated as plotted in Figure 10. For each dataset, ambient SQT and MT concentrations were linearly regressed against ambient PAR and air temperature. Ambient SQT concentrations correlated more strongly with ambient temperature ( $R^2_{\text{temp}} = 0.56 \pm 0.09$ ) than with PAR ( $R^2_{\text{PAR}} = 0.43 \pm 0.07$ ), (t-test,  $\alpha = 0.05$ ,  $R^2_{\text{temp}} \neq R^2_{\text{PAR}}$ ). In contrast, ambient MT concentrations correlated more strongly with PAR ( $R^2_{\text{PAR}} = 0.69 \pm 0.07$ ), than with ambient temperature ( $R^2_{\text{temp}} = 0.60 \pm 0.08$ ), (t-test,  $\alpha = 0.05$ ,  $R^2_{\text{temp}} \neq R^2_{\text{PAR}}$ ). This suggests that monoterpenes are more affected by

light, and SQT are more affected by temperature, related perhaps to their difference in biosynthetic pathway and/or whether or not the compounds are emitted from storage.

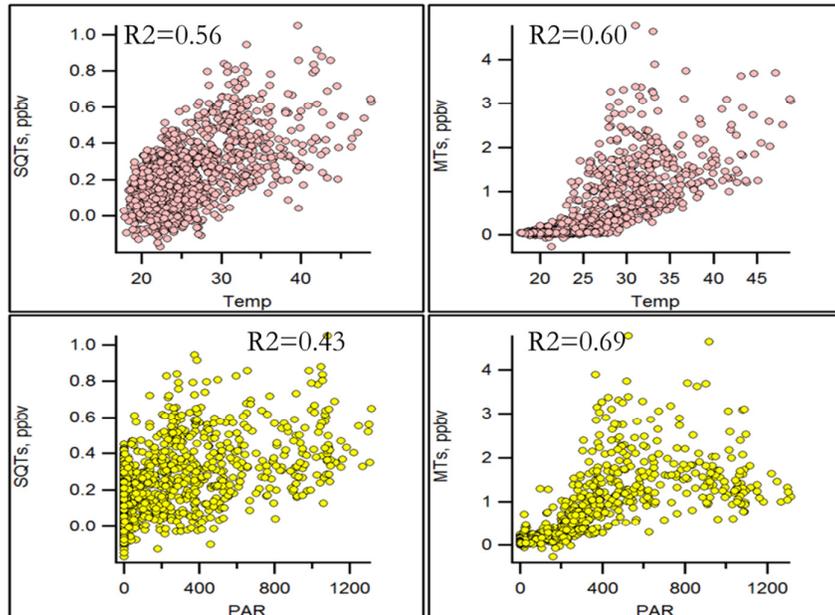


Figure 10 (courtesy of Kolby Jardine): Correlation of SQT (left column) and MT (right column) for temperature (top) and photosynthetically active radiation, PAR (bottom). R square values are shown at the top of each individual graph. PAR is expressed in  $\mu\text{mol per m}^2 \text{ per second}$  and temperature in  $^{\circ}\text{C}$ . Both MT and SQT are expressed in ppbv.

### 3.3. The Amazon Rainforest

#### 3.3.1. Time series

When zooming into a few days of the entire data series (see Figure 8), taken from the inlet at 17 m (half way into the canopy, as the average profile height), it can be seen how sesquiterpene concentration peaks at night (Figure 11). By contrast, concentration of monoterpenes peaked at noon, when light limitation was at its minimum; MT concentration was lowest (close to zero) during the night. Moreover, in the Amazon rainforest, the monoterpene concentrations throughout the day followed the same diurnal pattern as seen in the Biosphere 2 data, whereas quite a different picture emerged for SQT. Since SQT emissions have in principle similar controlling environmental variables than MT, such as temperature and light (which are also known to co-vary), the observed differences between monoterpenes and SQT were unexpected.

A proposed rapid oxidation of SQT by ozone provided the basis to compare sesquiterpene concentration data with ozone concentration data taken at inlet 6. Interestingly, ozone was found to be inversely related to sesquiterpene concentration (Figure 11), such that the sesquiterpenes concentration-peak at night, coincided with ozone concentrations being at their lowest (higher concentrations of ozone during the day were possibly due to enhanced photochemical formation) and vice versa. Figure 11 represents 4 days of data, but a similar pattern was seen throughout the whole measurement period. This suggested a very strong relationship between ozone and sesquiterpenes which was further investigated.

## Within-canopy sesquiterpene ozonolysis in Amazonia

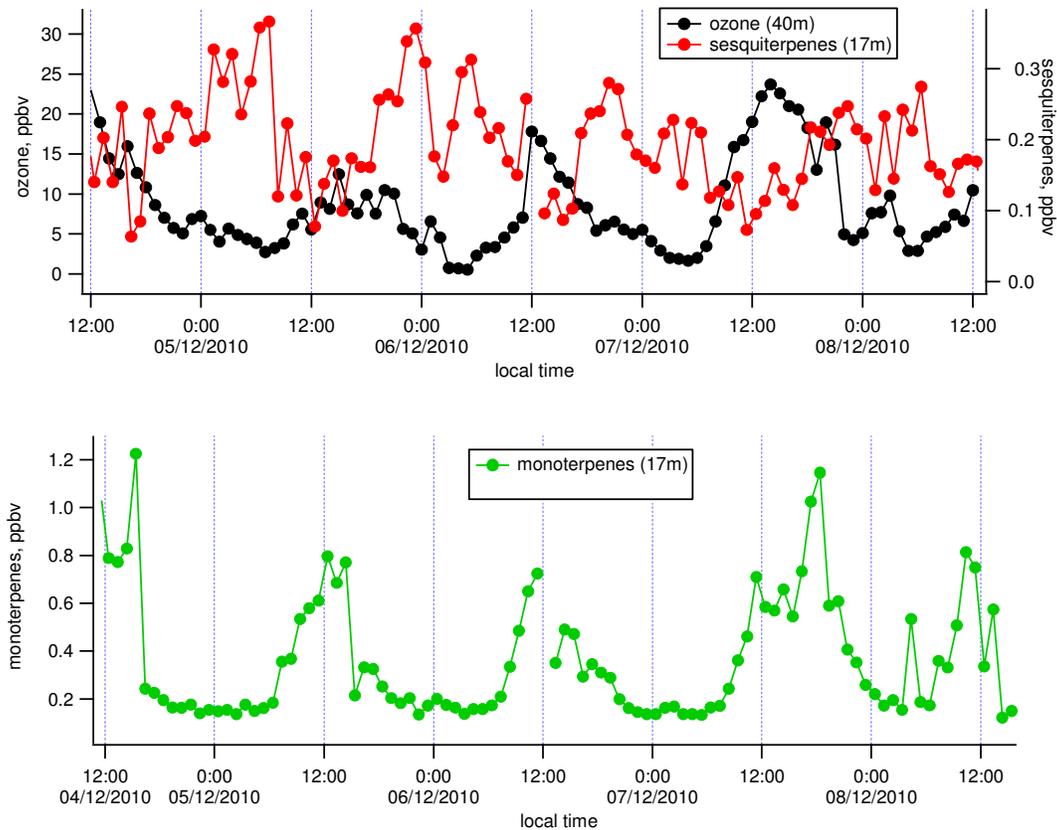


Figure 11: Top panel shows the inverse relationship between sesquiterpene concentration and ozone concentration. Sesquiterpene concentration at 17 m is represented by the red lines and markers (each marker represent actual time of measurement, once each hour) whereas the ozone concentration is represented by the black line and markers (each marker represents actual time of measurements coinciding with the sesquiterpene measurements). Both ozone (in the left y-axis) and sesquiterpenes (in the right y-axis) are expressed in ppbv but note the difference in axis-. The bottom panel shows the diurnal pattern for monoterpenes at 17m (green line and markers). They-axis represents monoterpenes concentration in ppbv with concentrations varying from 0-1.2 ppbv. Both x-axis for the top and the bottom graph represent the local time which spans from 12pm 4/12/2010 to 12pm 8/12/2010.

### 3.3.2. Average profiles

Figure 12 shows the averages vertical concentration profiles for the different seasons, one for the dry season (September-November) and another for the wet season (December-January), separated by daytime and night-time. The data show higher concentrations of both isoprenoids during the dry season, likely due to a strong dependence of emissions rates on light and temperature, since during the wet season, temperature and specially PAR is reduced with respect to the dry season. Furthermore, for the average profiles, again a diurnal difference emerges, with monoterpenes having higher concentrations during daytime hours (10:00-16:00), being the opposite case for sesquiterpenes, with higher concentrations at night.

While concentrations of monoterpenes peaked at 17 m, surprisingly, sesquiterpene concentrations peaked near the ground at 2 m, although they were also clearly elevated at 17 m. Monoterpene concentrations followed an almost straight vertical pattern in the canopy layers above peak-concentration height, however in the case of sesquiterpenes, concentrations decreased notably towards the top of the canopy. This suggested that

**Within-canopy sesquiterpene ozonolysis in Amazonia**

sesquiterpenes were getting lost at the top of the canopy, possibly due to rapid ozonolysis reactions.

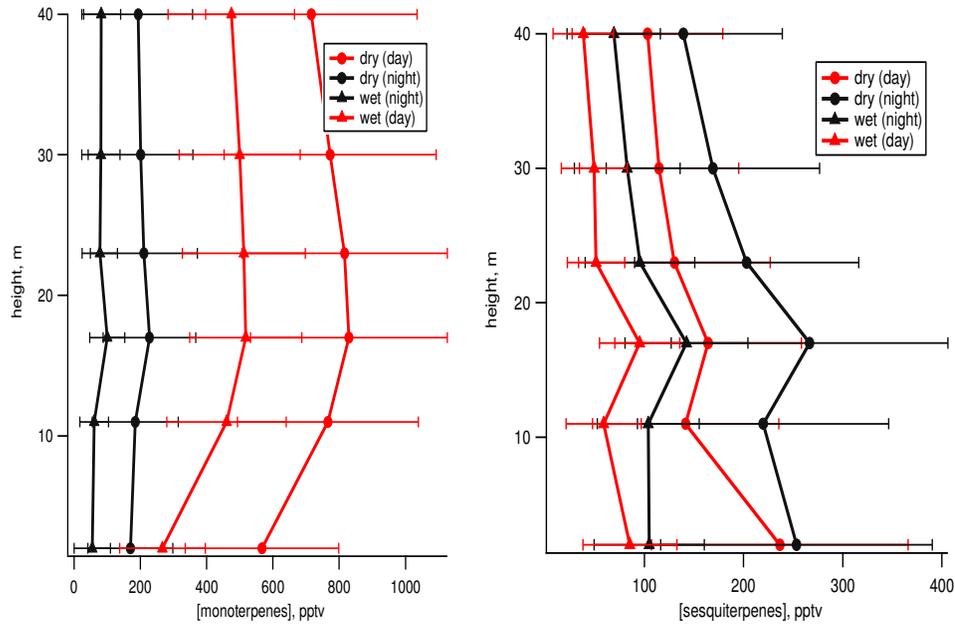


Figure 12: Average dry (dots) and wet (triangles) concentration profiles through 40 m height for monoterpenes (left panel) and sesquiterpenes (right panel). Red line and markers represents average profiles during the day and black line and markers represent the night average profiles. Both monoterpenes concentration and sesquiterpene concentration are expressed in pptv. The height of the profile on the y-axis is expressed in meters, with vegetation canopy reaching up to 30 m. Error bars, in terms of standard deviation, are shown for every average height concentration.

The ozone profile concentration was compared to the sesquiterpene profile concentration (see Figure 13). During the dry season, the average vertical profile of sesquiterpene concentrations was inversely related to that of ozone. While ozone concentrations decreased with decreasing height within the canopy, sesquiterpene concentrations increased, showing two types of inverse relationships for ozone and SQT both in time and in space.

**Within-canopy sesquiterpene ozonolysis in Amazonia**

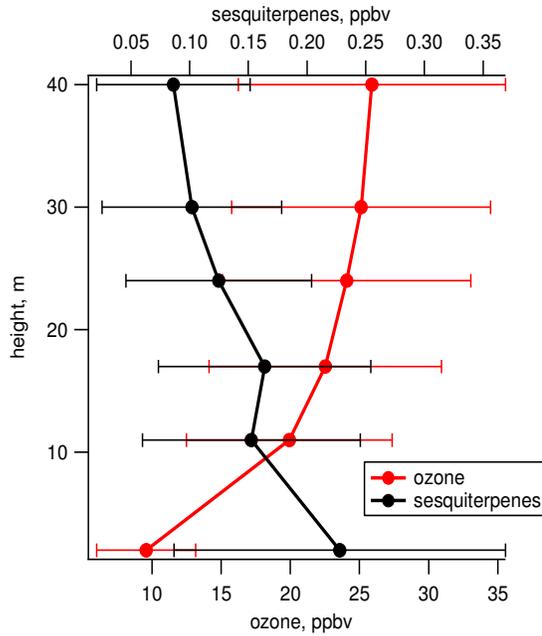


Figure 13: Graph showing the average diurnal profile concentrations during the dry season for ozone (red line and markers) and the average profile sesquiterpene concentrations during night (black line and markers). Ozone is represented in the bottom x-axis is expressed in ppbv, whereas sesquiterpene concentration is represented in the top x-axis and also expressed in ppbv. Height is represented in the y-axis and is expressed in meters. Error bars for both ozone and sesquiterpene concentrations are shown for each average measurement in height.

3.3.3. Ozonolysis

To further analyse the behaviour of sesquiterpenes and ozone within canopy I tested for the inverse relationship of ozone (at 40 m) with sesquiterpenes (average concentration for each height) (Figure 14). Except for the lowest measurement levels (2m), ambient concentrations at all heights decreased substantially during the day, with minima around 12:00 local time, and increase during the afternoon. These observations strongly suggest that within canopy sesquiterpene ozonolysis reactions in the dry season are chief modulators of the vertical concentration distribution, driving maximum concentration of SQT to ground level, where O<sub>3</sub> concentration was at its lowest.

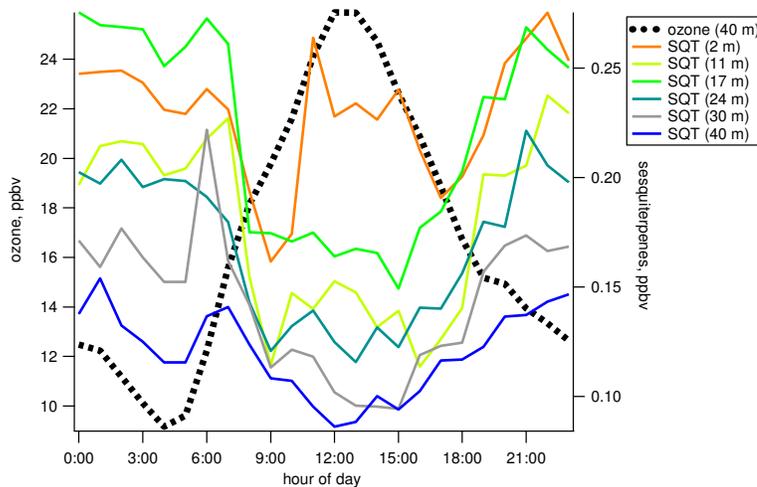


Figure 14: Graph showing a time series plot of the inverse relationship between dry-season average sesquiterpene concentrations at each height throughout the canopy and ozone concentration at 40 m. Sesquiterpene concentrations at 2 m height is represented by the orange line, at 11 m height by the pistachio line, at 17 m by the light green line, at 24 m by the turquois line, at 30 m by the grey line and at 40 m by the dark blue line. Ozone concentration at 40 m is represented by the thick black dotted line. Ozone concentration is expressed in ppbv and represented in the left y-axis with a range of 10-25 ppbv, and the sesquiterpene concentrations are expressed in ppbv with a range of 0.1-0.3 ppbv on the right y-axis. The x-axis represents the hour of the day of the diurnal average concentrations.

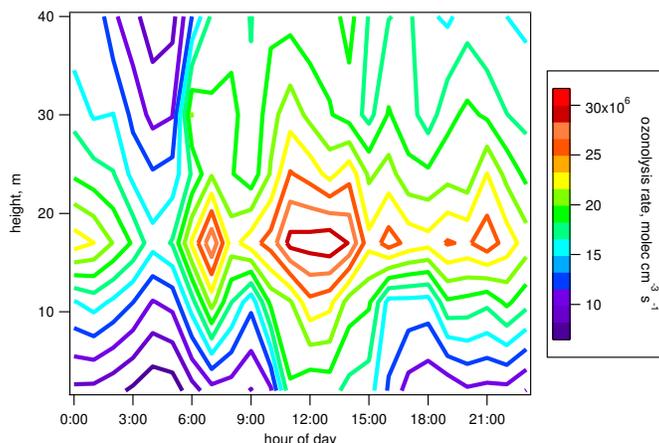


Figure 15: Contour plot of the average diurnal pattern of calculated sesquiterpene ozonolysis rates during the dry season throughout the canopy. Ozonolysis is shown at each height, represented by the y-axis and expressed in meters in an average day, represented in the x-axis and expressed in hours. The ozonolysis rate is expressed in  $\text{cm}^3$  per second ranging from 0 to  $30 \times 10^6 \text{ cm}^3/\text{s}$ , with colors from red shades at highest ozonolysis rates to green shades (medium ozonolysis rates) to blue shades being the lowest ozonolysis rates.

When the average dry season sesquiterpene ozonolysis rates at each height were estimated from the average diurnal ozone and sesquiterpene concentrations, using the ozonolysis reaction rate constant from  $\beta$ -Caryophyllene, a strong diurnal pattern emerged (Figure 15). Despite low ambient sesquiterpene concentrations during midday, maximum reaction rates (up to  $3 \times 10^7 \text{ cm}^3/\text{s}$ ) occur during the day at 17 m height within the canopy. Therefore, due to the roughly two orders of magnitude higher ambient ozone concentrations than those of sesquiterpenes, the diurnal pattern in ozone concentration seems to determine the pattern of sesquiterpene ozonolysis rate (maximum during the day not the night). Furthermore, the estimated mean daytime SQT ozonolysis rate integrated throughout the 40 m height was calculated by adding up all the ozonolysis at each height, giving a value of  $-1.1 \text{ mg}/\text{m}^2/\text{h}$ .

### 3.3.4. Pseudo-quantitative fluxes

To further investigate the source/sink behaviour, a qualitative analysis of the fluxes of monoterpenes and sesquiterpenes were obtained using an inverse Lagrangian transport model (Raupach, 1989) (Figure 16). Since model inputs, including profiles of the standard deviation of the vertical wind speed ( $\sigma_w$ ) divided by the friction velocity ( $u^*$ ), were obtained from AMAZE campaign at the TT34 tower in 2008 (Karl et al., 2009), VOC flux estimates (in  $\text{mg m}^{-2} \text{ hr}^{-1}$ ) are therefore can only be considered pseudo-quantitative. In these fluxes it can be seen how net emissions of sesquiterpenes dramatically decline from 25 m height as they go up the canopy, whereas monoterpenes remained strong after the start of emissions from 15 m height. For the SQT flux the

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estimated integrated canopy-scale emissions rates was also calculated, yielding a value of  $0.7 \text{ mg/m}^2/\text{h}$ , by adding all fluxes together (Figure 16 left panel).

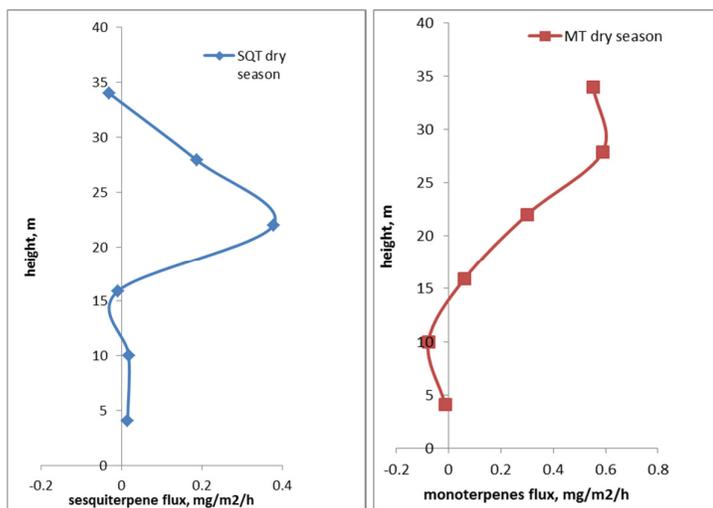


Figure 16: Graphs showing the estimated dry season fluxes through 30 m canopy. The left panel represents sesquiterpene flux, in blue, and the right panel represents the monoterpenes flux, in maroon. Fluxes are expressed in mg per meter square per hour all in the x-axis and the height in the y-axis is expressed in m.

## 4. Discussion

### 4.1. Relevance of this study

Even though monoterpene concentrations have been widely quantified in different ecosystems (Jordan et al., 2009; Karl et al., 2002; Filella and Penuelas, 2006; Baker et al., 2005; Karl et al., 2009; Baraldi et al., 2004), studies of within and above canopy sesquiterpene concentrations (and inferred fluxes) are scarce to-date due to experimental difficulties dealing with high reactivity and sampling losses of SQT (Kim et al., 2009; Boy et al., 2008; Bouvier-Brown et al., 2009a). The implications of this study are several. First, due to an optimized PTR-MS which lead to high primary ion intensity, low water clusters and low  $O_2^+$  contamination, we were able to measure SQT's low concentrations. Furthermore, the heated Teflon sampling lines minimised SQT loss to tubing walls. In addition, the fact that the Amazon has relatively low ozone concentration (<40 ppbv) aids the atmospheric quantifications since SQT were not so rapidly oxidised compared to more polluted environments. Additionally, the meteorological conditions in tropical locations such as high UV light, temperature and air humidity (SQT are more heavily emitted at higher humidity) stimulate high emissions, along with high biomass increasing the amount of BVOC emitted (Duhl et al., 2008; Kuhn et al., 2010).

### 4.2. Divergence between MT and SQT

#### 4.2.1. Temperature and light dependence

Previous work has shown that MT and SQT emissions correlate with each other at leaf and branch level (Ormeno et al., 2007a). In addition, the results from Biosphere 2, also indicate such correlation to exist, based on the relatively similar diurnal patterns of emissions, although MT are more strongly correlated with light whereas SQT are mainly correlated with temperature. This divergence in correlations could be done to the difference in biosynthetic pathway of both isoprenoids. Whereas SQT are synthesized in the cytosol (via MVA pathway), MT are synthesized in the plastids (Kesselmeier and Staudt, 1999; Ormeno et al., 2007b), nevertheless, this is a matter of crosstalk since MVA pathway also requires metabolites that are derived from photosynthesis. Moreover, a strong temperature dependence of emissions usually also relates to an emission from storage pools (often found for MT emissions from conifers), while a strong light dependence indicates emission directly after production (found for isoprene, and frequently for MT from broadleaved trees). In the Amazon, as temperature and light co-vary during the day, both MT and SQT concentrations were expected to be higher during the day due to their emissions (Vickers et al., 2009; Duhl et al., 2008). Nevertheless, there was a distinct pattern in the Amazon, where SQT diurnal concentration differed notably from MT concentrations.

The high SQT concentration at night as compared to MT could at least to some degree be related to differences in their biosynthetic pathways. In the absence of sunlight, MT emissions decline to zero due to the lack of photosynthesis, since MT biosynthesis is controlled upon recently photosynthesized carbon. By contrast, SQT emissions could occur at night, since SQT biosynthesis is not so strongly dependent on recently

photosynthesized carbon. Still, emission rates are expected to be lower than during the day, due to lower night-time temperatures.

Differences in leaf production and emission patterns are however only one factor to be considered. Concentration of compounds (if produced day and night, and without substantial chemical destruction) would be lower at daytime than at night due to greatly reduced night-time vertical mixing (Campbell and Norman, 1998; Vilà-Guerau de Arellano et al., 2011). Boundary layer effects would not affect diurnal monoterpene concentration patterns, because of the light inhibition of emissions at night which would also indicate that at the Amazon rainforest site, MT emission does not occur from storage. This is likely not the case of SQT where the concentration built-up at night reflects possibly a continued production, emission from storage, slow atmospheric break-down, as well micrometeorological conditions that determine atmospheric stability and boundary layer height.

#### 4.2.2. SQT ozone sensitivity and escape efficiency

Differences between storage pools and emission patterns of SQT and MT from Amazonian plants are to-date not well studied, and their importance for the observed patterns remains unclear. Furthermore, it does not explain the very high concentrations of SQT that were observed at the lowest measurement level (highest emissions of SQT could be expected to occur around 17 m, where the shaded and non-shaded canopy meet -mimicking the MT average profile-, or else it would have been expected to find similar higher concentration at the ground for MT). In fact, the most plausible possibility for the divergence of MT and SQT appears to be the high sensitivity of SQT towards ozone. The two inverse relationships found between ozone and SQT, both in time and space, suggest that SQT concentrations are determined mainly by its atmospheric sink: ozone. Rapid SQT oxidation by ozone is supported by the reaction rate constants of OH and NO<sub>x</sub> in comparison with the reaction rate constant of ozone. For OH the reaction rate constant with  $\beta$ -Caryophyllene is  $2.0 \times 10^{-10}$  molec/cm<sup>3</sup>/s, cm whereas the NO<sub>x</sub> reaction rate constant with the same compounds is  $2.2 \times 10^{-11}$ . In contrast the reaction rate constant for ozonolysis,  $1.16 \times 10^{-14}$ , is some orders of magnitude lower, and gives a faster reaction rate than any of the other oxidants (Bouvier-Brown et al., 2009b). Furthermore sesquiterpenes are around 100-times more reactive with ozone than monoterpenes (Kurpius and Goldstein, 2003; Bonn and Moortgat, 2003), providing yet another possible indication of rapid reactions depleting sesquiterpenes at the top of the canopy due  $\beta$ -Caryophyllene double bond reactivity (Winterhalter et al., 2009).

Possibly, sesquiterpene are being preferentially oxidized at the top of the canopy and less at the bottom, since ozone deposition fluxes decline when reaching the lower parts of the canopy due to previous consumption. The high concentration at 17 m could suggest highest plant emissions there; especially during daylight hours since the 17 m inlet coincided with the sunlight subcanopy (see Figure 7). Whole daytime (10:00-16:00) canopy integrated sesquiterpene emission flux (SQT emitted:  $0.7 \text{ mg}_{\text{SQT}}/\text{m}^2/\text{hr}$ ), as estimated using the inverse transport model, was less than the estimated whole canopy integrated sesquiterpene ozonolysis flux (SQT oxidized normal ozone depletion:  $-1.1 \text{ mg}_{\text{SQT}}/\text{m}^2/\text{hr}$ ); a more extreme case of ozone depletion through ozonolysis would yield a rate of  $-0.6 \text{ mg}_{\text{SQT}}/\text{m}^2/\text{hr}$  (SQT oxidized extreme ozone depletion). The escape efficiency refers to the percentage of SQT which are able to reach the above-canopy atmosphere. With these values it was possible to give a rough estimate of the SQT

canopy escape efficiency of 39-54% leading to 46-61% of SQT oxidized within the canopy. The way in which this was calculated was by adding together what it was emitted and oxidized, and then dividing the emission (SQT emitted:  $0.7 \text{ mg}_{\text{SQT}}/\text{m}^2/\text{hr}$ ) by the total emitted and oxidized ( $1.8 \text{ mg}_{\text{SQT}}/\text{m}^2/\text{hr}$ , for the normal ozone deposition case) to get the percentage of SQTs that has not escape outside the canopy. This estimate is comparable to the modelling estimates in a hardwood forest in the US for the summer time, of 30% SQT escape efficiency (Stroud et al., 2005). Although our ecosystem scale sesquiterpene emission flux is only a rough estimate due to uncertainty in the turbulence parameters used in the inverse transport model, these results could provide the first demonstration that a large fraction of sesquiterpene emitted into atmospheres can be rapidly oxidized within canopy due to ozonolysis.

#### 4.3. Ozone deposition

Even though our measurements allow first and foremost a qualitative analysis, a further discussion about the interactions of  $\text{O}_3$  flux and SQT emissions might be attempted. In the scientific community it was generally accepted that total ozone deposition is dominated by stomatal uptake, even though, recently, mid-latitude studies show ozone deposition is actually due to gas-phase chemistry (Fowler et al., 2001; Kurpius and Goldstein, 2003; Mikkelsen et al., 2000) which could be leading to high yields of SOA nucleation and growth (O'Dowd et al., 2002) and OH production (Paulson et al., 1999).

Nevertheless, the study of Rummel et al., 2007 in southwest Amazonia showed the opposite behaviour (dominated by stomatal deposition), with an ozone deposition flux of  $-6.6$  to  $-10.9 \text{ nmol}_{\text{O}_3}/\text{m}^2/\text{s}$  which was supported by enclosure studies on Amazonian plants which also indicated dominance of stomatal uptake (Rummel et al., 2007; Gut et al., 2002). By using the deposition velocity used by Rummel et al., 2007 we calculated the ozone deposition flux. The rates increased notably ( $-5.4$  to  $-10.8 \text{ nmol}_{\text{O}_3}/\text{m}^2/\text{s}$ , in agreement with Rummel's finding) compared to the ozone deposition inferred from the integrated ozonolysis ( $-0.6$  to  $-1.5 \text{ nmol}_{\text{O}_3}/\text{m}^2/\text{s}$ ). By subtracting the general ozone deposition flux, with the ozone deposition flux only from ozonolysis, we found 7-28 % of net deposition only due to ozonolysis. If this is true and decomposition of ozone is taking place by volatiles such as ozone, a great burden of ozone damaging pressure could be taken out of plants, since it would imply not so much stomatal uptake.

#### 4.4. SQT antioxidant role

Recent studies suggested that monoterpenes and sesquiterpenes can act as endogenous antioxidants within plants in order to reduce the oxidative damage of stress caused by the accumulation of ROS (reactive oxygen species) (Vickers et al., 2009; Duhl et al., 2008). Whereas no evidence has been shown for SQT to date, MT have been proven to aid protecting photosynthesis against high temperature or high ozone concentrations (Delfino et al., 2000; Loreto et al., 1998; Loreto and Fares, 2007). At our forest site, SQT were rapidly oxidized by ozone within the canopy, before  $\text{O}_3$  reached the leaf surface, creating a gas-phase chemistry ozone sink. This could potentially significantly reduce the amount of ozone taken up by plants, reducing the oxidative damage, which could be of especial importance in the Amazon due to the increasing annual average ambient ozone concentration, which has risen from 12 ppbv in 1987 to 40 ppbv in 2010 (Kirchhoff et al., 1990). This is of especial importance since it has been found that long-

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term exposure of Amazonian plant species to more than 50 ppbv can cause permanent plant damage (Rummel et al., 2007).

## 4.5. Possible SQT Feedback mechanisms in the climate system

Due to the interactions, effects and controls in SQT, a number of emission-climate feedbacks can be postulated. Emissions are affected by biotic and abiotic environmental drivers on local, regional and global scales. Although it is still difficult to quantify the atmospheric interactions and feedbacks due to the high reactivity of SQT, and due to uncertain process-understanding on SQT emissions, several feedback mechanisms are proposed in figure 17, adopted from Pacifico et al. (2009). These mechanisms are combined in the Figure but it is important to note that scales may vary in time and space. In particular, regional changes may or may not feed back to the global climate system.

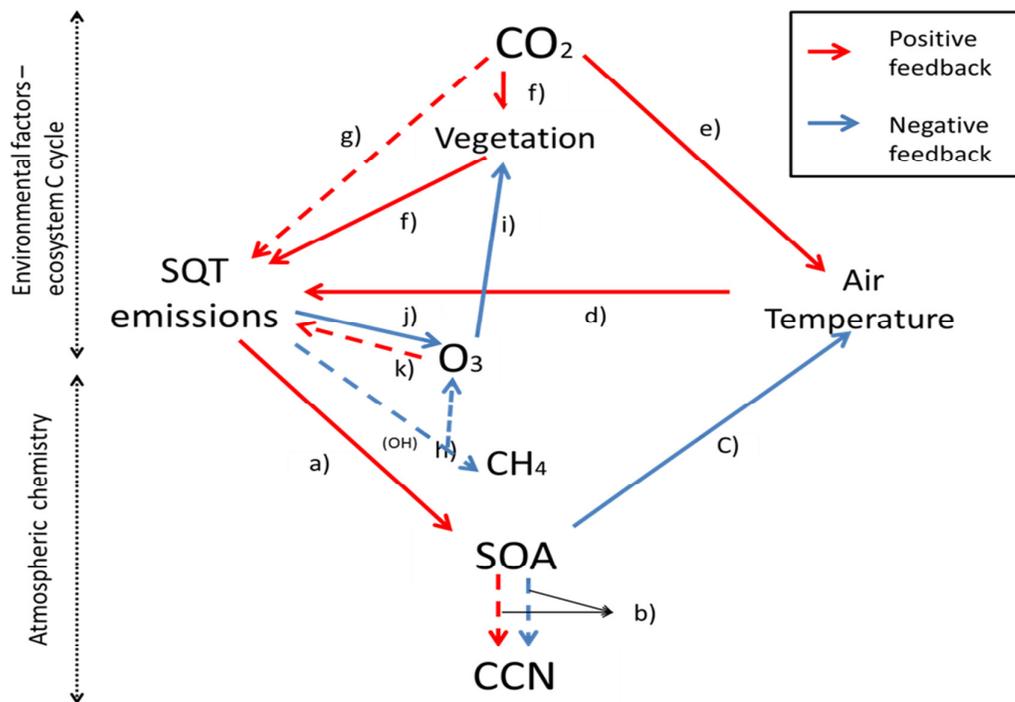


Figure 17: Schematic diagram showing the possible feedback mechanisms related to SQT emissions. This figure is adopted from Pacifico et al., 2009, who focussed on emissions and role of isoprene emissions. Their diagram has been modified for the possible feedback mechanisms including SQT. Feedbacks are separated into negative (blue arrows) and positive (red arrows), for instance, warmer air temperature leads to higher SQT emissions, which may bring SOA up, which has a cooling effect on air temperature (negative feedback). Another example is how higher CO<sub>2</sub> concentration leads to higher biomass which leads to more SQT emissions. Letters are given to each impact, and related feedbacks for later explanation. The dashed red arrow from ozone to sesquiterpene emissions is a hypothesized mechanisms exposed in the study by the very first time, thus still very doubtful of veracity of such mechanism. Furthermore, the blue dashed arrow between SQT emissions and methane is also not proven yet, so it is expressed as a hypothesis. The bottom part of the diagram represents the atmospheric chemistry and the upper part of the diagram represents the environmental factors and ecosystem carbon cycle.

When SQT react with ozone, the condensable vapours formed may be critical for formation and growth of new aerosols in the atmosphere; with secondary aerosols yields

of up to 100% from SQT their effect on SOA formation is considered much more important than from monoterpenes (Bonn and Moortgat, 2003; Ormeno et al., 2007a) (although numbers vary among literature (VanReken et al., 2006)). These high yields are due to the low volatility of SQT and their oxidation products with respect to other VOCs, having a significant heterogeneous nucleation, thus efficiently condensing into pre-existing aerosol loading, or forming new particles (Boy et al., 2008; Winterhalter et al., 2009; Zhao et al., 2010). This provides a positive feedback (a) in a global and regional scale, as the higher the SQT emissions, the more SOA are likely to be produced. Furthermore, when grown to size classes above ca. 50nm, SOA can act as cloud condensation nuclei (CCN), hence organic aerosols link components of the carbon and water cycles (Kulmala et al., 2004). For instance, ozonolysis of SQT (in a scenario with high ozone, thus high VOC concentration) can lead to high aerosol concentration environment and possibly, the cloud droplets formed won't be able generate high rain efficiency clouds; whereas if the CCN were formed in a low aerosol concentration environment, such cloud droplets will create clouds with higher rain efficiency (Rizzo, 2006; Artaxo et al., 2006; Kuhn et al., 2010). This could be supported by the finding that SQT emissions cease when there is drought, and this could be due to the fact that SQT may contribute negatively to precipitation anomalies at local scale (Ormeno et al., 2007b). Nevertheless, since this is highly unknown so it is difficult to say if it represents a positive or a negative feedback (b).

Although interactions between BVOC emissions and the formation of CCN act mostly on the regional scale, the radiation effect of SOA could be considered as a global scale feedback. Unless washed-out in precipitation, aerosol particles are transported over thousands of km over few days and changes in regional SOA burdens could possibly contribute to global changes in radiation. The direct effect of aerosols is the scattering or absorption of light. The aerosols formed from SQT oxidation can reflect UV radiation, and therefore can lead to less radiation reaching the earth surface creating a cooling effect. This feedback, is then considered negative, since the more SOA, the less warmer the air temperature (c) (Arneeth et al., 2009). Nevertheless, there are certain aerosols such the black carbon (biomass-burning particles are heavily enriched by black carbon) (Decesari et al., 2006) in which SQT could condense too, changing its optical properties (Kesselmeier et al., 2009).

Emissions of sesquiterpenes are also affected by air temperature at a plant scale. Raising temperature affects the vapour pressure at which sesquiterpenes are held within the plant storage pools (d), with a significant possibility of increasing emissions in a warmer climate (Helmig et al., 2006; Helmig et al., 2007; Duhl et al., 2008). Furthermore, atmospheric water vapour is also found to anticorrelate with the intensity of SQT condensable vapours nucleation's, reducing the formation of SOZ due to competitive reactions, thus, decreasing SOA formation (Bonn and Moortgat, 2003). On the other hand, in an ecosystem, temperature can affect SQT emissions indirectly, as climate feedbacks that go via ecology, by warming the region enhancing insects' outbreaks, in which as a defence mechanism plants will emit more sesquiterpenes, leading again to an indirect positive feedback at the regional scale. Nevertheless, even for regions that have experienced large insects outbreaks, such as certain parts of the boreal forests, it has not been possible to quantify any climatic effect, if any, such as the production of more SOA, due to enhanced emissions of SQT (Haapanala et al., 2009; Staudt and Lhoutellier, 2007).

Warmer temperatures leading to higher SQT emissions is one of the interactions related to increasing atmospheric CO<sub>2</sub> concentrations and their greenhouse effect (e). But CO<sub>2</sub> burdens in the atmosphere can act on SQT emissions in other ways as well. A positive effect relates to plant CO<sub>2</sub> fertilization (f), in which the more carbon available will lead to higher plant biomass, and larger emissions from the higher leaf area index. With a fertilization effect, there could also be an excess of photosynthetic material which can be used for the production of more BVOCs, therefore, in this case it could be said that more CO<sub>2</sub>, the more SQT emissions, due to more PEP available for SQT biosynthesis (Kulmala et al., 2004; Kesselmeier et al., 2002b). This could be considered a global scale process, since it is related to vegetation overall, but it needs to be further demonstrated by leaf-scale experiments (Penuelas and Staudt, 2010). Whether or not there is a direct effect of CO<sub>2</sub> on SQT leaf production (g), as found for isoprene (Possell et al., 2005; Rosenstiel et al., 2003; Arneth et al., 2007), and possibly also monoterpenes awaits further study.

In addition, methane lifetime can also be considered an important factor affecting climate at a global scale, which indirectly could be affected by SQT emissions. Most BVOCs are oxidized by OH, reducing the global OH concentration in the atmosphere, which is produced by the photolysis of ozone (Laothawornkitkul et al., 2009). Subsequently, if BVOC emissions are assumed to alter/increase drastically, methane lifetime can increase by several months, since it cannot be dissociated to methyl radical and water due to lack of OH (Poisson et al., 2000). However, for the case of SQT (h), the feedback could be opposite than that for isoprene or monoterpenes. Whereas isoprene and monoterpenes increase methane lifetime by consuming OH, SQT are mainly oxidized by ozone having OH as a by-product (Hakola et al., 2006; Kurpius and Goldstein, 2003), and although Winterhalter et al. (2009) states this can be regarded as a minor source to the OH radicals in the atmosphere, in a regional scale, methane could be oxidized much more readily possibly having significant impacts on the measurements of OH missing reactivity in forest (Pacífico et al., 2009; Poisson et al., 2000; Winterhalter et al., 2009; Bouvier-Brown et al., 2009b; Holzke et al., 2006; Goldstein et al., 2004).

As a last climate-relevant process, ozone has a major role in these feedback mechanisms. Vegetation is affected by ozone, since acute tropospheric ozone exposure damages plant leaf tissues creating a negative feedback (i), in which the more ozone, the less vegetation there is, due to death of plant tissue and reduced productivity (Sitch et al., 2007). As explained above, SQT are heavily oxidized by ozone, thereby reducing the concentration of ozone when more SQT are available (j). This could be considered a negative feedback at a local scale, since if SQT are emitted, the ozone concentration within canopy and just above the canopy will be reduced. Nevertheless, here I propose a new mechanism which could compromise this negative feedback. As proposed by Jardine et al., (submitted manuscript) and Vickers et al. (2009), oxidation products of isoprene could be produced within plant as a mean of endogenous protections, acting as a quenching agent of reactive oxygen species and membrane strengthening (Vickers et al., 2009; Jardine et al., submitted; Affek and Yakir, 2002). What I here propose is the possibility of sesquiterpenes acting as exogenous protection outside the plant. So if ozone starts to inflict plant tissue damage, SQT might be emitted as a wounding signalling response, emitted to the canopy helping reduce ozone concentration before entering the leaf. In this case a feedback can be postulated (k), in which higher concentration of ozone could inflict more SQT emissions, in turn reducing O<sub>3</sub> canopy

levels. Nevertheless, this is just a hypothesis and further studies are needed to support this idea.

#### 4.6. Limitations

Measurements in remote locations of highly reactive chemical species are fraught with difficulties. In terms of the experiment set up, a gradient scheme of such complexity and measurements over a relatively long period are hard to maintain. Small leaks were found in the isolation of the Teflon lines, and even though small cuts were made at the bottom of the isolation lines before entering the container in order to avoid water coming inside the PTR-MS system, new techniques should be developed to reduce these risks (Karl et al., 2004). Furthermore, within the PTR-MS setting, an increased dwell time for SQT is advisable for higher accuracy in measuring at low concentrations. This would be of striking importance especially if sensitivity is being reduced due to higher contamination of oxygen ions in the ion source and water cluster contamination in the drift tube. Furthermore, a very big limitation of PTR-MS is the lack of compounds speciation, only measuring mass to charge ratios. Therefore, for further studies it is suggested to couple a GC after the mass spectrometer to chemically identify the species in question for such mass to charge ions (Christian et al., 2004), since  $\beta$ -Caryophyllene was assumed to be the major contributor to  $205^+$  m/z (Kim et al., 2009).

Moreover, some plant species identification should be carried, in order to acknowledge specific emissions and how they interact in canopy height, such as understory growing in shaded environments, to further corroborate the behaviour of SQT governed by the sink (Kim et al., 2009). In addition, for future studies in which seasonality is further studied, it is important to look at the deforestation of the Amazon, and future modelling trends, since for sure it will be affecting the behaviour of not only SQT emissions but any other BVOC emitted by plants in that region, and the effect of burning biomass in the aerosol loading of the regional Amazonian atmosphere.



## 5. *Conclusion*

In conclusion, this thesis presents observed real-time sesquiterpenes dynamics within canopy obtained over dry and wet-season conditions in the Amazon rainforest. The data is novel, since it provides instantaneous diurnal concentration profiles without relying on the previously employed long term averaging or sample preconcentration. These data, together with O<sub>3</sub> concentrations, allowed the analysis of the relative concentration patterns of monoterpenes and sesquiterpenes. They indicated on the one hand notable differences in the effect of short-term environmental drivers (i.e., temperature and light) on emissions, and on the other hand a predominant role of in-canopy atmospheric oxidation for concentrations of sesquiterpenes, but not of monoterpenes.

In this study a possible role of SQT acting as exogenous protection against oxidative plant damage has been proposed, based on the high sensitivity SQT have with respect to ozone. Inverse relationships both in time and in space were found for SQT and ozone in the Amazon region, showing patterns opposite to what it was expected. SQT escape efficiency and ozone deposition flux was also calculated to support the proposed important role of SQT ozonolysis in Amazonia. This reaction between ozone and SQT can lead to feedback mechanisms which are different that the ones thought for other isoprenoids such as isoprene.



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