Yañez Serrano, Ana Maria; Bourtsoukidis, Efstratios; Gomes Alves, Eliane; [et al.]. «Amazonian biogenic volatile organic compounds under global change». Global Change Biology, Vol. 26, issue 9 (Sep. 2020), p. 4722-4751. DOI 10.1111/gcb.15185

Amazonian Biogenic Volatile Organic Compounds under Global Change

A.M. Yáñez-Serrano[1,2], E. Bourtsoukidis[3], E.G. Alves[4], M. Bauwens[5], T. Stavrakou[5], J. Llusia[1,2], I. Filella[1,2], A. Guenther[6], J. Williams[3], P. Artaxo[7], K. Sindelarova[8], J. Doubalova[8,9], J. Kesselmeier[3], J. Peñuelas[1,2].

[1]{CREAF, E08193 Cerdanyola del Vallès, Catalonia, Spain}

[2]{CSIC, Global Ecology Unit, CREAF-CSIC-UAB, E08193 Cerdanyola del Vallès, Catalonia, Spain}

[3]{Atmospheric Chemistry and Multiphase Chemistry Departments, Max Planck Institute for Chemistry, P. O. Box 3060, 55128, Mainz, Germany}

[4]{Department of Biogeochemical Processes, Max Planck Institute for Biogeochemistry, Hans-Knöll-Straße 10, 07745, Jena, Germany}

[5]{Royal Belgian Institute for Space Aeronomy, Avenue Circulaire 3, 1180, Brussels, Belgium}

[6]{Department of Earth System Science, University of California, Irvine 92697, USA}

[7]{Instituto de Física, Universidade de Sao Paulo (USP), Rua do Matão, Travessa R, 187, CEP 05508-900, São Paulo, SP, Brasil}

[8]{Charles University, Faculty of Mathematics and Physics, Dept. of Atmospheric Physics, Prague, Czechia}

[9]{Czech Hydrometeorological Institute, Modelling and Assessment Dept., Prague, Czechia}

Correspondence e-mail: ayanezserrano@yahoo.es

Keywords: Biogenic volatile organic compounds, BVOCs, Amazonia, air chemistry, climate, ecological interactions, depositional processes, land use, land cover, global change

Abstract

Biogenic volatile organic compounds (BVOCs) play important roles at cellular, foliar, ecosystem, and atmospheric levels. The Amazonian rainforest represents one of the major global sources of BVOCs, so its study is essential for understanding BVOC dynamics. It also provides insights into the role of such large and biodiverse forest ecosystem in regional and global atmospheric chemistry and climate. We review the current information on Amazonian BVOCs and identify future research priorities exploring biogenic emissions and drivers, ecological interactions, atmospheric impacts, depositional processes, and modifications to BVOC dynamics due to changes in climate and land cover. A feedback loop between Amazonian BVOCs and the trends of climate and land-use changes in Amazonia is then constructed. Satellite observations and model simulation time series demonstrate the validity of the proposed loop showing a combined effect of climate change and deforestation on BVOC emission in Amazonia. A decreasing trend of isoprene during the wet season, most likely due to forest biomass loss, and an increasing trend of the sesquiterpene to isoprene ratio during the dry season, suggest increasing temperature stress induced emissions due to climate change.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are emitted by vegetation, bacteria, algae, fungi, and animals. Their rates of emission vary greatly in response to biotic (e.g. herbivory) and abiotic (meteorological) factors (Šimpraga et al., 2019). They have diverse roles at multiple scales, from cellular protection and defence at the foliar level, through chemical signalling at regional level, up to influencing rainfall at the ecosystems scale (Laothawornkitkul et al., 2009). BVOCs profoundly affect biosphere-atmosphere interactions by atmospheric reactivity, aerosol growth processes, and cloud formation, and therefore radiative balance (Kulmala et al., 2013; Nölscher et al., 2016; Pöschl et al., 2010). As BVOCs are precursors of aerosols, they can impact the regional radiative forcing directly through aerosol scattering and indirectly by influencing cloud processes. Furthermore, higher cloud cover leads into increased diffuse radiation, boosting net primary productivity and thereby BVOC emissions (Rap et al., 2018). However, BVOCs can have further impacts on the radiative forcing by their influence on tropospheric ozone formation or by increasing the lifetime of methane by suppression of its major sink, the OH radical (Peñuelas & Llusià, 2003).

Vegetation is the largest source of BVOC emissions, with tropical trees responsible for ca. 80% of global terpenoid emissions and 50% of other BVOC emissions (Guenther et al., 2012). With half of the global tropical forests, Amazonia is the largest remaining pristine continental area (Andreae et al., 2015; Pöhlker et al., 2019). Amazonia stores 50% of tropical-forest carbon, plays a vital role in the global cycles of energy, water, and carbon, and has the largest biodiversity in the world (Levine et al., 2016; Malhi et al., 2008; Swift et al., 1998; ter Steege et al., 2013). This dynamic system emits large quantities of chemically diverse BVOCs to the atmosphere, with implications both within and above Amazonian forest canopies. Amazonia is highly sensitive to changes in climate and land use due to its strong energy and biochemical cycling (Levine et al., 2016). It has been established that recent human action is already altering Amazonian conditions and feedbacks (Sena et al., 2018; Shrivastava et al., 2019), complicating the understanding of BVOCs in this region. In fact, BVOC emission decrease due to forest conversion to croplands in the tropics has been shown to result in a positive radiative forcing (Jia et al., 2019; Scott et al., 2018). Additionally, the impact of Amazonian BVOCs on global primary production through diffuse radiation has large implications for the global carbon balance (Rap et al., 2018). Furthermore, by participating in cloud formation processes, Amazonian BVOCs play a key role in the regional hydrological cycle, since Amazonian rainforests contribute to precipitation throughout the South American continent (Boers et al., 2017; Rocha et al., 2018). Therefore, it is critical to understand the BVOC response to environmental stresses caused by changes in climate and land use in Amazonia, and how these changes will feedback into the Earth system (Peñuelas & Staudt, 2010).

We here review the recent advances in Amazonian BVOC research and estimate potential future BVOC dynamics using information currently available for emission processes, resulting ecological interactions and atmospheric impacts, depositional processes, and effects and feedbacks of climate and land use change. We propose a feedback loop, which is supported by satellite observations and model simulations of BVOC fluxes, to identify research priorities in Amazonian BVOCs.

2. Advances on BVOC scientific research in Amazonia

a. History of measurements

Measurements of BVOCs in Amazonian ecosystems are logistically difficult due to accessibility, and power constrains. Research on this topic began in the 1970s and 1980s, when tethered balloon observations demonstrated that Amazonia is a major source of BVOC emissions to the atmosphere (Crutzen et al., 1985; Greenberg & Zimmerman, 1984; Zimmerman et al., 1988) providing understanding into atmospheric chemistry (Grosjean, 1995). The establishment of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) provided the first large-scale estimates of isoprene emissions and oxidation products from data collected by aircraft and tower-based stations (Kesselmeier et al., 2009). Nevertheless, understanding of the controlling processes was still scarce due to the lack of data on temporal and spatial variability and the very limited number of BVOCs species studied (Kesselmeier et al., 2009). The most commonly used prominent technique in early studies was BVOC collection in cartridges, followed by transportation of field samples to laboratories outside of Amazonia for analysis by gas chromatography. The logistical difficulties for sample transport were addressed by establishing more locations for tower-based measurements, long term field campaigns, new sampling approaches such as the use of drones (McKinney et al., 2019), along with more advanced analytical tools such as proton-transfer-reaction mass spectrometry (Bracho-Nunez et al., 2013; Crutzen et al., 2000; Fuentes et al., 2016; Jardine et al., 2011b, 2011a, 2011c, 2014, 2016b; Karl et al., 2009; Kesselmeier et al., 2009; Kuhn et al., 2007; Liu et al., 2016; Rinne et al., 2002; Williams et al., 2001; Yáñez-Serrano et al., 2015), the comparative reactivity method (CRM) (Nölscher et al., 2016; Pfannerstill et al., 2018; Sinha et al., 2008), photoionization detector (PID) (Harley et al., 2004), semi-volatile thermal desorption aerosol gas chromatography (SV-TAG) (Yee et al., 2018), and isoprene portable monitoring system (T. Taylor personal communication). Extensive campaigns and projects such as GoAmazon and ATTO provided integrated investigations of emissions, chemistry, transport, and cloud processes (Andreae et al., 2015; Martin et al., 2017). Seasonality was clearly addressed (Alves et al., 2016, 2018; Nölscher et al., 2016; Yáñez-Serrano et al., 2015, 2018b) and greater effort was expended towards obtaining a mechanistic understanding that was provided by foliar-level measurements under natural and controlled experiments (Alves et al., 2014; Bourtsoukidis et al., 2018; Bracho-Nunez et al., 2012, 2013). Despite the increasing number of observation datasets and efforts toward addressing horizontal heterogeneity (Batista et al., 2019), comparing ecosystems remains difficult due to the spatial diversity of Amazonia (see S.I.1) and the inadequate information over controlling processes. Figure 1 shows the number and location of BVOC measurements available since 1984, when the first measurements were published, showing the lack of spatial variability in the Amazonian BVOC studies to date.

b. History of modelling

There are still too few observations of BVOC emissions for accurate representation of the regional variability, resulting in large uncertainty in model predictions. Initially, the BVOC emissions algorithm proposed by Guenther et al., (1995) included light- and temperature-dependent emissions of isoprene, but all other emissions were regarded as only temperature-dependent, a potentially misleading assumption (Kesselmeier & Staudt, 1999). The algorithm was updated in 1999 by a simple leaf-age activity factor to determine the dependence on meteorological conditions. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) then simulated net emission rates, accounting for losses of primary emissions (Guenther et al., 2006), with the latest update adding a longer list of compounds and their emission factors (Guenther et al., 2012; Sindelarova et al., 2014). Further BVOC emissions modelling included Organizing Carbon and Hydrology in Dynamic EcosystEm (ORCHIDEE) (Messina et al., 2016) and Lund-Potsdam-Jena-General Ecosystem Simulator (LPJ-GUESS) (Acosta Navarro et al., 2014). Amazonian modelling has thus been improved, but a reliable predictive framework for emission capacities in Amazonia requires an improved mechanistic understanding of BVOC variation across plant populations and of their interactions with other living organisms and abiotic factors (Alves et al., 2018; Kuhn et al., 2004a; Salazar et al., 2018; Taylor et al., 2018).

c. Satellite applications

Amazonian isoprene fluxes can be derived at regional, or global scales via satellite measurements (Barkley et al., 2009, 2013; Bauwens et al., 2016; Fu et al., 2019; Gu et al., 2017). This can improve our knowledge of the dynamics in scale and time. Formaldehyde is formed during the oxidation of most VOCs released in the atmosphere. It is a major intermediate product in isoprene oxidation, and therefore satellite observations of formaldehyde (HCHO) have been used to infer isoprene emissions at global and regional scales (Millet et al., 2008; Pamler et al., 2003; Stavrakou et al., 2009). The variability of emissions estimated with these satellite data generally lies within the variability of the surface observations. Direct observations of isoprene recently acquired by the satellite-borne Cross-track Infrared Sounder (CrIS) (Fu et al., 2019) will open new avenues in the isoprene emission estimation from satellites. A global study using these data found a regional reduction (-2% y^{-1}) of biogenic emissions over Amazonia during the period of 2005 to 2013 but no plausible cause could be identified (Bauwens et al., 2016).

3. Emission

The BVOCs in the Amazonian rainforest have many sources, with vegetation being the most prominent (Kesselmeier et al., 2009) (Figure 2). A large variety of BVOCs are emitted from Amazonian ecosystems. Isoprene is the most strongly emitted compound, with reported ambient mixing ratios of 0.5-15 ppb and fluxes of 0.7-12.1 mg m^{-2}_{ground} h^{-1}, although other isoprenoids have been reported such as monoterpenes (with mixing ratios typically below 1 ppb but in some cases up to 5.5 ppb (Greenberg & Zimmerman, 1984; Kesselmeier et al., 2002b)), sesquiterpenes (SQT) (with mixing ratios up to 0.16 ppb), and even diterpenes (0.0002 ppb) (Yee et al., 2018). Methanol is the second most emitted compound, with measured mixing ratios reported up to 6 ppb (Kesselmeier et al., 2002b; Yáñez-Serrano et al., 2015). Other oxygenated compounds have also been reported, such as acetaldehyde, acetone, methyl ethyl ketone (MEK) (Bracho-Nunez et al., 2012; Rottenberger et al., 2008; Yáñez-Serrano et al., 2016), ethanol (Bracho-Nunez et al., 2012; Rottenberger et al., 2008), formaldehyde (Karl et al., 2009; Kesselmeier et al., 2000), acetic and formic acid (Jardine et al., 2011b; Kuhn et al., 2002a), green-leaf volatiles (GLVs) (Jardine et al., 2015b), isoprene oxidation products (including methyl vinyl ketone (MVK), methacrolein (MACR), isoprene hydroperoxide (ISOPOOH), and hydroxyacetone (Karl et al., 2009), aromatics (Paralovo et al., 2015), sulphurous compounds such as dimethyl sulphide (Jardine et al., 2014) as well as chlorine compounds such as methyl chloride and chloroform (Gebhardt et al., 2008; Gregory et al., 1986; Yokouchi et al., 2002) (Table 1, figure 3 and 4). Additionally, the emission, and consequent atmospheric abundance is given as the sum of enantiomers due to analytical constrains, yet BVOCs are generated by enzymes and are therefore chiral. Although chemically identical, they can induce differing biological responses. Thus examining the different enantiomers would lead to a doubling of information (Williams et al., 2007).

Vegetation emits BVOCs, as *de novo* compounds from recently photosynthesised carbon or as volatilised compounds from storage pools or resins and waxes (Kesselmeier & Staudt, 1999). These emissions may represent a substantial loss of carbon previously assimilated by photosynthesis (up to 2% of carbon fixed for tropical forests) (Kesselmeier et al., 2002a). Isoprene is the most common *de novo* biosynthesised compound, with isoprene-emitting plants found as a typical component in tropical forests (Harley et al., 2004; Šimpraga et al., 2019; Taylor et al., 2018). Further species, such as monoterpenes are also released *de novo* from leaves, glands, and resin ducts (Kesselmeier & Staudt, 1999) in Amazonia (Jardine et al., 2015a; Kuhn et al., 2002b; Piva et al., 2019; Yáñez-Serrano et al., 2018b).

In addition to living vegetation, leaf litter is an important source of BVOCs (Greenberg et al., 2012), particularly during the start of the dry season when litterfall peaks, and decomposition is further aided by wetness with the upcoming wet season. Little is known about this BVOC source in Amazonia, but monoterpene addition to soils from leaf fall and excreted from plant resins and roots have been reported elsewhere (Delory et al., 2016; Marmulla & Harder, 2014), suggesting a potential, unquantified role of Amazonian ecosystems with a rapid turnover of biomass.

Soils are a poorly explored BVOC source in the Amazonian rainforest, including their microorganisms, roots, and surface reactions (Tang et al., 2019). SQTs have recently been found to be strongly emitted by soil bacteria (Bourtsoukidis et al., 2018), with responses to soil conditions, because microorganisms are highly spatially heterogeneous (Buscardo et al., 2018), dynamic and able to produce and consume BVOCs strongly interacting within the soil ecosystem. Also reduced sulphur compounds such as dimethyl sulphide, carbon disulphide or carbonyl sulphide can be released by soils (Bunk et al., 2017), including Amazonian soils (Jardine et al., 2014).

Similar to soil, microorganisms in the phyllosphere (both endo- and epiphytic) can be an important source of BVOCs. The phyllosphere contains bacteria, fungi, bryophytes, and lichens and are extremely diverse in tropical forests (Roy & Banerjee, 2018). Little is known about the relationship between the phyllosphere and BVOCs, but typical colonizers of the phyllosphere can emit and metabolise BVOCs (Farré-Armengol et al., 2016a; Kesselmeier et al., 1999; Rundell et al., 2015), therefore, the contribution of phyllospheric emissions to net ecosystem emission may be important given their abundance in rainforests (Roy & Banerjee, 2018). In addition to phyllospheric interactions, other processes at the foliar level can be a source of BVOC emissions to the atmosphere, e.g. oxidation products formed interactions at the surface of leaves (Jud et al., 2016) and adsorption/desorption onto/from surfaces.

Lastly, animals are a relatively unexplored source of BVOCs in Amazonian rainforests. In particular, arthropods such as ants and termites contribute 1/3 of the animal biomass in Amazonian upland forests, constituting several tonnes per hectare (Rinker & Lowman, 2004). Induced volatile emissions from animals, such as emissions from wood-eating termites of different social ranks (Himuro et al., 2011), or emissions of formic acid from ants for defensive purposes (Brütsch et al., 2017), have been reported. However, the types and magnitudes of the emissions from Amazonian ecosystems have not been really deepened since the reports by Zimmerman et al., (1982) or Khare et al., (1999).

The emission rates of BVOCs from all the aforementioned sources may vary considerably as a function of driving factors. Temperature is a key driver of BVOC emissions, both for plants and soils, because it promotes enzymatic reactions in pathways of BVOC biosynthesis and their diffusion in biological tissues and soil substrates (Llusià & Peñuelas, 2000). For example, monoterpenes have been described as leaf "thermometers", increasing in emission with temperature (Jardine et al., 2017). Emissions of SQTs and methanol are also temperature-dependent (Alves et al., 2016; Jardine et al., 2011c, 2016b) and isoprene has been found to protect against thermal stress in Amazonia (Garcia et al., 2019). Soil temperature is also a determinant because it increases decomposition and subsequent BVOC emission, but such processes have not been adequately addressed.

Photosynthetically active radiation and its relationship to photosynthesis are essential drivers for compounds emitted *de novo*, including isoprene and monoterpenes such as cis-β-ocimene (Alves et al., 2014; Harley et al., 2004; Jardine et al., 2013, 2015a, 2017; Kesselmeier & Staudt, 1999; Kuhn et al., 2002b, 2004a; Llusià & Peñuelas, 2000). For example, isoprene emissions from *Hymenaea courbaril* have been strongly correlated with gross primary productivity under non-stress conditions (Kuhn et al., 2004b) and protect plants under high solar radiation conditions (Garcia et al., 2019). Rapidly changing light conditions, e.g. during a sudden thunderstorm, can also induce emissions of acetaldehyde and ethanol (Holzinger et al., 2000). The effect of solar radiation on soils has not been well explored, but radiation would both heat the surface and decrease the water content due to evaporation, though only about one third of the radiation that arrives at the top of the canopy reaches the soil (Alves et al., 2016).

The availability of water within ecosystems affects BVOC production, whether as humidity, foliar uptake, or content in soil. Drought reduces stomatal conductance, decreases intracellular CO_2 mixing ratios and as a result, increases isoprene emissions (Pegoraro et al., 2004a), although this is dependent on the severity of drought (Niinemets, 2010; Otu-Larbi et al., 2020; Pegoraro et al., 2004b; Potosnak et al., 2014). GLV emission can be stimulated at high temperatures and under drought conditions (Jardine et al., 2015b; Pfannerstill et al., 2018). The general reduction of BVOC emissions by plants due to drought depends on both changes in plant physiology and to lower foliar biomass. Emissions from Amazonian soils depend on moisture, because bacteria may become activated by water, with an emission burst after a large rainfall event and an optimal pattern of emissions, where SQT emissions are the highest under moderate levels of soil water (Bourtsoukidis et al., 2018). The soil water also affects the gas permeability of the soil. The soil water content is therefore an essential parameter for BVOC production and release from Amazonian soils.

The atmospheric abundance of gaseous constituents is an additional regulator of BVOC emissions. The mixing ratios of BVOCs in the atmosphere, particularly of oxygenated compounds that are bidirectionally exchanged (Niinemets et al., 2014), is driven by a compensation point (i.e. a compound is emitted if the foliar concentration is higher than the ambient mixing ratios, otherwise the plant will take up the compound), as has been observed in Amazonia (Jardine et al., 2011b; Kuhn et al., 2002a; Rottenberger et al., 2004). The amount of oxidants in the atmosphere can induce emissions to quench oxidation (Jardine et al., 2011a, 2015a; Peñuelas & Llusià, 2001) and oxidise BVOCs generating oxidation products. Biotic and abiotic stressors at the foliar level lead to the formation of reactive oxygen species (ROS), altering plant BVOC emissions coordinated to quench the ROS (Jardine & Jardine, 2016; Sampaio Filho et al., 2018). Regional and global models currently have a module for deposition and another for emissions. For these bidirectional exchange compounds such modules must be combined. One step forward in this matter is the addition of a bidirectional exchange compound class in the MEGAN model (Guenther et al., 2012).

Increasing atmospheric CO_2 mixing ratios can affect BVOC emissions (Possell et al., 2005; Wilkinson et al., 2009) directly, with higher biomass due to higher substrate availability (Lerdau et al., 1994), and thus higher foliar surface area for BVOC emission, as demonstrated for monoterpene emissions (Staudt et al., 2001). However, no information on these processes is available for Amazonian ecosystems. These increasing CO_2 mixing ratios can also indirectly suppress the emission of compounds such as isoprene (Young et al., 2009), due to a competition of phosphoenolpyruvate (PEP) (Fasbender et al., 2018; Possell et al., 2005; Rosenstiel et al., 2003), which at the same time may be offset by warming and increased growth (Garcia et al., 2019; Sharkey & Monson, 2017).

Phenology, ontogeny, and canopy structure play important roles in BVOC emissions in Amazonian rainforests (Alves et al., 2018; Kuhn et al., 2004b; Wei et al., 2018). The quantity of BVOCs emitted by leaves varies with the stage of maturity as a consequence of resource availability (maturity) and defensive demand (bud break and early stages) (Kuhn et al., 2004b). For example, young *Vismia Guianensis* leaves emit higher quantity of methanol than mature leaves (Jardine et al., 2016b), whereas mature leaves *Vismia Guianensis* and *Eschweilera coriacea* have been found to higher emissions than other leaf ages (Alves et al., 2014, 2016; Jardine et al., 2016b); and light-dependent monoterpenes are emitted exclusively during the period between bud-break and foliar maturity for *Hymenaea courbaril* (Kuhn et al., 2004b). Additionally, canopy structure plays a role in BVOC dynamics as shown with high sesquiterpene emissions in the lower canopy (Alves et al., 2016). Foliar flushing in Central Amazonia peaks during the transition from the wet to the dry season, with a consequent peak in leaf litter and foliar turnover at the onset of the dry season (Goulden et al., 2004; Huete et al., 2006; Roberts et al., 1998). This factor has been reported to be essential for modelling BVOC emission in Amazonia (Alves et al., 2018).

Nutrient availability is another important driver of BVOC emissions (Fernández-Martínez et al., 2018). In this regard, the role of litterfall have recently been demonstrated to be important for supplying soil with nutrients that affect microbial composition in Amazonian ecosystems (Buscardo et al., 2018), but no information is available with respect to the effect of nutrient availability on BVOC dynamics at canopy level in Amazonia.

Biotic factors such as pathogens, herbivores, herbivorous predators, pollinators, and phyllospheric organisms influence the emission rates of BVOCs. Plants emit BVOCs as defensive mechanisms or for signalling within plants and ecosystems (Šimpraga et al., 2019). Alterations to these biological controls can thus affect the average BVOC emissions from plants. Little is known about the role of the phyllosphere in BVOC dynamics in the Amazonian rainforest, but some possible implications can be derived from studies elsewhere. The phyllosphere affects plant biogeography and ecosystem function, thereby affecting plant physiology. The phyllosphere reduces the amount of photosynthesis by blocking light (Huete et al., 2006), protects plants against heat (Stuntz et al., 2002), can retain water in the leaves (Coley et al., 1993; Stuntz et al., 2002), fixes nitrogen, and protects plants against herbivores and abiotic stresses by the production of phytohormones and other secondary metabolites (Roy & Banerjee, 2018). The phyllosphere is also subjected to environmental conditions that can alter its role from beneficial to pathogenic. Such environmental conditions can be leaching, changes in temperature, variations in exposure to sunlight, ROS concentration (Bringel & Couée, 2015), the phyllospheric cover itself, effects of irrigation, cohabitation, foliar texture, and phenology (Coley et al., 1993; Saikkonen et al., 1998).

Lastly, species diversity can influence the total emission of BVOCs, as has been reported for terpenoids, with substantial variation within species (Guenther, 2013). In Amazonia, an elevation gradient in isoprene emissions was attributed to the plant species distribution which differ topographically (Gu et al., 2017). The Amazonian rainforest contains a variety of ecosystems, from upland forests to flooded or seasonally flooded forests (see SI for more information). Differences in environmental conditions and adaptive strategies can be implied from differences in BVOC emission (Bracho-Nunez et al., 2012). Investigation on the effects of root anoxia on BVOC exchange is thus important for understanding the functioning of Amazonian ecosystems. Plants may react to flooding with fermentation, accompanied by emissions of ethanol and acetaldehyde to remove the large amounts of ethanol produced under root anoxia (Bracho-Nunez et al., 2012; Kreuzwieser et al., 1999; Rottenberger et al., 2008). The quantities and ratios of such emissions can indicate the metabolic and morphologic adaptations of flooded ecosystems (Parolin et al., 2004).

The vast amount of BVOC sources in the Amazonian rainforest (i.e. diverse species of insects, vegetation, soil and phyllosphere microorganisms) is regulated by a plethora of biotic and abiotic emission drivers (i.e. temperature, radiation, water and nutrient availability, ambient CO_2 and BVOC mixing ratios) leading to a strong seasonality (Alves et al., 2016, 2018; Barkley et al., 2009; Kesselmeier et al., 2002b; Kuhn et al., 2004a; Yáñez-Serrano et al., 2015, 2018b). While increasing research addresses BVOC emissions over single or combined emission drivers, the large-scale biodiversity and interplay of biotic and abiotic processes remains challenging. Within such large ecosystems, ecological interactions may have an important, but poorly explored, role in regulating the BVOC emissions of the Amazon rainforest.

Table 1: Isoprene ambient mixing ratios reported in literature over Amazonian ecosystems in a within or above canopy and season basis. Data is organized by height with a line separating between within canopy mixing ratios and above canopy mixing ratios and between seasons. We considered 35m to be the average top of the Amazonian canopy. Values reported are in ppb and as presented in literature. They are usually means or medians. The values in parenthesis represent either standard deviation or interquartile range when available. Where only graphical data was available we used the software Plot Digitizer to derive means and standard deviations. The locations are classified according to the area where the measurements were taken, namely, Central Amazonia, Western Amazonia, South-western Amazonia, Guyana Shield and Central-east Amazonia. The techniques are PTR-MS: Proton Transfer Reaction Mass Spectrometer; GC-MS: Gas Chromatography Mass Spectrometer, GC-FID: Gas Chromatography Flame Ionization Detector and IEC: Ion-Exchange Chromatography. The seasons are specified together with the exact timing of sampling: Dry, dry season; Wet, wet season; D-t-W, transition from dry to wet season; and W-t-D, transition from wet to dry season. X stands for laboratory experiments or satellite retrievals.

For a more extended table with all reported values for Amazonian ecosystems in ppb, please refer to Table1 in S.I.2. Note that in some cases fluxes in mg m^{-2} h^{-1} are reported (these cases are identified by (flux), or by an *). The compounds are presented in the following order: Acetaldehyde, acetic acid, acetone, acetonitrile, acetylene, benzaldehyde, benzene, butanal, butane, butene, 1,4-cyclohexadiene, p-cymene, decanal, dichloromethane, diterpenes, dimethylsulphide, estragole, ethane, ethanol, ethylbenzene, ethylene, formaldehyde, formic acid, heptane, 1-heptene, 2-heptene, hexane, hexanol, hexene, hydrogen sulphide, hydroxyacetone (flux), isoprene (flux), linalool, methyl ethyl ketone (MEK), methanol, 2-methyl-2-butene, methyl chloroform, 2-methyl-furan, 3-methyl-furan, 6-methyl-5-heptene-2-one, methyl mecarptan, methyliodide, total monoterpenes, total monoterpene (flux), methyl vinyl ketone and methacrolein (MVK+MACR), MVK+MACR (flux), nonanal, octane, pentanal (flux), pentane, propane, propylene, propyne, total sesquiterpenes, total sesquiterpene (flux), styrene, sulphur dioxide, α-terpineol, toluene and m-, p- and o-xylene.

Isoprene

Site	***Season***	***Height (m)***	***Isoprene (ppb)***	***Technique***	***Reference***	***Observations***
Central Amazonia	Dry	0.05	3.13	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	0.5	3.77	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	1	2.77(0.4)	GC-FID	(Rasmussen & Khalil, 1988)	Daytime mean (11:00-15:00, LT). Canister sampling. Near ground level.
Western Amazonia	Dry	2	3.31	GC-MS	(Helmig et al., 1998)	Daytime mean.
Central Amazonia	Dry	4	5.35	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	0-30	2.40(1-5.24)	GC-FID	(Greenberg & Zimmerman, 1984)	Daytime mean. Canister sampling. Near ground to 30m
Central Amazonia	Dry	24	19.9(2.0)	PTR-MS	(Andreae et al., 2015)	Daytime mean.
Central Amazonia	Dry	24	7.62	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	30	2.65(1.39-3.38)	GC-FID	(Zimmerman et al., 1988)	24 h median. Sampling on teflon bag on tethered balloon (30m).
Central Amazonia	Dry	38	6.13	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	40	2.68(0.9)	PTR-MS	(Alves et al., 2016)	Daytime mean (10:00-14:00, LT).
Central Amazonia	Dry	40	7.94(1.67)	PTR-MS	(Wei et al., 2018)	Daytime mean.
Central Amazonia	Dry	45	5 max.	GC-MS	(Rinne et al., 2002)	Afternoon values. Fluxes 30 ºC and 1000 µmol m^{-2} s^{-1}. Cartridge on Disjunct Eddy Accumulation.
Southwestern Amazonia	Dry	50	4.6(2.7)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Central Amazonia	Dry	51	3.4(1.8)	GC-FID	(Kuhn et al., 2007)	Daytime mean (10:00-15:00, LT). Cartridge on Relaxed Eddy Accumulation.

Central Amazonia	Dry	53	5.72	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	54	7.80	PTR-MS	(Rizzo et al., 2010)	Maximum at noon. Disjunct Eddy Covariance.
Central Amazonia	Dry	55	7.8(3.7)	PTR-MS	(Karl et al., 2007)	Daytime mean (12:00-14:00, LT). Disjunct Eddy Covariance.
Southwestern Amazonia	Dry	60	4.0(2.5)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Central Amazonia	Dry	79	4.81	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Dry	305	1.73(1.03-2.15)	GC-FID	(Zimmerman et al., 1988)	24 h median. Sampling on teflon bag on tethered balloon (305m).
Western Amazonia	Dry	91-1167	1.69	GC-MS	(Helmig et al., 1998)	Daytime mean.
Central Amazonia	Dry	100-1200	5.5(2.6)	PTR-MS	(Karl et al., 2007)	Daytime mean (10:00-11:30, LT). Mixed Layer Gradient.
Central Amazonia	Dry	150-1500	1.5(0.75)	GC-FID	(Rasmussen & Khalil, 1988)	Daytime. Canister sampling. Aircraft flights.
Central Amazonia	Dry	35-2000	2.27(0.38-4.08)	GC-FID	(Greenberg & Zimmerman, 1984)	Daytime mean. Canister sampling. Flights from treetop to 2 km.
Western Amazonia	Dry	1481-1554	0.16	GC-MS	(Helmig et al., 1998)	Daytime mean.
Central Amazonia	Dry	2000-17000	0.19(0.14-0.22)	GC-FID	(Greenberg & Zimmerman, 1984)	Daytime mean. Canister sampling. Flights from 2km to Tropopause.
Central Amazonia	Dry & D-t-W	2	1.54(1.37)	PTR-MS	(Jardine et al., 2011a)	
Central Amazonia	Dry & D-t-W	11	2.86(1.61)	PTR-MS	(Jardine et al., 2011a)	
Central Amazonia	Dry & D-t-W	17	2.86(1.53)	PTR-MS	(Jardine et al., 2011a)	
Central Amazonia	Dry & D-t-W	24	2.71(1.37)	PTR-MS	(Jardine et al., 2011a)	
Southwestern Amazonia	Dry & D-t-W	08-52	9.5(4)	GC-FID	(Kesselmeier et al., 2002b)	Daytime mean (11:00-18:00, LT).
Central Amazonia	Dry & D-t-W	30	2.47(1.26)	PTR-MS	(Jardine et al., 2011a)	
Central Amazonia	Dry & D-t-W	40	2.36(1.26)	PTR-MS	(Jardine et al., 2011a)	
Central Amazonia	Dry & Wet	40	2.5(2.2)	PTR-MS	(Fuentes et al., 2016)	
Central Amazonia	D-t-W	40	2.65(1.33)	PTR-MS	(Alves et al., 2016)	Daytime mean (10:00-14:00, LT).
Central Amazonia	D-t-W	40	6.76(2.35)	PTR-MS	(Wei et al., 2018)	Daytime mean.
Southwestern Amazonia	D-t-W	50	3.4(1.2)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Southwestern Amazonia	D-t-W	60	3.0(0.5)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Central Amazonia	Wet	0	6.90	GC-MS	(Kesselmeier et al., 2000)	Daytime mean (15:00, LT).
Central Amazonia	Wet	0.05	0.57	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Wet	0.5	0.57	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Wet	1	3.2(0.9)	GC-MS	(da Silva, 2010)	Daytime mean (07:00-17:00, LT). Cartridge sampling.
Central Amazonia	Wet	1.5	4.33(2.02)	GC-MS	(Kesselmeier et al., 2000)	Daytime mean (09:30-16:00, LT). Outside forest.
Central Amazonia	Wet	1.5	3.01(0.85)	GC-MS	(Kesselmeier et al., 2000)	Daytime mean (09:30-16:00, LT). Inside canopy.
Central Amazonia	Wet	4	0.86	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central-East Amazonia	Wet	8.1	0.13(0.61)	GC-MS	(Jardine et al., 2016a)	Nighttime mean.

Central-East Amazonia	Wet	8.1	8.95(4.2)	GC-MS	(Jardine et al., 2016a)	Daytime mean.
Central Amazonia	Wet	10	4.6(0.94)	GC-MS	(da Silva, 2010)	Daytime mean (07:00-17:00, LT). Cartridge sampling.
Central Amazonia	Wet	20	6.17(1.03)	GC-MS	(da Silva, 2010)	Daytime mean (07:00-17:00, LT). Cartridge sampling.
Central Amazonia	Wet	24	2.29	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Wet	30	7.90	GC-MS	(Kesselmeier et al., 2000)	Daytime mean (14:00, LT).
Central Amazonia	Wet	38	2.39	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Wet	40	1.66(0.9)	PTR-MS	(Alves et al., 2016)	Daytime mean (10:00-14:00, LT).
Central Amazonia	Wet	40	4.66(2.21)	PTR-MS	(Wei et al., 2018)	Daytime medan.
Central Amazonia	Wet	50	6.3(1.32)	GC-MS	(Kesselmeier et al., 2000)	Daytime mean (12:00-16:00, LT).
Southwestern Amazonia	Wet	50	4.5(0.9)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Central Amazonia	Wet	53	1.85	PTR-MS	(Yáñez-Serrano et al., 2015)	
Southwestern Amazonia	Wet	60	4.0(1.2)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Central Amazonia	Wet	60	2.40	GC-MS/FID	(Batista et al., 2019)	Mean of overall dataset. Slope forest. Cartridge sampling with drones.
Central Amazonia	Wet	60	4.40	GC-MS/FID	(Batista et al., 2019)	Mean of overall dataset. Plateu forest. Cartridge sampling with drones.
Central Amazonia	Wet	79	1.69	PTR-MS	(Yáñez-Serrano et al., 2015)	
Central Amazonia	Wet	200-500	~3	GC-MS	(Kesselmeier et al., 2000)	24 hr mean. Sampling with thetered balloon.
Guyana Shield	Wet	400	~2.3	GC-FID	(Gregory et al., 1986)	Canister sampling.
Central Amazonia	Wet	500	~3	PTR-MS	(Martin et al., 2017)	During periods of clean conditions (above threshold).
Central Amazonia	Wet	200-1000	2.86(2.25-3.64)	GC-MS	(Greenberg et al., 2004)	Daytime median and interquartiles (12:00-15:00, LT). Cartridge sampling on tethered balloon.
Southwestern Amazonia	Wet	200-1000	6.89(2.78-7.73)	GC-MS	(Greenberg et al., 2004)	Daytime median and interquartiles (12:00-15:00, LT). Cartridge sampling on tethered balloon.
Central Amazonia	Wet	200-1000	0.74(0.6-1)	GC-MS	(Greenberg et al., 2004)	Daytime median and interquartiles (12:00-15:00, LT). Cartridge sampling on tethered balloon.
Guyana Shield	Wet	3000	3.30	PTR-MS	(Warneke et al., 2006)	
Guyana Shield	Wet	3000	1.70	PTR-MS	(Williams et al., 2001)	
Southwestern Amazonia	W-t-D	25	~4	GC-FID	(Kuhn et al., 2002b)	
Southwestern Amazonia	W-t-D	08-52	3.7(0.6)	GC-FID	(Kesselmeier et al., 2002b)	Daytime mean (11:00-18:00, LT).
Central Amazonia	W-t-D	40	4.17(1.81)	PTR-MS	(Wei et al., 2018)	Daytime mean.
Southwestern Amazonia	W-t-D	50	2.1(2.0)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Southwestern Amazonia	W-t-D	60	1.8(1.8)	GC-FID	(Aquino, 2006)	Daytime mean (11:00-16:00, LT). Canister sampling.
Central Amazonia	W-t-D	100	2.38(1.16)	GC-FID	(Kuhn et al., 2010)	Mean vertical profiles of isoprene and α-pinene from 8 background flights.
		Satellite	X		(Barkley et al., 2009)	
		Satellite	X		(Bauwens et al., 2016)	
Southwestern Amazonia	Dry	Leaf level	X	GC-FID/MS	(Kuhn et al., 2004b)	

Southwestern Amazonia	Dry	Leaf level	X	GC-FID/MS	(Kuhn et al., 2004a)
		Leaf level	X		(Bracho-Nunez et al., 2012)
		Leaf level	X		(Bracho-Nunez et al., 2013)
		Leaf level	X		(Garcia et al., 2019)
		Leaf level	X		(Harley et al., 2004)
		Leaf level	X		(Jardine et al., 2013)
		Leaf level	X		(Jardine et al., 2016b)
		Leaf level	X		(Pegoraro et al., 2005)
		Leaf level	X		(Taylor et al., 2019)
		Leaf level	X		(Taylor et al., 2018)

4. Ecological interactions

BVOCs are assumed to play a strong role in ecological interactions in Amazonia (Figure 2). BVOC sources create volatile blends that can serve to identify the species of a recipient (Piva et al., 2019), allowing us to understand the nature of such communication (e.g. the identity and density of an attacking herbivore; Pinto-Zevallos et al., 2018), and can also direct the evolution of plant chemical diversity (Salazar et al., 2018).

Signalling within plants can be based on cascading signals of jasmonates, salicylates, and ethylene, but also other types of BVOCs such as GLV, methanol or isoprenoids (Filella et al., 2006; Matsui, 2016; Matsui et al., 2012; Seco et al., 2011). The function of their emission can be involved in: inducing the production of BVOCs that can downregulate floral volatiles to produce BVOCs associated with fruit ripening, inducing BVOC production for defensive purposes, or for individual plant coexistence (Kigathi et al., 2019; Ninkovic et al., 2019). However, to our knowledge, these processes have not been investigated in Amazonia.

Another type of signalling occurs between plants and other living organisms in ecosystems for reproduction, defence, awareness of neighbouring plants, and modulating adaptation and evolution (Fine et al., 2004; Laothawornkitkul et al., 2009; Salazar et al., 2018). Plants emit floral blends to attract specific pollinators to aid reproduction. As rewards for pollination they offer pollen, and also resins, although the latter more rarely, as for some Amazonian *Clusia* species (Bittrich & Amaral, 1997). Guarana trees emit higher amounts of (E)-β-ocimene during night to attract nocturnal bees (Krug et al., 2018). The preferences of bees for collecting pollen from other Amazonian plant species are nevertheless still unclear (Kaminski & Absy, 2006). Furthermore, the role of phyllospheric floral bacteria has been pointed out to be of importance for BVOC emissions (Peñuelas et al., 2014), although no information is available for the Amazonian rainforest. Other types of communication associated with reproduction involve the production of fruit odours for seed dispersal (Laothawornkitkul et al., 2009), for the seeds of a plant or of neighbouring plants (Gfeller et al., 2019), particularly in Amazonia with seed-ant mutualism (Youngsteadt et al., 2009).

BVOCs emitted for defensive purposes have characteristic blends, in both abundance and chemical diversity, are species-specific (Courtois et al., 2009; Sharifi et al., 2018), serve an awareness role with neighbouring plants (De Moraes et al., 2001; Kessler & Baldwin, 2001), and can affect plant chemical diversity (Salazar et al., 2018). Such interactions can also occur between aboveground plants and roots, with important implications for BVOC interactions within the soil ecosystem (Delory et al., 2016). Herbivory in tropical rainforests has been estimated to consume 12-30% of the foliar area annually, with insects dominating foliar consumption, at 680 kg ha^{-1} y^{-1} (Rinker & Lowman, 2004). The role of BVOC emission in the Amazonian rainforest induced by herbivory is thus expected to be substantial but has not been characterized on regional scales.

Plants, including their roots, can emit BVOCs to attract predators of herbivores (Aartsma et al., 2017; Sharifi et al., 2018). SQTs are good attractors of plant bodyguards (Rasmann et al., 2005) whereas isoprene repels them (Loivamäki et al., 2008). For example, the Amazonian ant *Allomerus octoarticulatus* can be attracted to damage from herbivory by its mutualistic plant *Hirtella myrmecophila* (Romero & Izzo, 2004), showing the complex interaction between plants and ants. In fact, the relationship between ants and plant size in Amazonia can shape arthropod communities (Izzo & Vasconcelos, 2005). The extent of the damage from herbivory feeds back on the defensive blends, as for cassava (Pinto-Zevallos et al., 2018), sometimes jeopardising the plant's protection (von Dahl et al., 2006).

Plants, microbes, and animals can emit BVOCs as direct toxins, deterrents, or repellents against herbivores (De Moraes et al., 2001; Kessler & Baldwin, 2001; Laothawornkitkul et al., 2009; Prestwich, 1984; Saikkonen et al., 1998; Sharifi et al., 2018). For example, Formicinae ants emit formic acid as a defensive strategy (Brütsch et al., 2017) or GLV plant emissions can prime neighbouring plants against herbivores (Engelberth et al., 2004). On the other hand, signalling can be negative, like isoprene that serves as a negative cue, informing insects where not to forage (Gershenzon, 2008; Laothawornkitkul et al., 2008).

Protection against pathogens and sealing wounds are also drivers for BVOC emissions (Laothawornkitkul et al., 2009; Ninkovic et al., 2019; Šimpraga et al., 2019). For example, the biosynthesis of natural rubber by *Hevea brasiliensis* is stimulated by wounding, releasing methyl jasmonate and ethylene (Duan et al., 2010), which is then oxidized during latex coagulation, sealing the wound (Piva et al., 2018). *Nicotiana tabacum* plants emit methyl salicylate when pathogenic infections are present, inducing the expression of defensive genes in neighbouring plants (Shulaev et al., 1997) and phytopathogenes can turn plants into sources of carbonyl sulphide (Bloem et al., 2012) rather than sinks as generally seen (Whelan et al., 2018). The role of the phyllosphere in defence against pathogens has been established for Amazonia (Azevedo et al., 2000; Gazis & Chaverri, 2015; Sia et al., 2013; Vaz et al., 2018), where pathogenic disease such as anthracnose can be especially important for modulating the expansion and production of guarana plantations (Bogas et al., 2015). BVOC emissions to protect against pathogens may thus be important for identifying plant diseases.

Lastly, abiotic factors driving BVOC emission can also alter ecological interactions. Amazonian plants have been shown to protect themselves against excessive heat: by emitting isoprene (Jardine et al., 2016b) and distinct monoterpene species (Jardine et al., 2017), by oxidizing isoprene within leaf tissues and therefore releasing MVK+MACR (Jardine et al., 2011a), or by emitting GLV due to high temperatures and drought as part of induced senescence processes (Jardine et al., 2015b). There are other abiotic factors altering ecological interactions. In Amazonia, rain can alter sesquiterpene speciation from soils (Bourtsoukidis et al., 2018). Ozone can affect plant physiology (Loreto et al., 2004). BVOC oxidation can disrupt plant olfactory cues (Vuorinen et al., 2004). Masking of BVOCs or ovipositional stimulants induced by herbivory may affect the range of the signal (Farré-Armengol et al., 2016b; Pinto et al., 2010). SQTs emitted by soils and vegetation have been shown to quench ozone within the canopy of an Amazonian rainforest (Bourtsoukidis et al., 2018; Jardine et al., 2011c). Thus, the abundance of ambient ozone regulates the distance over which the ecological BVOC signals are transported (Conchou et al., 2019). In fact, given the toxicity of ozone, trees have been shown to emit reactive BVOCs to quench the ozone levels (Bourtsoukidis et al., 2012). Additionally, ozone mixing ratios increase after biomass burning and urban pollution plumes in Amazonia (Wei et al., 2019), so these processes could be important for plant fitness and ecological interactions in the future Amazonia. At last, atmospheric CO_2 increase is expected to alter ecological interactions either by increasing BVOC emissions due to higher substrate availability, decrease BVOC emissions due to BVOC synthases competition in biosynthesis, or due to a modification of the emitted compounds (Yuan et al., 2009).

While the role of BVOCs in ecological interactions is widely accepted, it is currently unknown how these will regulate the cumulative BVOC release from Amazonia. Disturbing established communication links among trees and between trees and insects may have unforeseen consequences for the ecosystem and species protection from pathogens. Anthropogenic activity alters ecological interactions; therefore, the rapidly changing atmospheric conditions may be a highly important piece of the puzzle in understanding the BVOC dynamics within Amazonia.

5. Atmospheric impact

The impact of Amazonian BVOCs on atmospheric chemistry is highly dynamic, with strong diel and seasonal characteristics. The vast emissions of reactive BVOCs, in combination with high emissions of other trace gases, insolation, high temperature and humidity, and high OH concentrations make the Amazonian atmosphere a tropical photoreactor (Andreae, 2001). BVOCs emitted to the Amazonian atmosphere are rapidly oxidized by OH radicals during the day and more slowly by ozone, or by NO_3 radicals at night (Paulson & Orlando, 1996). Some of the BVOCs emitted are very reactive, such as isoprene towards OH (Nölscher et al., 2016) and SQTs towards O_3 (Jardine et al., 2011b). Isoprene, in particular, can deplete tropical OH concentrations, thus indirectly affecting BVOC oxidation (Taraborrelli et al., 2012) and the lifetimes of climate relevant gases such as methane.

OH reactivity is a measurable parameter quantifying the total loss frequency of OH radicals in the atmosphere, including BVOCs and other reactive trace gases. It can be used to assess how comprehensively the reactivity of BVOCs can be accounted for in Amazonia. The difference between the calculated OH reactivity vs. the observed OH reactivity indicates that there is a large portion of unexplained reactivity (OH missing reactivity) possibly due to unmeasured compounds not accounted for in the calculation of OH reactivity from the sum of the individual compounds. Missing reactivity measured at a single Amazonian rainforest location was strongly seasonal, being lower during the wet season (10 s^{-1}; missing OH reactivity of 5-15%) and higher during the dry season (62 s^{-1}; missing OH reactivity of up to 79%), suggesting that more unknown reactive compounds are present in the atmosphere during the dry season (Nölscher et al., 2016; Yang et al., 2016). Lower reactivity leads to a more oxidative atmosphere in the wet season, with high deposition of oxidation products onto wet surfaces and possible enhanced microbial activity on foliar surfaces that could influence the OH reactivity budget (Nölscher et al., 2016).

The gas-phase oxidation of BVOCs can form new particles by nucleation (Kirkby et al., 2016), or the oxidised BVOCs can condense onto pre-existing particles, undergo heterogeneous reactions on particle surfaces, be processed in clouds, or undergo further atmospheric degradation and deposition. Photochemistry is an important Amazonian source of oxygenated VOCs (Yáñez-Serrano et al., 2015), particularly for short-chain compounds (Seco et al., 2007). A recent study has demonstrated the strong role of isoprene oxidation, which contributes ca. 20% of the organic aerosols (OAs) produced in Amazonia (Schulz et al., 2018). The contribution of other BVOCs to aerosol formation in the tropical rainforest is more difficult to estimate, but SQTs have been estimated to contribute 0.4-5% to submicron OAs (Yee et al., 2018). Shrivastava et al. (2019) recently reported that isoprene and terpenes can contribute almost half of the Amazonian biogenic secondary organic aerosols (SOAs).

Aerosols have profound implications on the radiation balance locally, regionally and globally, either directly by scattering (Artaxo et al., 2013a; Kulmala et al., 2013) or absorbing solar radiation (Boucher et al., 2013) or indirectly by impacting cloud and rain formation processes. Furthermore, they can boost global primary production up to 25% for Amazonian ecosystems via diffuse radiation fertilization (Cirino et al., 2014; Koren et al., 2012; Rap et al., 2018). Therefore, the presence of BVOCs influences the associated albedo by modifying the number and size of cloud condensation nuclei (CCN) and cloud droplets, affecting how the clouds reflect and absorb light (Boucher et al., 2013) and thus the radiation balance (Andreae & Crutzen, 1997; Artaxo et al., 2009; Sena et al., 2013) and hydrological cycle (Sheil, 2018). BVOCs and their role in SOAs, dominant type the fine-mode aerosol mass (Martin et al., 2010), could ultimately affect the radiative cooling of the Earth (Ehn et al., 2014), particularly in Amazonia where sulphur compounds are at low concentrations (Kirkby et al., 2016) and the radiation balance is driven by organic aerosols (Artaxo et al., 2013a). A significant fraction of SOAs can act as CCN formed from BVOCs in the Amazonian wet season (Pöschl et al., 2010). The low CCN particle concentrations lead to larger cloud droplets producing clouds at lower altitudes that have higher rain efficiency (Rosenfeld, 1999), intensifying the role of BVOCs in aerosol and cloud dynamics. The formation of new particles at the planetary boundary layer has not been observed in Amazonia. BVOC species are instead elevated by deep convection and converted into condensable species in the upper troposphere, forming new aerosol particles and increasing the loading of OAs, which can then be transported down to the planetary boundary layer (Andreae et al., 2018; Schulz et al., 2018; Figure 2).

BVOCs can also affect radiative forcing by their degradation in the atmosphere (with CO_2 as an end product) and by their perturbation of the lifetime of other greenhouse gases such as methane, ozone (Guenther, 2002), and further reactive gases such as CO (Collins et al., 2002). This is estimated to add 0.16 Pg C y^{-1} to the amount of global atmospheric CO_2 (Suntharalingam et al., 2005), which can increase CO_2 levels by 0.07 ppm y^{-1}, and can have a significant impact on the results of inverse model investigations of CO_2 sources. Because BVOCs deplete OH faster than methane (for which the primary sink is OH), methane will have a longer lifetime in the atmosphere (Collins et al., 2002). Alternatively, tropospheric ozone is formed via BVOC oxidation when sufficient NOx is available, adding to the radiative forcing of greenhouse gases.

NOx levels are low (ca. 0.4 ppb) in the atmosphere over the undisturbed Amazonian rainforest (Liu et al., 2016), particularly during the wet season when air masses arrive predominantly from the northeast over mostly pristine rainforest (Pöhlker et al., 2019). NO from soils that reacts with O_3 to form NO_2 inside the canopy is the main source of NOx. This NO_2 is deposited on the leaves of the very dense rainforest canopy, reducing the contribution of soil NO emissions to the levels of NOx above the canopy (Jacob & Wofsy, 1990). The direct loss by reaction of O_3 with BVOCs outcompetes O_3 formation under these pristine conditions, thereby leading to a decrease in O_3 (Jacob & Wofsy, 1990; Scott et al., 2018). O_3 budgets are thus mainly controlled by transport from above (downdrafts from convective storms (Dias-Júnior et al., 2017; Gerken et al., 2016) and deposition to the canopy, with little net effect from photochemistry (Jacob & Wofsy, 1990).

NOx levels increase significantly during the dry season due to changes in wind direction from the easterly and southeasterly fetch regions, transporting considerable amounts of pollution from burning biomass and human activities (Bela et al., 2015; Pacifico et al., 2015). Consequently, O_3 levels also increase during this season (8-15 ppb in the wet season, 15-50 ppb in the dry season at midday) (Andreae et al., 2015; Artaxo et al., 2013a, Figure 5). The concentrations of trace gases and particles are thus strongly seasonal. In fact, an increase in NOx mixing ratios (to >1 ppb) can affect the oxidative pathways (i.e. HO_2 or NO pathway; Liu et al., 2016) of BVOC peroxy radicals, thus altering photochemistry, even in this region where NOx levels are generally low. The central Amazonia plume has been reported to significantly increase O_3 levels by 35% at 70 km downwind of Manaus, whereas NOx levels increased by <20% relative to remote areas, indicating the strong role of BVOC oxidation in forming O_3, in areas where NOx levels have increased due to pollution (maxima of up to 6 ppb; Wei et al., 2019). Enhanced urban pollution and plumes from burning biomass alter BVOC emissions by inducing further emissions of highly reactive BVOCs (Bolsoni et al., 2018) and thus, altering the dynamics of natural aerosols, with an increase in SOAs formed by BVOC oxidation (Shrivastava et al., 2019). The burning of biomass can profoundly alter SOA composition, although increases in organic submicron particulate matter during the dry season are also due to increased BVOC emissions combined with reduced deposition (de Sá et al., 2019; Williams et al., 2016).

Canopy structure is another very important parameter in determining the impact of BVOCs in the atmosphere. The dense and tall canopy of the Amazonian rainforest can stratify air masses, with an intermittent coupling of the upper canopy and the atmosphere above. Air is poorly mixed within the canopy, particularly at night when conditions are stable, with occasional exceptions of periods with bursts of intermittent turbulence (Freire et al., 2017). The lower part of the canopy is characterized by a thermal inversion, hindering mixing between the canopy and the forest floor (Nölscher et al., 2016; Santana et al., 2018).This feature can affect the residence times of emitted BVOCs and their turbulent transport out of the forest canopy (Bakwin et al., 1990; Fitzjarrald et al., 1988; Gerken et al., 2017). BVOCs can thus remain trapped within the canopy, becoming oxidised before reaching the atmosphere above. For example, 50-70% of O_3 reactivity within the canopy has been attributed to the ozonolysis of highly reactive SQTs (Bourtsoukidis et al., 2018; Jardine et al., 2011c; Yee et al., 2018).

Isoprene oxidation by OH produces, among many other products, isoprene peroxide radicals (ISOPOO). These radicals can react with HO_2 to form isoprene hydroxyhydroperoxides (ISOPOOH) or with nitric oxide (NO) to produce mostly methyl vinyl ketone and methacrolein. Both pathways (HO_2 and NO) are important in Amazonia, despite their strong seasonality (Liu et al., 2016). The formation of isoprene epoxydiols can lead to the growth/formation of SOAs, mostly in the upper troposphere (Schulz et al., 2018). ISOPOOH levels can nevertheless decrease in polluted conditions (Liu et al., 2016), with implications for OA levels, because higher NOx levels can suppress the production of SOAs derived from isoprene epoxydiols (IEPOX) (de Sá et al., 2017; Schulz et al., 2018). Isoprene was previously thought to yield very low quantities of condensable material under low NOx levels (Pandis et al., 1991). More recently, gas-phase IEPOX, second-generation products of isoprene oxidation under RO_2+HO_2 chemistry (Surratt et al., 2010), and reactive uptake have been proposed as an additional pathway. The IEPOX may be responsible for the production of observed SOA isoprene tracers, such as 2-methyltetrols found in the particle phase of Amazonian samples (Carlton et al., 2009; Claeys et al., 2004; Kroll et al., 2005).

In summary, BVOCs can have very strong impacts on the atmospheric chemistry over Amazonia. BVOC emissions determine oxidant regimes, as they modulate the major atmospheric oxidant, OH, and they can lead to pollutant production (e.g. tropospheric ozone) when the pristine Amazonian conditions are altered.

6. Depositional processes

Deposition of BVOCs can be divided into wet and dry deposition onto surfaces, biological uptake, and physicochemical processes at the leaf-atmosphere interface (Figure 2). In Amazonia, wet deposition can be an important sink for trace gases. Polar compounds are particularly well washed off by rain. Moreover, BVOC oxidation products can be formed in the water layer of leaves and other surfaces. This process is especially important during the wet season and periods of rain and contributes to the observed general decrease in the concentrations of trace gases. For example, organic acids such as formic and acetic acid can contribute up to 90% of rain acidity in Amazonia (Andreae & Andreae, 1988; Jardine et al., 2011b). Dry deposition depends on the movement of air, the vertical stability of the boundary layer, the chemical properties of the species, and the nature of the depositional surface (Stickler et al., 2007), which may be important in Amazonia, particularly at night with 78% of isoprene lost to surface deposition (Wei et al., 2018). Further information is needed to understand dry deposition in Amazonian ecosystems, which may have been underestimated as has been demonstrated over a dense tropical rainforest in Costa Rica (Karl et al., 2004).

Vegetation takes up compounds via stomatal or non-stomatal processes, where re-metabolisation can occur (Matsui, 2016). The ambient mixing ratio of a compound regulates its uptake or emission depending on the compensation point. Compensation points for Amazonian ecosystems have been reported to be <0.6 ppb for acetaldehyde and formaldehyde (Rottenberger et al., 2004) and <0.3 for formic and acetic acid (Kuhn et al., 2002a) based on leaf level measurements. Data estimated on an ecosystem level were found to range around 1.4 and 2.1 ppb for formic and acetic acid, respectively (Jardine et al., 2011b). In view of the possible bio-facilitation for plant VOC uptake (Matsui, 2016), more information is needed to understand the function of bi-directional BVOC exchange by Amazonian ecosystems.

Bacteria are another sink or source for BVOCs. They can take up BVOCs as a source of carbon (Ginkel et al., 1987) when levels are not toxic and can detoxify BVOCs above toxic levels (Marmulla & Harder, 2014). For example, isoprene can be taken up by tropical soils (Cleveland & Yavitt, 1997), depending on the atmospheric mixing ratio of isoprene and with decreasing rates of uptake under drought conditions (Pegoraro et al., 2005). Bacterial communities in the phyllosphere may also be a BVOC sink (Farré-Armengol et al., 2016a). Phenol degradation has been observed in phyllospheric communities elsewhere (Sandhu et al., 2007). All these phyllospheric sink processes for BVOCs could be especially important in Amazonia, given its abundant phyllospheric communities.

Processes taking place at the leaf surface such as oxidation and adsorption/desorption are important for ecological interactions, plant physiology, and accounting for gross and net BVOC emissions. Oxidation can occur in the stomatal cavity or at the leaf surface as it serves to quench ROS damage in vegetation. Examples have been reported for monoterpenes (Loreto et al., 2004), by semi-volatile organic compounds exuded by glandular trichomes (Jud et al., 2016), and specifically in Amazonia for isoprene (Jardine et al., 2011a). This oxidation can lead to the production of oxygenated BVOCs such as ketones and aldehydes (Jardine et al., 2011a; Jud et al., 2016; Pinto et al., 2010). This within-leaf oxidation process is of particular importance for dry deposition estimates worldwide. When fast metabolic conversion of oxygenated BVOCs was incorporated into a global chemistry transport model, Amazonia showed an increased annual dry deposition flux of 75% (Karl et al., 2010).

Adsorption/desorption can occur on surfaces, such as plant cuticles (Müller & Riederer, 2005) and water films and may be important in humid places such as Amazonia, even though their functioning is not yet fully understood. Water layers on the upper surfaces of leaves may strongly influence the absorption of water by leaves, stomatal conductance, pathogenic infection, nutrient leaching, and adsorption of pollutants (Aryal & Neuner, 2010). Oxygenated BVOCs may thus be adsorbed onto water films and are then released upon the evaporation of the films. This process may occur in wet environments such as Amazonia.

In summary, BVOC deposition is dependent on many factors, including the nature and concentration of the compound and the existent meteorology. Despite high uncertainties, in an attempt to quantify the magnitude of BVOC deposition, we used approximations from literature. Dry deposition has been estimated to occur onto leaf surfaces as well as to soil surfaces with shares of 70% and 30%, respectively (Karl et al., 2010). These estimates are expected to be higher for leaf surfaces in Amazonia due its larger leaf area. On the other hand, in Amazonia, rain wet deposition occurs 90% to soil surfaces, with only 10% being intercepted by vegetation (Czikowsky & Fitzjarrald, 2009). In addition, fog wet deposition is expected to occur at high percentage values (Shimadera et al., 2011), although no estimates have been found so far for Amazonia. A proper characterization of Amazonian BVOC deposition flux could result in higher estimates of gross BVOC production, larger than previously thought. The aforementioned processes may account for active and partly unexplored sinks, which have to be considered in regional and global modelling exercises.

7. Climate change, land-use change, and feedbacks

Amazonian ecosystems may be moving towards tipping points. For example, a temperature increase of 4°C or deforestation exceeding 40% of the forested area (Nobre et al., 2016) due to human intervention as land-use change possibly lead to savannisation (Marengo et al., 2011) and limit rainfall in synergistic interactions with the impacts of climate change.

Climate change is expected to alter Amazonian ecosystems, since increased warming will be combined with decreased precipitation (IPCC, 2013). Accompanying effects are drought associated with El Niño–Southern Oscillation (ENSO) anomalies and changes in the surface temperature of the Atlantic Ocean (Leitold et al., 2018), increased frequency and intensity of heat waves (Perkins-Kirkpatrick & Gibson, 2017), and increased duration and intensity of dry (Adams et al., 2017) and intensity of wet (Leite-Filho et al., 2019; Mori and Becker, 1991) seasons. Increasing temperatures and drought (Aragão et al., 2018; Feldpausch et al., 2016; Leitold et al., 2018; Li et al., 2008; Marengo et al., 2016; Pfannerstill et al., 2018; Yang et al., 2018) and intensified dry seasons (Sena et al., 2018), which are slowly drying Amazonia (Esquivel-Muelbert et al., 2018), have already been observed.

These conditions of thermal and drought stress have multiple effects in Amazonian ecosystems. An intensified dry season can particularly increase the frequency of fires (Silva Junior et al., 2019), reduce net primary productivity, and accelerate canopy turnover (Leitold et al., 2018). Drier conditions can lead to an overall decrease in BVOC production (although drought may induce transient GLV emission (Jardine et al., 2015b) (Figure 6). Other effects are higher irradiance due to lower cloud cover (Sena et al., 2018) and higher temperatures, which ultimately lead to a net increase in BVOC production (Jardine et al., 2017; Pfannerstill et al., 2018) of both BVOCs associated with stress (Jardine et al., 2015b) and other unknown highly reactive compounds (Pfannerstill et al., 2018). If threshold limits for heat and radiation are exceeded, increased tree mortality will naturally reduce BVOC emissions. Altered ecological interactions (e.g. insect outbreaks or altered floral compositions) and increasing pollution can modify BVOC emissions, with unforeseen consequences. However, an intensified wet season, could lead to stronger storms (Nelson et al., 1994) and floods (Barichivich et al., 2018), increasing BVOC production associated with root anoxia. Tree mortality associated with storms (Aleixo et al., 2019) have potential implications for atmospheric chemistry because of increased BVOC emission associated with anoxia from floods.

These effects ultimately lead to increased tree mortality (Aleixo et al., 2019; Brando et al., 2019) aggravated by deforestation, and, therefore, to decreased BVOC production due to biomass reduction, which further feeds back on a changing climate by altering ecological interactions and aerosol dynamics. Additionally, the loss of biodiversity (Nobre et al., 2016) caused by climate change (Chapin III et al., 2000) and deforestation (Barlow et al., 2007) can alter ecological interactions and associated BVOC emissions.

Agricultural practices, including but not limited to biomass burning, and urbanisation are the two main impacts of land-use change affecting Amazonia. Twenty percent of the original forest in the Brazilian Amazonia has been cleared in the last three decades (Bullock et al., 2020; Davidson et al., 2012), particularly from the so-called arc of deforestation in southern and southwestern Amazonia (Leite-Filho et al., 2019; Pöhlker et al., 2019), with a sharply increasing trend during the past several years. Deforestation has implied substantial environmental changes (Davidson et al., 2012) and forest disturbance (Bullock et al., 2020), such as water stress due to shallower roots (Huete et al., 2006) that causes an energy imbalance, loss of biodiversity, changes to carbon storage (Huete et al., 2006), and an overall decrease in BVOC emissions due to the loss of biomass (Scott et al., 2018). Biomass burning also profoundly affects the oxidation pathways of BVOCs and increases emissions of air pollutants (Bulbovas et al., 2014) by clearing land mainly for soy production (Bulbovas et al., 2007), oil palm production (Jardine et al., 2016a) and cattle ranching (Figure 5). Soy crops are very sensitive to tropospheric ozone (Bulbovas et al., 2007), so higher ozone mixing ratios will feed back to more deforestation to counteract decreased soy productivity (Pimentel, 2011).

Increasing urbanisation (Richards & VanWey, 2015) and rural development (Nobre et al., 2016) are also drivers of land-use change in Amazonia. The urban population of the region has increased from about 1 million to 11 million in the last 50 years (1960–2010) (Medeiros et al., 2017). In central Amazonia, the city of Manaus has 2 million inhabitants, and pollution sources include vehicular emissions, refinery operations, and electricity generation. Even though anthropogenic emissions are lower than for other regions around the world, Amazonian air chemistry is highly sensitive, amplified by the high solar irradiance and concentrations of water vapour in an environment with plentiful BVOC emissions. NOx and ozone production are much higher in urban plumes (Kuhn et al., 2010; Trebs et al., 2012; Wei et al., 2019) and have profound impacts on atmospheric chemistry and physics by increasing biogenic SOA production by 60-200% (Shrivastava et al., 2019) and altering gaseous (Liu et al., 2016) and particle (de Sá et al., 2017) chemical pathways. A programmed change from fuel oil and diesel to natural gas is nevertheless projected to improve urban air quality (Medeiros et al., 2017).

At a global scale BVOC emissions may increase in a warmer climate (Peñuelas & Staudt, 2010) due to higher plant metabolism and diffusion, but in Amazonia, the effects of climate could increase the emission of stress-related BVOCs and the effects of land-use change could lead to a decrease in BVOCs due to loss in biomass. An increase of BVOCs due to warmer temperatures would lead to more SOA having a cooling impact through the direct light scattering or indirectly by the increase in cloud cover. This would lead to a negative radiative forcing. Additionally, more SOA would lead to more diffuse radiation, boosting GPP (Rap et al., 2018) and thus the uptake of atmospheric CO_2. On the other hand, an increase in BVOCs would lead to an increase of the CH_4 lifetime. In the presence of sufficient NOx, an increase in tropospheric ozone could be a consequence resulting in a warming effect. A decrease in BVOC emissions, however, would have opposite effects on the radiative balance. Moreover, the net effects of altered ecological interactions (Niederbacher et al., 2015), higher oxidation capacity, changes in species composition, and increased flooding on BVOC responses remain unknown for Amazonian ecosystems. Unfortunately, there is almost no information about the impact of BVOCs in the Amazonian hydrological cycle, with effects for the rest of the South American continent (Boers et al., 2017; Rocha et al., 2018). Thus, a substantial change in Amazonian BVOC emission may have strong climatic impacts at a regional and even at global levels, but there are large uncertainties in current estimates.

8. Recent evolution of isoprene emissions in Amazonia

We investigated the evolution of isoprene fluxes in Amazonia using modelled isoprene emissions from the CAMS-GLOB-BIO dataset (Granier et al., 2019), and satellite-based estimates (Bauwens et al., 2016) for 2005-2014. The CAMS-GLOB-BIO global dataset is based on the Model of Emissions of Gases and Aerosols from Nature (MEGANv2.10; Guenther et al., 2012) and includes monthly isoprene emissions at 0.5ºx0.5º resolution. The MEGAN model was driven by re-analysed ERA-Interim meteorological fields (Dee et al., 2011). Global annual land cover was provided by the ESA-CCI dataset (Climate Change Initiative of the European Space Agency, ESA, 2017), processed in order to be consistent with plant functional types (PFT) used in the MEGAN model (see S.I.3). On the other hand, for the satellite data we used formaldehyde columns from the OMI satellite sensor and an inverse modelling framework (see S.I.4.). Both techniques were used successfully for estimating isoprene fluxes in this region in the past (Barkley et al., 2009; Pacifico et al., 2011). Seasonal and inter-annual variations of the modelled and satellite-based isoprene fluxes over the Amazonian region (5°N-13°S, 46-77°W) are shown in Figure 7. Both approaches display similar magnitudes and seasonal patterns, with slightly higher fluxes for modelled isoprene. The decrease of isoprene fluxes during the wet season is observed in the complete time series of modelled isoprene (1992-2015) (Figure S.I.2). Since biomass burning during the dry season affects the formaldehyde columns, only wet season data are used for the trend calculation, but it has to be noted that both modelled and satellite isoprene fluxes show a decrease for the reported period. The decrease of isoprene fluxes during the wet season can be partly attributed to large and rapid changes in land cover (Acosta Navarro et al., 2014). Even though the rate of deforestation decreased in the period of 2005-2014 (Artaxo et al., 2013b), studies point out that drought-related fires may have increased during this period (Aragão et al., 2018). In fact, satellite observations suggest a widespread forest degradation due to deforestation (Bullock et al., 2020).

The modelled isoprene flux indicates an increase of isoprene emissions during the dry season for 1992-2015, with peaking fluxes in El Niño years (1997, 2015; Figure S.I.2). Given that sesquiterpenes are temperature-dependent and emitted as a plant response to environmental stresses (Zhao et al., 2017), we have calculated the sesquiterpene to isoprene ratio as a proxy of environmental stress (Figure 8). The ratio significantly increases over time, suggesting that Amazonian forest is undergoing increased heat stress due to climate warming.

These results underline the combined effect of climate change and land use change affecting BVOC fluxes. During the dry season, strong environmental stresses to Amazonian vegetation occur at higher intensity and frequency over time. This view is supported by the increasing ratio of sesquiterpene to isoprene fluxes. During the wet season, the decrease in isoprene emissions may be partly explained by the rainforest loss due to deforestation, although further analysis is needed to prove this hypothesis.

9. Research priorities

Kesselmeier et al. (2009) identified several research priorities that need to be addressed to better understand BVOC dynamics in Amazonia. However, some of them remain unaddressed even one decade later. Intensive efforts towards integrated investigations of emissions, chemistry, transport, and cloud processes, with campaigns such as Brazilian-Air 2010, GOAMAZON (2014-2015), ACRIDICON (2014), and ATTO (2012-present), which comprised observations from tower-based measurements (at TT34, K34, ATTO) and aircraft-based studies (ACRIDICON and GOAMAZON) have been made or planned for the near future (CAFÉ-Brazil 2020). These studies provided essential information, particularly in understanding the fate of emitted isoprene in the atmosphere. Many studies have now addressed a wide range of biogenic VOCs, including oxygenated BVOCs, aromatic compounds, sulfurous compounds, and oxidation products (Alves et al., 2016; Bourtsoukidis et al., 2018; Jardine et al., 2011b, 2011a, 2014, 2015a, 2015b, 2017; Liu et al., 2016; Paralovo et al., 2015; Yáñez-Serrano et al., 2015, 2016, 2018b; Yee et al., 2018), although new studies should aim to characterize unknown reactive compounds to better understand atmospheric reactivity, particularly in the dry season (Nölscher et al., 2016; Pfannerstill et al., 2018). Progress has been made in understanding of the impact of BVOCs on oxidant and aerosol distributions (Andreae et al., 2018; de Sá et al., 2017, 2019; Liu et al., 2016; Nölscher et al., 2016; Pfannerstill et al., 2018; Schulz et al., 2018; Shrivastava et al., 2019), the processes controlling the seasonal (Alves et al., 2016, 2018; Wei et al., 2018; Yáñez-Serrano et al., 2015, 2018a) and spatial (Barkley et al., 2009, 2011; Bauwens et al., 2016; Salazar et al., 2018; Taylor et al., 2018, 2019) variations of BVOCs, flooding (Bracho-Nunez et al., 2012), and ecological interactions (Salazar et al., 2018). However, more process-based studies are essential, such as those using laboratory and enclosure methods, to understand mechanistically what is happening at foliar surfaces, including phyllospheric processes, BVOC sink processes, relationships between BVOCs and the carbon and water cycles, ecological interactions, and the response of BVOCs to climate change and deforestation in Amazonia. Model simulations could thus become more process-based, reducing the uncertainty of predictions. For example, strong efforts are currently being made to understand BVOC variation across plant populations beyond plant functional type, which is too broad to represent variability in Amazonian ecosystems (Taylor et al., 2018).

Understanding how BVOC emissions would affect CCN and rain formation, including rain acidity (Jardine et al., 2011b), is important as clouds can have an effect on the radiative forcing by reflecting radiation and by increasing diffuse radiation thereby increasing GPP, as well as having impacts on the hydrological cycle (Koren et al., 2012). But the effect of increased flooding, as a response to climate change, must also be understood at an ecosystem level, particularly the role of anoxia BVOCs in CH_4 and CO_2 cycles in flooded ecosystems. More effort is needed to obtain a more regional and long-term vision of BVOCs in Amazonia, which can only be approached with synergistic investigations of different Amazonian ecosystems, to understand the timing and duration of the response dependency of BVOC dynamics. This review demonstrates the necessity of understanding the signals of BVOC feedback loops in response to climate and land-use changes in Amazonia, for which understanding the potential impacts of the role of BVOCs in ecological interactions is crucial, a subject rarely studied in Amazonia despite its enormous biological productivity and biodiversity. Understanding how these interactions can be modulated by climate change is also critical. Some ecological theories have been proposed to account for hyperdominant species in Amazonia (ter Steege et al., 2013), which study the evolution and distribution of defensive compounds as a function of species composition. For example, *Protium* genus produces large quantities of phenolics, which may increase colonisation of its species (Salazar et al., 2018). This approach may be used to study the ecological interactions of BVOCs in Amazonia. Climate change and pollution increase the oxidative capacity of the Amazonian atmosphere (Nölscher et al., 2016; Pfannerstill et al., 2018; Yáñez-Serrano et al., 2015), but the signals of the BVOC responses in the feedback loops remain unknown. Similarly, the signal of the BVOC response to an intensified wet season remains unknown. The responses of BVOCs to global change in Amazonia, either as a direct response to stress (e.g. increase drought, increase in UVB or nutrient availability) or as an indirect response due to the extinction of BVOC sources (e.g. tree mortality or agricultural expansion), are key research priorities for understanding how Amazonian ecosystems function and how they will be modified in the future. This review suggests that warming and associated drying, combined with the rate of deforestation, deforestation and associated drying is and will be the most determinant in the fate of BVOCs in Amazonia (both for chemistry and physics), impacting the radiative forcing of the atmosphere and the hydrological cycle. Deforestation is a major threat to Amazonia, with >10000 km^2 between the period between August 2018 and July 2019, the highest annual loss since 2008 (Barlow et al., 2020). Even the most optimistic climatic scenarios where forest protection policies are implemented predict substantial deforestation in Amazonia (Pöhlker et al., 2019; Soares-Filho et al., 2006). This trend indicates a major loss of forest biomass, potentially reaching threshold levels with difficult recovery. This loss will affect not only the tropical and extra tropical carbon and water cycles, but also the BVOC exchange between the surface and the atmosphere. Actions such as large-scale forest restoration (Bastin et al., 2019) and the promotion of services (Šimpraga et al., 2019) provided by Amazonian ecosystems may therefore help to mitigate these impacts of deforestation. Human action will thus delineate also the future of BVOCs in Amazonia.

10. Acknowledgments

AMYS, JP, IF and JL acknowledge funding for their research provided by the Spanish Government grant CGL2016-79835-P, the European Research Council Synergy grant ERC-SyG-2013-610028 IMBALANCE-P and the Catalan Government grant SGR 2017-1005. Furthermore, AMYS acknowledges the Spanish Ministry of Education and Science for her Juan de la Cierva-Incorporación grant. She also truly thanks Paloma Yañez for her help in the design of Figure 6. Research on the satellite-derived emission estimates was supported by the SOLFEO project funded by the European Space Agency (ESA), by the TROVA PRODEX and the ALBERI STEREO III projects funded via the Belgian Science Policy Office (BELSPO). AG acknowledges his funding source: US NSF AGS award #1829074. PA acknowledge support from FAPESP – Fundação de Apoio à Pesquisa do Estado de São Paulo, grant number 2017/17047-0. JW and EB acknowledge the support by the German Federal Ministry of Education and Research (BMBF contract 01LB1001A and 01LK1602B) and the Brazilian Ministério da Ciência, Tecnologia e Inovação

(MCTI/FINEP contract 01.11.01248.00) as well as the Amazon State University (UEA), FAPESP, CNPq, FAPEAM, LBA/INPA, and SDS/CEUC/RDS-Uatumã. E.G.A. was funded by a BMBF (Bundesministerium für Bildung und Forschung). KS and JD acknowledge the Copernicus Atmosphere Monitoring Service project CAMS-81: Global and Regional Emissions funded by European Commission through European Center for Medium-Range Weather Forecast (ECMWF). Neither the European Commission nor ECMWF is responsible for any use that may be made of the CAMS Information.

11. Additional Information

Competing Interests: The authors declare no competing interests.

Data accessibility: Data is available upon request to corresponding author.

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13. Figures

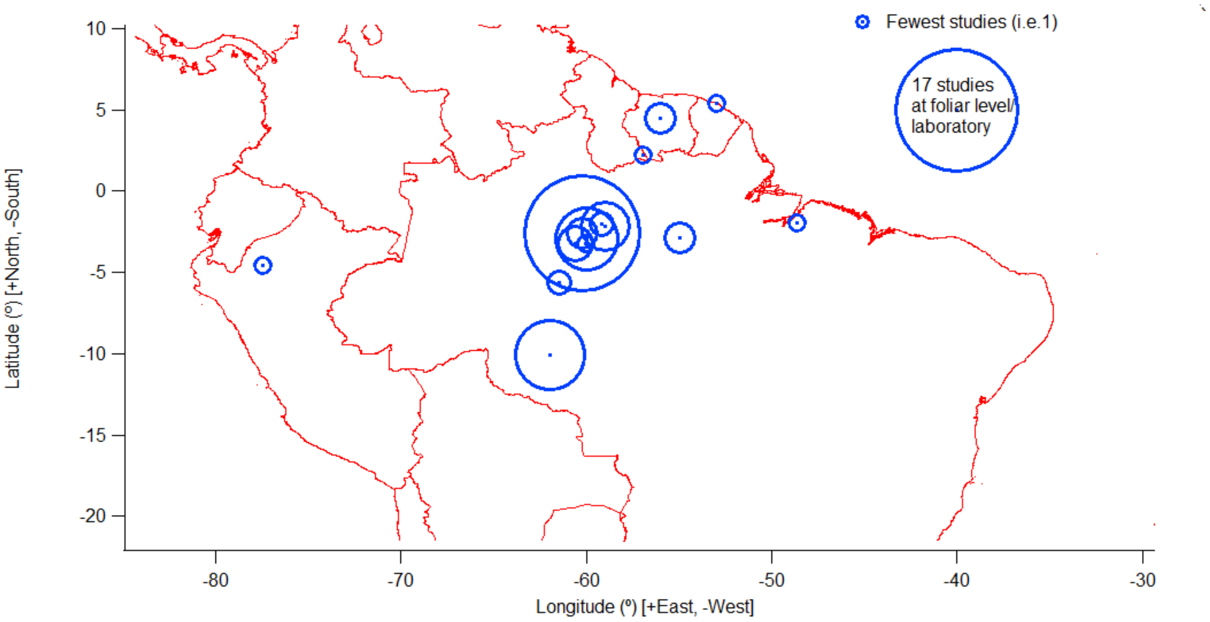

Figure 1: Map of Amazonia with the distribution and frequency of published BVOC measurements. The centres of the circles represent the locations of the measurements, and the sizes of the circles represent the number of published studies of BVOCs. This graph was derived from the information of Table 1 and S.I.1.

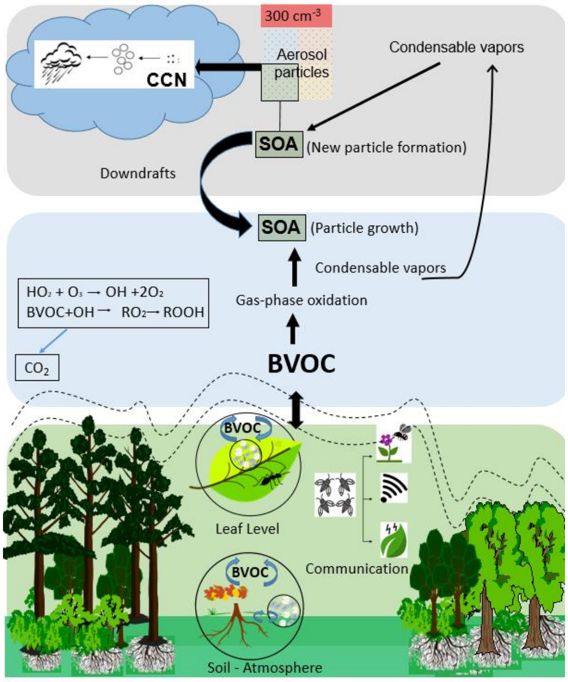

Figure 2: Schematic showing the BVOC dynamics in a pristine Amazonian atmosphere, including sources and interactions, BVOC oxidation in the atmosphere, and subsequent aerosol production influencing cloud droplet formation and cloud dynamics. CCN stands for cloud condensation nuclei and SOA stands for secondary organic aerosol.

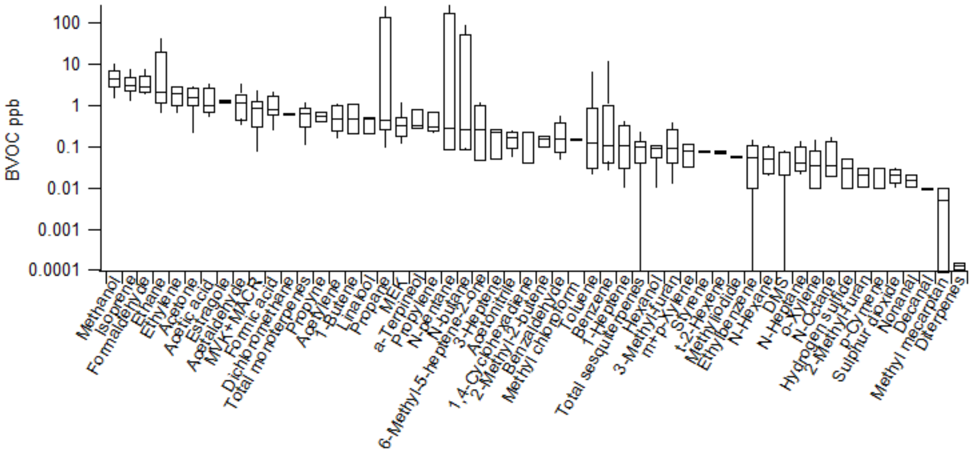

Figure 3: Whiskers box plot of all measured ambient concentrations (in ppb) of BVOCs in Amazonia to date. The ends of the box are the upper and lower quartiles showing the interquartile range, and the median is marked by a horizontal line inside the box. The whiskers are the two lines outside the box that extend to the highest and lowest observations.

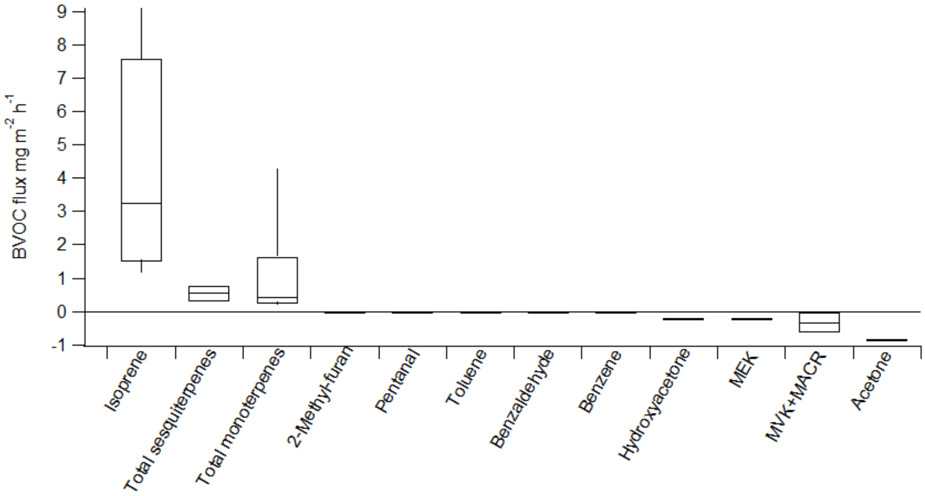

Figure 4: Whiskers box plot of all measured ecosystem fluxes (in mg m^{-2} h^{-1}) of BVOCs in Amazonia to date. The ends of the box are the upper and lower quartiles showing the interquartile range, and the median is marked by a horizontal line inside the box. The whiskers are the two lines outside the box that extend to the highest and lowest observations.

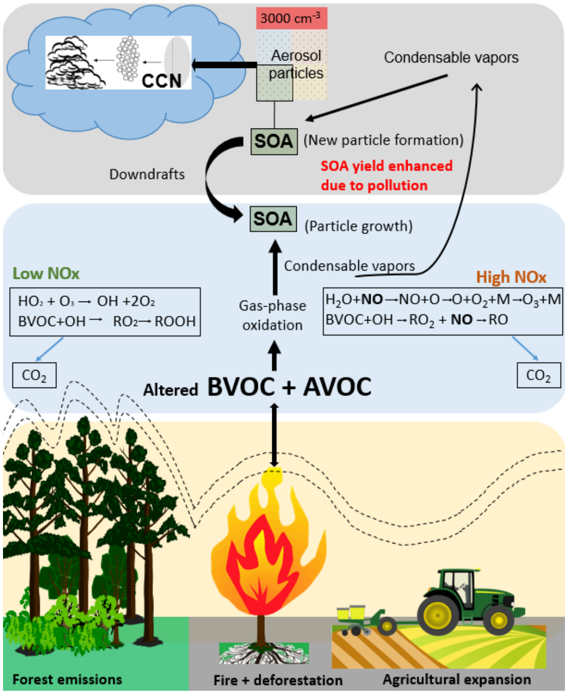

Figure 5: Schematic showing BVOC dynamics in a polluted Amazonian atmosphere, including BVOC sources and interactions, interaction with anthropogenic volatile organic compounds (AVOCs), BVOC oxidation in the atmosphere, and subsequent aerosol and cloud dynamics. CCN stands for cloud condensation nuclei and SOA stands for secondary organic aerosol.

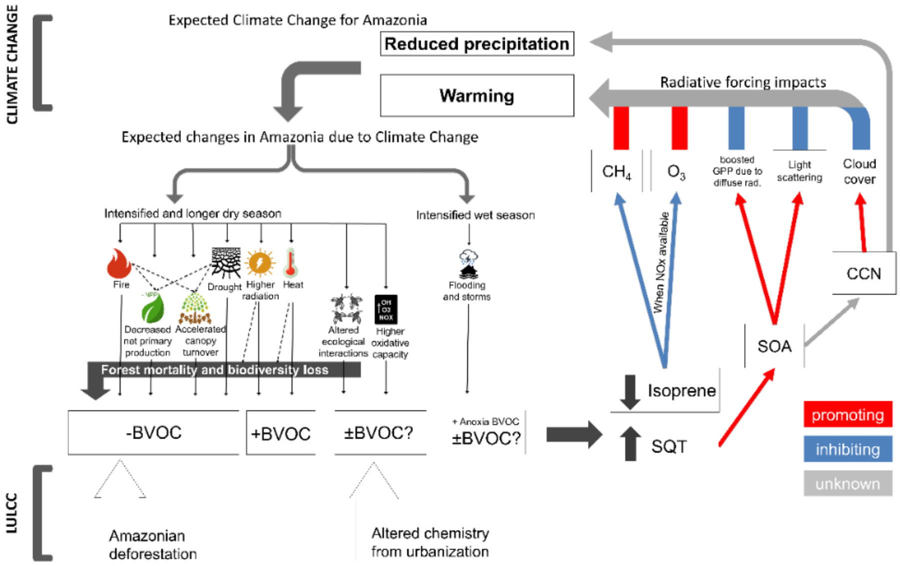

Figure 6: Proposed feedback loops for the impacts of climate and land-use changes in Amazonian BVOCs and how these impacts will feed back into the system. The dashed arrows represent the situation where threshold limits are reached (i.e. heat can stimulate BVOC emissions until the point where heat is detrimental to plant fitness, thereby decreasing BVOC emissions). Red colour stands for promoting and blue colour for inhibiting. Grey arrows indicate inconclusive/unknown effects. LULCC stands for Land Use Land Cover Change.

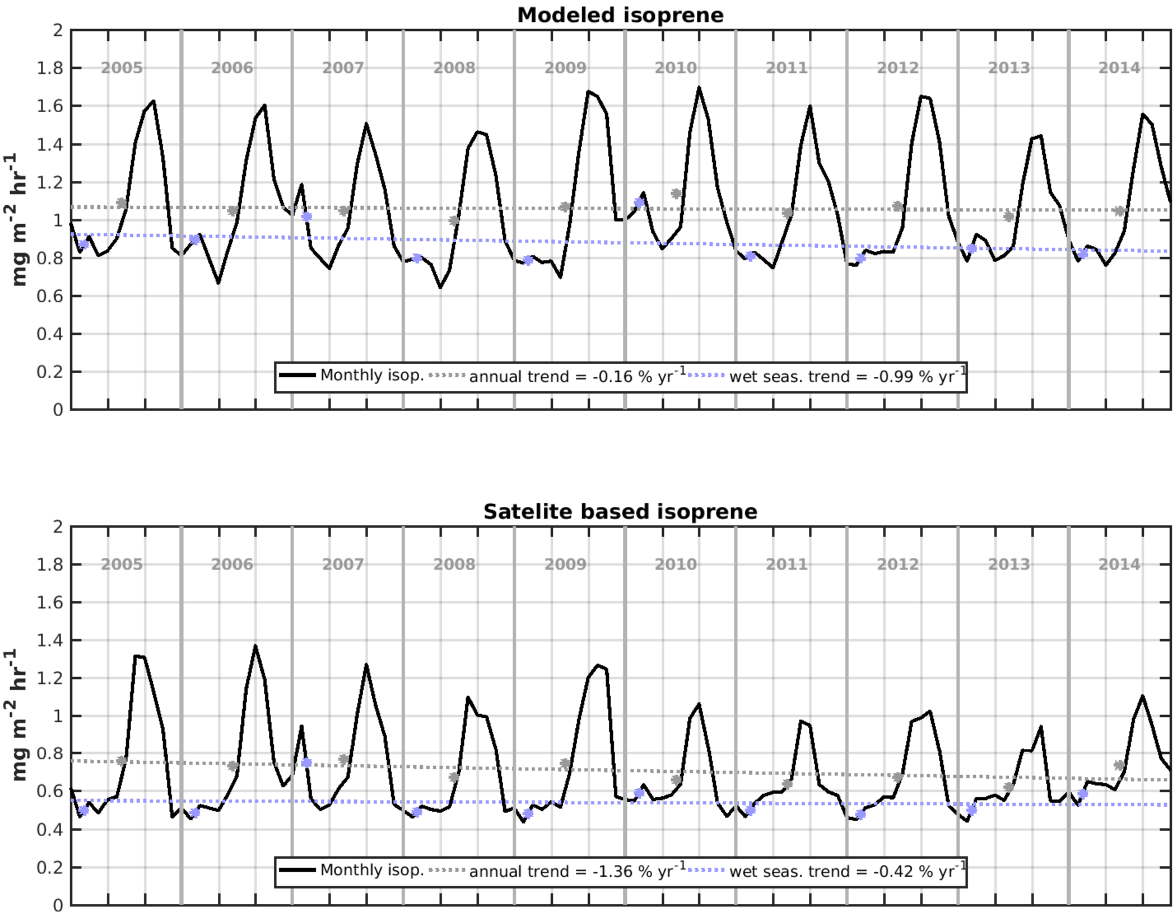

Figure 7: Monthly top-down isoprene flux estimates based on global model simulations using MEGAN (top) and based on the OMI satellite formaldehyde columns (bottom) over 2005-2014 averaged over the Amazon region. Grey dots represent yearly averages whereas the blue dots represent the wet season average.

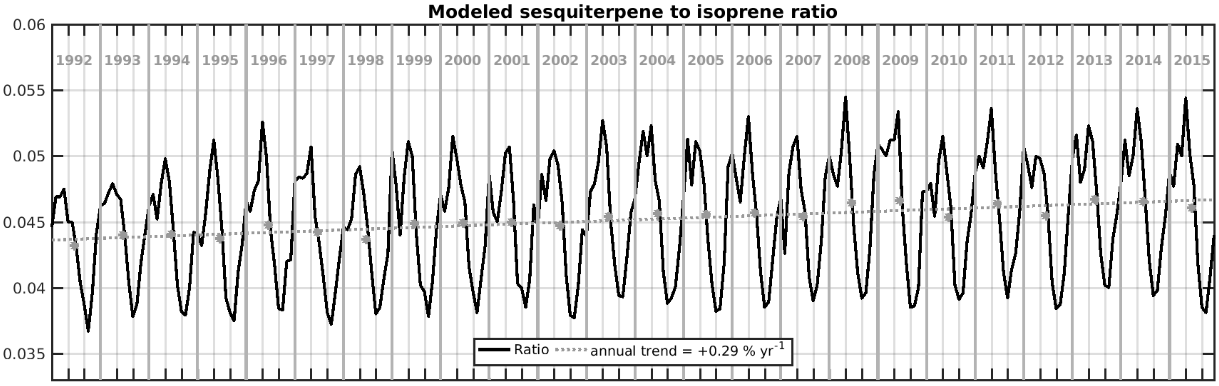

Figure 8: Time series of the sesquiterpene to isoprene ratio fluxes from model simulations. Dots represent yearly averages from which the trend is calculated. Grey dots represent yearly averages.