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RESEARCH ARTICLE

Seasonal shifts in isoprenoid emission composition from three hyperdominant tree species in central Amazonia

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ABSTRACT

- Volatile isoprenoids regulate plant performance and atmospheric processes, and Amazon forests comprise the dominant source to the global atmosphere. Still, there is a poor understanding of how isoprenoid emission capacities vary in response to ecophysiological and environmental controls in Amazonian ecosystems.
- We measured isoprenoid emission capacities of three Amazonian hyperdominant tree species – *Protium hebetatum*, *Eschweilera grandiflora*, *Eschweilera coriacea* – across seasons and along a topographic and edaphic environmental gradient in the central Amazon.
- From wet to dry season, both photosynthesis and isoprene emission capacities strongly declined, while emissions increased among the heavier isoprenoids: monoterpenes and sesquiterpenes. Plasticity across habitats was most evident in *P. hebetatum*, which emitted sesquiterpenes only in the dry season, at rates that significantly increased along the hydro-topographic gradient from white sands (shallow root water access) to uplands (deep water table).
- We suggest that emission composition shifts are part of a plastic response to increasing abiotic stress (*e.g.* heat and drought) and reduced photosynthetic supply of substrates for isoprenoid synthesis. Our comprehensive measurements suggest that more emphasis should be placed on other isoprenoids, besides isoprene, in the context of abiotic stress responses. Shifting emission compositions have implications for atmospheric responses because of the strong variation in reactivity among isoprenoid compounds.

INTRODUCTION

Isoprenoids are volatile organic compounds (VOC) that are emitted to the atmosphere, mostly by plants. They have diverse functional roles at multiple scales, from cellular protection and defence at the foliar level, through chemical signalling within and among plants, to the regulation of large-scale biogeochemical processes, such as effects on atmospheric chemical composition and contribution to aerosol formation (Laothawornkitkul *et al.* 2009). Volatile isoprenoids are represented by isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$), and their largest source is tropical trees, which contribute ca. 80% of global emissions (Guenther *et al.* 2012). The high contribution of isoprenoid emissions from tropical vegetation is probably mostly related to the high plant biomass of such regions, since the percentage of plant species emitting isoprene (the largest emitted VOC) is similar when comparing the tropics with other ecosystems in the world (Loreto & Fineschi, 2015); although some studies in the Amazon indicated that the fraction of isoprene emitters in the tropics may be higher than anticipated (*e.g.* Taylor *et al.* 2018; Jardine *et al.* 2020).

With half of the world's tropical forests, Amazonia is recognized as the most important global source of isoprenoids to the atmosphere (Sindelarova *et al.* 2014). Since the early 1980s, multiple investigations have studied canopy flux, canopy concentrations and, to a lesser degree, leaf-level emissions of isoprenoids. These studies have reported meaningful insights into the emission drivers and how these compounds are involved in subsequent atmospheric processes (Yáñez-Serrano *et al.* 2020). These combined findings have contributed to developing and optimizing an isoprenoid emission model (Guenther *et al.*

2012). Despite such efforts, emission estimates from tropical vegetation still carry a high degree of uncertainty because of a poor understanding of the biological controls that determine the *capacity* for emission and its plasticity in response to ecological and environmental conditions, as well as the environmental controls that determine *rates* of emissions (Alves *et al.* 2018).

The constitutive emission capacity of isoprenoids is determined by the emission under 'standard' leaf conditions (*i.e.* 1000 $\mu mol \cdot m^{-2} \cdot s^{-1}$photosynthetically active radiation at 30°C), even though this physiological property might vary plastically (across individuals) under different ecological and physiological conditions. Actual emission rates are a function of emission capacity and variations in light and temperature (Niinemets *et al.* 2011). This implies that, in order to model isoprenoid emissions, it is first necessary to quantify emission capacities across species, as well as their plasticity across individuals, to then quantify the emission variation driven by environmental factors, such as light and temperature (Duhl *et al.* 2008; Niinemets *et al.* 2011; Guenther *et al.* 2012). For several practical reasons, such as the remoteness and high plant species diversity of Amazonia, most studies so far have only investigated isoprenoid emission rates at the ecosystem level and how they vary with environmental factors. The majority of these studies measured canopy concentration or flux of isoprenoids, focusing on isoprene, which is known to be the strongest of the emitted compounds (Eerdekens *et al.*2009). Only a few studies have measured monoterpenes, and very few studies have quantified sesquiterpenes (Jardine *et al.* 2011; Yáñez-Serrano *et al.* 2020).

A first attempt to address isoprene emission capacities at the leaf level and the upscaling to ecosystems was made by Harley *et al.* (2004). Knowing that not all plant species emit isoprene (Monson *et al.* 2013), the aforementioned study aimed to quantify the isoprene emission capacity for multiple plant species from different Amazonian regions, and a method was created to impute the isoprene trait to other non-measured trees by using species identification and phylogenetic proximity; after which the results were used to upscale the isoprene emission capacity to the ecosystem level based on the fraction of tree isoprene emitters. Subsequent studies further expanded the number of species measured (Jardine *et al.* 2020; Taylor *et al.* 2021). Recent work has derived more mechanistic approaches to scaling isoprene emission across the landscape by determining how the fraction of emitters relates to mean climate conditions (Taylor *et al.* 2018) due to differences in performance between isoprene-emitting and non-emitting species (Taylor *et al.* 2019). These studies were important as they identified the emission capacity of isoprene, and in a few cases, also of monoterpenes. This has certainly contributed to the overall body of work covering nearly 30 years of research on modelling of isoprenoid emission in Amazonia.

Yet, it is also known that the isoprenoid composition is conserved within a plant species, but that emission capacity for these compounds may vary significantly within species and individuals according to photosynthetic capacity, carbon and nutrient investment trade-offs, habitat and the environment (Harrison *et al.* 2013). This variability in emission capacity is an essential factor to explain why we observe seasonal variations in isoprenoid emission (for a synthesis of studies, see Yáñez-Serrano *et al.* 2020) which does not entirely follow the seasonal variations in solar radiation and temperature in central Amazonia (Alves *et al.* 2016, 2018).

Seasonal factors such as leaf demography and phenology are important drivers of variability in leaf emission capacity and the composition of emitted isoprenoids. During early leaf development, young leaves synthesize less isoprene and more monoterpenes and sesquiterpenes (Gershenzon & Croteau 1991; Kuhn *et al.* 2004b), while the opposite pattern occurs with leaf maturation (Alves *et al.* 2014). This shift in emission composition is the result of physiological and ecological factors, which cannot be explained by atmospheric observations and direct abiotic effects alone. Variations in leaf physiology with ontogeny scale up through leaf age distributions – with a higher proportion of young leaves during the dry season (Lopes *et al.* 2016; Wu *et al.* 2016; Gonçalves *et al.* 2020) – to influence seasonal variations in isoprenoid emission capacities and total ecosystem emissions (Alves *et al.* 2014, 2016, 2018).

Given such reports, we can infer that most of the studies in Amazonia have focused on emission *rates* — *i.e.* canopy-level sensitivity to environmental factors and landscape-level sensitivity to leaf quantity and emitter fraction. Few studies have focused on mechanisms of variation in emission *capacity*, either within or between species, and such studies have focused exclusively on leaf age and primarily on isoprene (Alves *et al.* 2014, 2016, 2018). There is still a lack of understanding of the different physiological roles of the other light-dependent isoprenoids. Only by measuring all of them across habitats and seasons within species, can we begin to infer conditions under which one or the other compound is favoured and how this can be more accurately scaled to the ecosystem. Therefore, the determination of intraspecific variations in emission capacities of different isoprenoids is a critical knowledge gap that this study addressed.

In this study, we present a unique comprehensive set of leaf-level isoprenoid emission measurements that allow us to characterize variations in emission capacities and chemical compositions within species, across habitats and across seasons. We performed our measurements on trees of three hyperdominant species from central Amazonia – *Protium hebetatum, Eschweilera grandiflora* and *Eschweilera coriacea* (ter Steege *et al.* 2013) – distributed along a topographic and edaphic environmental gradient at the Amazon Tall Tower Observatory (ATTO) site, during both the wet and the dry season. Simultaneous measurements of photosynthesis and emissions allowed us to assess shifting isoprenoid investments in the context of the leaf carbon balance and infer the availability of photosynthetic substrates for isoprenoid synthesis.

MATERIAL AND METHODS

Study site

The study was conducted at the Amazon Tall Tower Observatory (ATTO) within the PELD-MAUA (PELD is the acronym in Portuguese for Long-term Ecological Research) experimental plots. This experimental site is in the Uatumã Sustainable Development Reserve (USDR), about 150 km northeast of the city of Manaus (02 08.9°S, 059 00.2°W), in central Amazonia (Fig. 1). The climate is tropical humid, with mean annual temperature and precipitation of 28°C and 2376 mm, respectively, and is marked by a pronounced rainy season from November

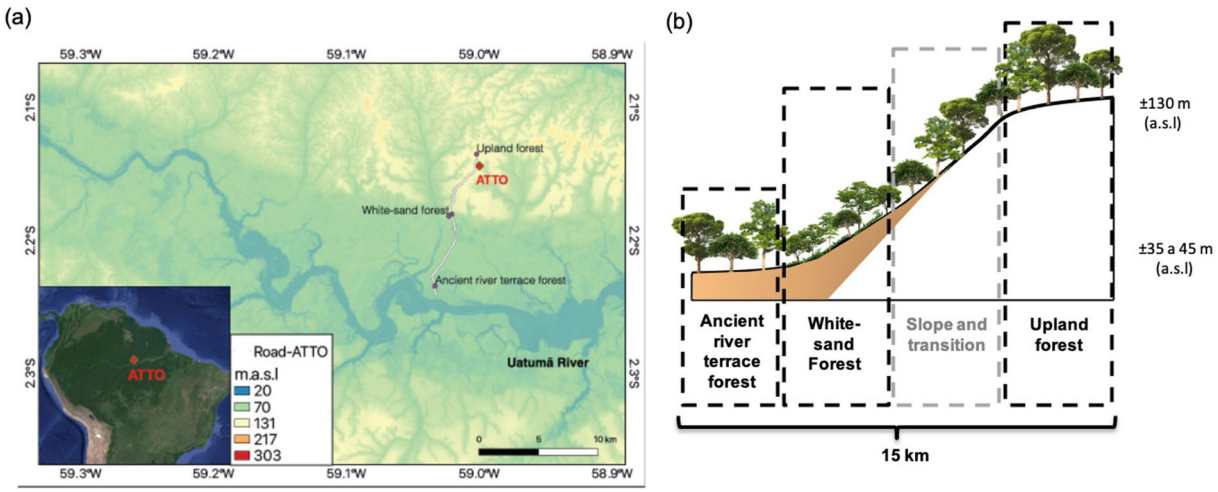

Fig. 1. Experimental site location. Composite map showing the location of the forest types investigated in this study – upland forest, white-sand forest and ancient river terrace forest – and their location relative to the ATTO tower, to an affluent of the Amazon River – Uatumã River and to South America (a). Scheme of the three forest types with their respective above sea elevation (a.s.l.) (b). Map drawn by Santiago Botía, MPI-BGC; scheme drawn by Murielli Caetano, INPA.

to May and a drier season from June to October (Andreae *et al.* 2015). The reserve covers 4244 km² with a mosaic of dense non-flooded upland forest vegetation, dense non-flooded forest upon ancient river terraces and shrubland/closed-canopy vegetation on white sands (Yáñez-Serrano *et al.* 2015). These three forest types are characterized with differences in soil and vegetation attributes. In the upland forest, soils are classified as ferralsols, which are highly weathered and well-drained (Chauvel *et al.* 1987).

Soils in the white-sand forests are classified as arenosols, with characteristic properties of high water permeability, low waterholding capacity, low specific heat capacity, and often low nutrient content, mostly on organic matter (Quesada *et al.* 2011). Also, white-sand forests can be subject to extremes of flooding and drought at different times of the year. Through intense leaching, Fe, Al, Mg and other compounds are deposited in the lower layers of the soil, forming a hard layer that can block water drainage. Thus, in the dry season the vegetation can suffer severe water deficit, and in the rainy season waterlogged soils or even superficial inundation of the root system for months (Kubitzki 1989).

Soils in the ancient river terrace forests are classified as alisols, which represent a more recent pedogenetic status compared to the ferralsols from the upland forest and therefore have a greater capacity to supply nutrients, as observed with higher total phosphorus and higher total reserve bases (Andreae *et al.* 2015). However, some ancient river terrace soils show signs of anoxia (mottling) in deeper horizons, which may influence forest structure (Quesada *et al.* 2012; Emilio *et al.* 2013) and dynamics (Cintra *et al.* 2013), and possibly restrict tree height and individual biomass storage (Martins *et al.* 2015) compared to upland forests.

The vegetation across the three forest types presents differences in tree species richness, with the highest number of species on upland forest (137 ± 5 sp.·ha^{-1}), followed by ancient river terrace forest (127 ± 8 sp.·ha^{-1}) and white-sand forest (64 ± 18 sp.·ha^{-1}) (Andreae *et al.* 2015). Carbon stocks in aboveground biomass follow the same pattern as species richness by increasing from 79 ± 26 Mg·ha^{-1} in the white-sand and 101 ± 13 Mg·ha^{-1} in the ancient river terrace to a maximum of 170 ± 13 Mg·ha^{-1} in the upland forests. The ATTO site combines high alpha-diversity with high beta-diversity within a small geographic range, where tree species diverge mostly in relation to local edaphic conditions (Andreae *et al.* 2015).

Sampling

We sampled isoprenoid emissions from 30 trees across two permanent plots for each forest type: upland forest, white-sand forest and ancient river terrace forest. Plots were distributed at least 1 km from each other along the ATTO access road (Fig. 1). Tree species were previously identified (with individual vouchers collected) and confirmed taxonomically. Two species were chosen from a preliminary selection based on: (i) their abundance in the PELD MAUA tree species inventory (Andreae *et al.* 2015), (ii) their contribution to a wider distribution in central Amazonia (ter Steege *et al.* 2013; Fauset *et al.* 2015) and (iii) their occurrence in at least two of the forest types of the study experimental site. *Protium hebetatum* (Burseraceae) and *Eschweilera grandiflora* (Lecythidaceae) are hyperdominant species in central Amazonia, with biomass ranking at 51 and 22, respectively (Fauset *et al.* 2015). *P. hebetatum* occurs across the three forest types: upland forest (first most abundant species), white-sand forest (tenth most abundant species) and ancient river terrace forest (third most abundant species) (Andreae *et al.* 2015). *E. grandiflora* was present in two forest types: upland forest (second most abundant species) and ancient river terrace forest (first most abundant species) (Andreae *et al.* 2015). In addition, we selected the second most dominant species in terms of stem abundance, biomass and productivity in central Amazonia – *Eschweilera coriacea* (Lecythidaceae) (ter Steege *et al.* 2013; Fauset *et al.* 2015), but this species was only present in the plots of white-sand forest, where it was

the fourth most abundant species (Andreae *et al.* 2015). For each species we selected and sampled five trees with similar diameter in each forest type where the species occurred. All trees assessed were of canopy height, and we collected only leaves from the crown top, which receives direct light at least around noon and therefore leaves are light-adapted. We sampled leaves that were visually healthy and mature. Although, we do not have precise information on leaf age, we avoided senescent and young leaves. Leaf traits and isoprenoid emission were repeatedly assessed in May 2019 (wet season) and September 2019 (dry season). In addition, a smaller subset of samples had previously been taken in December 2018 (dry-to-wet transition season). See Table 1 for more details on weather and climatic conditions for each campaign.

Isoprenoid emission

Leaf-level gas fluxes were measured on site from one leaf per tree and repeated in the same tree across the seasons. Measurements were made using a commercial, portable gas exchange system with an infrared gas analyser (IRGA), LI6400XT (LiCor, Lincoln, NE, USA). A hydrocarbon filter (Restek Pure Chromatography; Restek, Bellefonte, PA, USA) was installed at the air inlet of the IRGA to remove hydrocarbons from incoming ambient air. All tubing in contact with the sampling air was PTFE (a material that is non-reactive to hydrocarbons). Before each measurement, a blank sample was taken from the empty leaf chamber (see Table S1). A single leaf was enclosed in the leaf chamber under standard conditions (PPFD 1000 $\mu mol \cdot m^{-2} \cdot s^{-1}$, leaf temperature 30°C) and net CO_2 assimilation (A_n), stomatal conductance (g_s) and internal CO_2 concentration (C_i) measured when stable. The stability criterion for measurements was ±1 SD of mean A_n. The flow rate of air into the leaf chamber was 400 $\mu mol \cdot s^{-1}$, CO_2 and H_2O concentrations were 400 $\mu mol \cdot mol^{-1}$ and 21 $mmol \cdot mol^{-1}$ (relative humidity ~60%), respectively. Air exiting the leaf chamber was routed through adsorbent cartridges (stainless silicon steel tubes filled with Tenax TA and Carbograph 5 TD adsorbents) at a rate of 200 sccm (standard cubic centimetres per minute) for 10 min, which resulted in 2-l air samples for isoprenoid chemical analysis. The isoprenoids that accumulated in the adsorbent cartridges were determined subsequently by laboratory analysis. Samples from December 2018 and May 2019 were analysed at the State University of Amazonas (UEA, BR, Brazil) and samples from September 2019 were analysed at the Max Planck Institute for Chemistry (MPIC, DE, Germany).

In UEA, cartridges were analysed with a thermal desorption system (TD; Markes International) interfaced with a gas chromatograph-mass spectrometer and flame ionization detectors (GC-MS-FID; 7890B-GC and 5977A-MSD series; Agilent, Santa Clara, CA, USA). The cartridges were loaded into the TD automatic sampler (TD-100; Markes International, Sacramento, CA, USA) connected to the thermal desorption system. Samples were then dried by purging for 5 min with 50 sccm ultrahigh-purity helium (all flow vented out of the split vent) and transferred (300°C for 10 min with 50 sccm ultrapure nitrogen) to the thermal desorption cold trap held at −10°C (Unity Series 1; Markes International). During GC injection, the trap was heated to 300°C for 3 min while backflushing with carrier gas (helium) at a flow rate of 6.0 sccm directed into the column (Agilent HP-5; 5% phenyl methyl siloxane capillary, 30.0 m × 320 μm × 0.25 μm). The oven ramp temperature was programmed with an initial hold of 6 min at 27°C, followed by an increase to 85°C at $6°C \cdot min^{-1}$, followed by a hold at 200°C for 6 min. We confirmed the identification of emitted isoprenoids from the samples by comparison of retention times with a solution of authentic liquid standards in methanol (Sigma-Aldrich, MO, USA) and comparison to the library of the National Institute of Standards and Technology (NIST). The GC-MS-FID was calibrated at least three times before analysis of the sample cartridges; calibration curves were generated by injecting different amounts of gas standard (27 biogenic VOCs gas mixture: Apel & Riemer Environmental, Broomfield, CO, USA) into separate cartridges, a mean correlation coefficient ≥0.98 was obtained, and LOD quantified as 27 pptv (parts solute per thousand parts solution by volume).

In MPIC, the cartridges were analysed through thermal-desorption gas chromatography time of flight mass spectrometry (TD-GC-TOF-MS; Bench ToF Tandem Ionisation from Markes International, Bridgend, UK). The analysis consisted of three main steps: desorption of the analytes from the cartridges (TD), separation of the analytes through gas chromatography (GC) and quantification and identification of the analytes through time-of-flight mass spectrometry (ToF-MS). Samples were first dried by purging for 5 min with a flow of ultrapure N_2 at 50 $ml \cdot min^{-1}$, then transferred to the thermal-desorption unit. Thermal-desorption was carried out in two stages – tube desorption and trap desorption, both performed at 250°C for

Table 1. Air temperature, relative humidity (RH), photosynthetic active radiation (PAR) and precipitation for the days of each intensive campaign and monthly average from 2013 to 2019.

year	month	campaign days	season	air temp. (°C)	RH (%)	PAR ($\mu mol \cdot m^{-2} \cdot s^{-1}$)	precipitation (mm)
2018	December	4th	dry-to-wet transition	26.03 (1.9)	90.3 (8.3)	742.8 (555.0)	–
2019	May	from 1st to 5th	wet	25.8 (2.3)	94.8 (7.9)	732.2 (626.0)	23.6
2019	September	from 21st to 24th	dry	28.3 (3.1)	77.3 (12.8)	1060.6 (756.6)	–
2013–2019[a]	December		dry-to-wet transition	26.4 (2.8)	87.7 12.6)	749.3 (574.0)	170.7 (79.1)
2013–2019[a]	May		wet	25.7 (2.4)	93.6 (8.7)	722.5 (584.4)	245.2 (73.9)
2013–2019[a]	September		dry	27.4 (3.3)	81.4 (14.3)	975.3 (680.2)	53.6 (21.9)

Note: Values within brackets represent 1 SD of mean.

[a]Monthly average of data provided by the weather station since its installation at the INSTANT tower.

10 min through a TD 100xr (Markes International). The desorbed components were carried in a flow of helium into the GC column (dimethyl T.B.S. β-cyclodextrin 0.15 μm × 0.15 mm ID, 25 ml; MEGA, Legnano, Italy). The temperature ramp consisted of an initial 5 min at 40°C, after which the temperature was increased at a rate of 1.5°C·min^{-1} from 40°C to 150°C, and further increased at a rate of 30°C·min^{-1} from 150°C to 200°C. After the GC column, the analytes were fragmented through electron impact ionization at −70 eV in the ToF. Identification was obtained by comparing the MS spectra with the MS NIST library for the same ionization energy and by injection of gas mixtures (162 VOCs gas mixture and 25 biogenic VOCs gas mixture; Apel & Riemer Environmental, Broomfield, CO, USA) and liquid standards. The obtained chromatograms were integrated with TOF-DS (Markes International). Gas standard cartridges were used to calibrate the instrument, determine the precision and LOD of the analysis, which was quantified as 23% and ~1 pptv, respectively. More information on the materials and methods can be found in Zannoni *et al.* (2020).

For the final flux calculation, isoprenoid concentrations were determined using the sample volume that was passed through each cartridge. This volume is the integration of the mass flow rate measured and controlled by the pump used to sample the air coming out of the IRGA leaf chamber. Once the volume mixing ratios of isoprenoids (ppbv; parts per billion volume) were obtained, leaf emission fluxes were determined using the equation ($F = R\text{ppbv} \times Q/A$), where F (nmol·m^{-2}·s^{-1}) is leaf flux of isoprenoid emission; *Rppbv* (nmol·mol^{-1}) is isoprenoid concentration of the sample; Q is flow rate of air into the leaf chamber (400×10^{-6} mol·s^{-1}); and A is the area of leaf within the chamber (0.06 m²). To calculate isoprenoid emission on a mass basis, we measured Leaf Mass per Area (LMA). LMA was calculated as the ratio of leaf dry weight to leaf area. We did not include petioles in the LMA calculation since they can be quite large in rainforest species and are usually more related to leaf positioning rather than biomass efficiency (Poorter *et al.* 2018). With LMA, isoprenoid emissions were then calculated to μg C·g^{-1}·h^{-1}.

Emission metrics and statistical analysis

Isoprenoid emission and photosynthetic rates were analysed in common units of μg C·g^{-1}·h^{-1}. This enabled us to produce integrated metrics related to the leaf C balance. We analysed total isoprenoid emissions both as the sum of all C emitted in the form of isoprenoids, and as a percentage of photosynthetic C assimilation rates. The three compound classes vary in mass (5C isoprene, 10C monoterpenes, 15C sesquiterpenes). We developed an 'isoprenoid mass investment' metric to assess the partitioning of C among the different classes of emitted isoprenoids, calculated by multiplying the emission rates of each compound (in μg C·g^{-1}·h^{-1}) by their respective masses (number of C atoms), then dividing by the combined total emission rate (*i.e.* emission rate weighted mean mass of emitted compounds). The mass investment metric reflects how much carbon is allocated to lighter *versus* heavier compounds. For example, the average mass investment of pure isoprene emission is 5C. Since sesquiterpenes contain three times as much C as isoprene, a 2:1 molar ratio of sesquiterpenes to isoprene gives an average mass investment of $(2(15C \times 3) + 1(5C \times 1))/7 = 13.6C$. Variation in metrics among habitats within species and seasons was analysed with Tukey Honestly Significant Difference (HSD) test (alpha = 0.05). Variation between dry and wet seasons was analysed by paired *t*-test (alpha = 0.05) on measurements taken from the same individuals in both seasons.

RESULTS

Here we present results of isoprenoid emission capacity (including isoprene, monoterpenes, and sesquiterpenes), photosynthesis and carbon allocation strategies across habitats and seasons for three tree species – *P. hebetatum, E. coriacea* and *E. grandiflora*.

Isoprenoid emission variation among habitats and seasons

Isoprenoid emissions and their habitat and seasonal associations varied among plant species (Fig. 2, Table 2). Isoprene emissions were mostly indistinguishable among habitats, except that emission capacities were higher from *P. hebetatum* in the ancient river terrace (AR) and upland (Up) forest habitats than in the white-sand (WS) forest in the dry season. Isoprene emission capacities were generally lower in the dry than the wet season (Fig. 2), although only significantly so for *P. hebetatum* in two habitats. When aggregating all trees, isoprene emissions were significantly lower in the dry than the wet season (a factor of 0.33, paired *t*-test '$p < 0.05$; Figure S1). Among the subset of trees sampled during the dry-to-wet transition season (December 2018), isoprene emissions were significantly higher than in either the dry or the wet season (Tukey HSD, $P < 0.05$), averaging 3.3 and 2.4 times higher than wet season emissions for *E. coriacea* (n = 5 trees) and *P. hebetatum* (n = 3 trees) (Figure S2).

Monoterpene emission capacities were highly variable in magnitude and chemical diversity among individuals within species, even in the same habitat and season (Table 3). Total monoterpene emission capacities were mostly indistinguishable among habitats, except for higher rates from *E. grandiflora* in AR than in Up in the wet season, tracking patterns of isoprene emission. The species that emitted most monoterpenes was *P. hebetatum*, with emissions frequently exceeding 15 μg C·g^{-1}·h^{-1}. Comparing monoterpene emission capacities between seasons, we found that *E. coriacea* only emitted monoterpenes during the dry season. No significant seasonal differences were detected within habitats (Fig. 2) or when aggregating by tree and species (Figure S1). However, the number of chemical species of monoterpene increased from the wet season to the dry season, both in WS and AR habitats (Table 3). During the dry-to-wet transition season, no monoterpene emissions were detected from *E. coriacea* or *P. hebetatum*.

Sesquiterpene emissions were only detected from *P. hebetatum*, reaching rates comparable to isoprene (when analysed in units of C emitted, but not as moles emitted). These emissions only occurred during the dry season, and significantly increased from WS to AR and Up habitats (Fig. 2). Measurements of leaf stored terpenes were carried out in the wet season, and high concentrations of sesquiterpenes were observed in leaves from *P. hebetatum*, with values up to seven orders of magnitude higher than for monoterpenes (Figure S4),

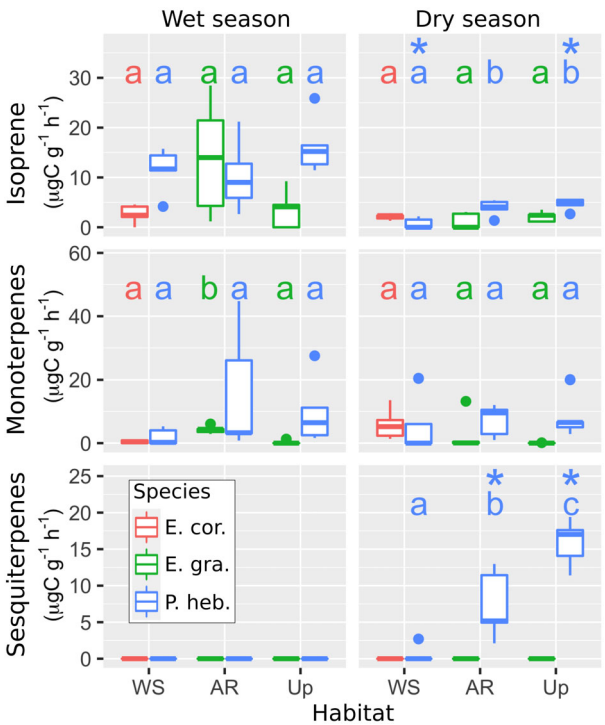

Fig. 2. Variation in emission rates of the three isoprenoid classes between seasons (wet, dry) and habitats (WS = white sand, AR = ancient river terrace, Up = upland), grouped by plant species. Letters indicate significant differences in emission rates between habitats, within species and seasons (Tukey Honestly Significant Difference test, alpha = 0.05). Stars indicate significant differences between seasons, within habitats and species (paired *t*-test, alpha = 0.05). Boxes show median and first and third quartiles, with whiskers and points distinguished at 1.5 times the interquartile range.

indicating that high sesquiterpene emissions from *P. hebetatum* resulted from leaf storage. No sesquiterpene emissions were detected during the dry-to-wet transition season. For chemical species of monoterpenes and sesquiterpenes, see Table 3.

Photosynthesis and carbon investment in isoprenoid emissions

Photosynthesis significantly decreased in most species and habitats during the dry season, while trends varied among species in total isoprenoid emissions and their associated carbon investments (Fig. 3). Photosynthesis was significantly lower in the dry than in the wet season in most habitats for *E. grandiflora* and *P. hebetatum*, but not for *E. coriacea*. Total C emitted in the form of isoprenoids varied among habitats, being significantly higher from *E. grandiflora* in AR than Up habitats in the dry season, and higher from *P. hebetatum* in AR and Up than in WS habitats in the wet season (mainly due to the trend in sesquiterpene emissions, see Fig. 2). Total C investment in emissions as a percentage of photosynthesis was generally <2% and could not be distinguished between habitats in either season, although it reached an average 6.1% in *P. hebetatum* in the Up habitat in the dry season. In *P. hebetatum*, isoprenoid mass investment was significantly larger in AR and Up than in WS habitats in both wet season (attributable to higher

Table 2. Emission capacities of isoprene, total monoterpenes and total sesquiterpenes, photosynthesis for the three forest types – white-sand forest (WS), ancient river terrace forest (ART) and upland forest (UP) – during the dry-to-wet transition season (December 2018), the wet season (May 2019) and the dry season (September 2019).

tree species	season	forest type	isoprene [µg C·g^{-1}·h^{-1}]	isoprene [mg·m^{-2}·h^{-1}]	sum MT [µg C·g^{-1}·h^{-1}]	sum MT [mg·m^{-2}·h^{-1}]	sum SQT [µg C·g^{-1}·h^{-1}]	sum SQT [mg·m^{-2}·h^{-1}]	photosynthesis [µg C·g^{-1}·h^{-1}]	photosynthesis [mg C·m^{-2}·h^{-1}]
Eschweilera coriacea	*DWT*	WS (n = 5)	10.71 (1.75)	1.19 (0.19)					1897.45 (372.89)	189.74 (37.28)
	wet	WS (n = 5)	3.30 (1.24)	0.36 (0.13)	0.75 (0.24)	0.08 (0.02)			2634.05 (692.45)	263.40 (69.24)
	dry	WS (n = 5)	2.11 (0.58)	0.23 (0.06)	5.96 (4.85)	0.66 (0.54)			2283.18 (407.46)	228.31 (40.74)
Eschweilera grandiflora	*wet*	ART (n = 5)	17.07 (10.37)	1.91 (1.16)	4.26 (1.19)	0.47 (0.13)			4053.90 (663.38)	405.39 (66.33)
		UP (n = 5)	5.95 (2.87)	0.66 (0.32)	1.29 (0)	0.14 (0)			2429.67 (821.09)	242.96 (82.10)
	dry	ART (n = 5)	2.89 (0.25)	0.32 (0.02)	2.74 (5.85)	0.30 (0.65)			2321.95 (800.14)	232.19 (80.01)
		UP (n = 5)	2.10 (1.06)	0.23 (0.11)	0.04 (0.05)	0.004 (0.005)			1983.25 (707.86)	198.32 (70.78)
Protium hebetatum	*wet*	WS (n = 5)	11.49 (4.48)	1.28 (0.50)	3.19 (2.63)	0.35 (0.29)			1977.45 (533.87)	197.74 (53.38)
		ART (n = 5)	10.30 (7.14)	1.15 (0.79)	15.61 (19.28)	1.74 (2.15)			2065.45 (256.60)	206.54 (25.66)
		UP (n = 5)	16.32 (5.69)	1.82 (0.63)	9.86 (10.56)	1.10 (1.18)			2195.56 (371.22)	219.55 (37.12)
	dry	WS (n = 5)	1.86 (0.46)	0.18 (0.04)	13.22 (10.16)	1.33 (1.02)	2.7	0.27	655.03 (487.07)	58.95 (43.83)
		ART (n = 5)	3.90 (1.60)	0.34 (0.14)	7.20 (4.92)	0.64 (0.44)	7.32 (4.64)	0.65 (0.41)	1412.10 (349.11)	112.96 (27.92)
		UP (n = 5)	4.61 (1.18)	0.46 (0.11)	8.21 (6.76)	0.82 (0.68)	15.90 (3.16)	1.60 (0.31)	635.14 (281.49)	57.16 (25.33)

Note: Values in parenthesis represent 1 SD of mean.

Table 3. Chemical species of monoterpenes and sesquiterpenes emitted by *Eschweilera coriacea*, *E. grandiflora* and *Protium hebetatum* measured in three forest types – white-sand forest (WS), ancient river terrace forest (ART) and upland forest (UP), during the wet season (May 2019) and the dry season (September 2019). Emissions are in μg $C \cdot g^{-1} \cdot h^{-1}$.

		wet season			dry season		
tree species	compound	WS	ART	UP	WS	ART	UP
Eschweilera coriacea[a]	α-Pinene	0.34; n = 1			1.17; n = 1		
	β-Pinene				0.36; n = 1		
	Camphene	0.53; n = 1			0.13; n = 1		
	3-Carene				3.14; n = 1		
	Limonene				1.53 (1.54); n = 2		
	β-Phellandrene	0.91; n = 1					
	α-Terpinene				3.285 (1.92); n = 2		
	γ-Terpinene	0.47; n = 1					
Eschweilera grandiflora[b]	α-Pinene		0.24 (0.15); n = 4			0.04 (0.51); n = 3	0.03 (0.02); n = 2
	β-Pinene					0.01 (0.004); n = 4	0.01 (0.0005); n = 2
	Camphene					0.26 (0.12); n = 2	0.04 (0.03); n = 2
	3-Carene					3.20; n = 1	
	D-Limonene		1.78 (0.15); n = 5				
	Limonene					3.63 (3.60); n = 2	
	α-Phellandrene		0.26 (0.07); n = 4				
	β-Ocymene			1.29; n = 1			
	o-Cymene		2.04 (0.65); n = 5				
	γ-Terpinene		0.49; n = 1				
Protium hebetatum	α-Pinene	0.24; n = 1	4.56 (7.21); n = 4	0.41 (0.19); n = 3	1.57 (0.15); n = 2	0.83 (3.43); n = 5	2.13 (1.49); n = 5
	β-Pinene		7.24 (4.05); n = 2		0.67 (0.65); n = 2	0.17 (0.76); n = 5	0.36 (0.14); n = 5
	Camphene	0.35 (0.01); n = 2		0.16; n = 1	0.18 (0.15); n = 2	0.23 (0.45); n = 5	0.15 (0.16); n = 5
	3-Carene			5.27 (7.59); n = 5	2.51 (2.46); n = 2	1.57 (3.12); n = 3	0.06 (0.02); n = 3
	D-Limonene		6.59 (12.57); n = 4	0.48 (0.63); n = 3			
	Limonene				8.27 (3.75); n = 2	1.05 (1.23); n = 5	1.01 (1.21); n = 5
	α-Phellandrene			0.26 (0.07); n = 2			
	β-Phellandrene		1.34; n = 1				
	o-Cymene	4.32 (0.62); n = 2		0.30 (0.20); n = 3			
	α-Terpinene				0.01; n = 1		1.53 (1.31); n = 4
	γ-Terpinene			0.05; n = 1		0.03 (0.48); n = 3	1.46 (1.29); n = 4
	α-Cubene						1.10 (0.42); n = 5
	α-Copaene						7.89 (1.34); n = 5
	Caryophyllene				2.70; n = 1	5.17 (6.48); n = 5	7.71 (1.29); n = 5

Note: [a]*Eschweilera coriacea* was only found in the white-sand forest type.
[b]*Eschweilera grandiflora* was not found in the white-sand forest type.

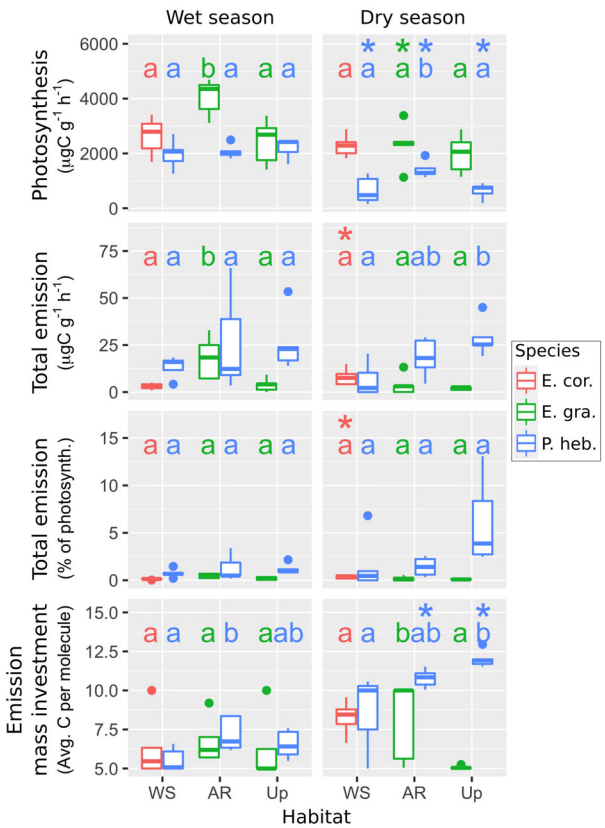

Fig. 3. Variation in photosynthesis, total isoprenoid emissions and metrics of carbon investment between seasons (dry, wet) and habitats (WS = white sand, AR = ancient river terrace, Up = upland), grouped by plant species. 'Isoprenoid mass investment' is the average mass (C) of emitted compounds, weighted by their relative emission rates. Letters indicate significant differences in emission rates between habitats, within species and seasons (Tukey Honestly Significant Difference test, alpha = 0.05). Stars indicate significant differences between seasons, within habitats and species (paired *t*-test, alpha = 0.05). Boxes show the median and first and third quartiles, with whiskers and points distinguished at 1.5 times the interquartile range.

monoterpene emissions; Fig. 2) and dry season (attributable to higher sesquiterpene emissions; Fig. 2) and was significantly higher in the dry than the wet season in AR and Up habitats (Fig. 3).

When aggregated across forest habitats and species, seasonal variation was strongest in photosynthesis and isoprenoid mass investment, and less pronounced in total isoprenoid emission and carbon emitted as a percentage of photosynthesis (Fig. 4). Statistical significance reflects paired *t*-tests for individuals measured in both seasons (alpha = 0.05), while Fig. 4 visualizes the dry season values as a factor of wet season values measured from the same individuals ('dry/wet factor'). Photosynthesis was not significantly lower in the dry season in *E. coriacea* (mean dry/wet factor = 0.94), significantly lower in *E. grandiflora* (mean dry/wet factor = 0.73) and *P. hebetatum* (mean dry/wet factor = 0.43), and in all species combined (mean dry/wet factor = 0.62). Total emission was not significantly higher in the dry season (mean dry/wet factor for all species combined = 1.47), even though emissions were strongly suppressed in many individual trees, except for *E. coriacea* in which emissions were significantly higher (mean dry/wet factor = 2.97). Carbon emitted as a percentage of photosynthesis was not significantly higher in the dry season overall (mean dry/wet factor for all species combined = 3.22) but highly variable among trees, except *E. coriacea* which had a significantly higher percentage (mean dry/wet factor = 3.43). Isoprenoid emission mass investment in the dry compared to the wet season was not significantly larger in *E. coriacea* (mean dry/wet factor = 1.41) and *E. grandiflora* (mean dry/wet factor = 1.07), but was significantly larger in *P. hebetatum* (mean dry/wet factor = 1.65), as well as significantly larger in all species combined (mean dry/wet factor = 1.41). Total emissions were positively correlated with photosynthesis in *E. grandiflora* (linear regression on all measurements combined, $P < 0.01$, $r^2 = 0.37$), while there was no detectable correlation in the other two species (Figure S3).

DISCUSSION

Previous studies examined constitutive leaf isoprenoid emission from tropical trees with a focus on isoprene (*e.g.* Keller & Lerdau 1999; Harley *et al.* 2004; Kuhn *et al.* 2004b; Pegoraro *et al.* 2006; Alves *et al.* 2014; Jardine *et al.* 2014, 2016; Taylor *et al.* 2019), followed by monoterpenes (*e.g.* Kuhn *et al.* 2004a; Jardine *et al.* 2017, 2020). These studies gave meaningful insights into how isoprene and monoterpenes respond to light, temperature and drought, and suggested their roles in plant stress tolerance. Nevertheless, constitutive sesquiterpene emission has only been found in tropical species in one study from Borneo (Llusia *et al.* 2014); therefore, most of our scarce knowledge on sesquiterpene production by tropical species comes from the content of these compounds either in leaves or resins (*e.g.* Salazar *et al.* 2018), which only suggest the potential for induced emissions. In this study, we found that Amazonian hyperdominant tree species emit isoprene, monoterpenes and sesquiterpenes constitutively, and that the amount and proportion of emissions change seasonally. The plasticity of emission capacity and chemical composition of isoprenoids emitted by trees distributed across different forest types, their seasonal behaviour and the significance of our findings are discussed in the following sections.

Isoprenoid emission capacity of hyperdominant tree species distributed along a topographic and edaphic environmental gradient

We found that, on average, isoprene emission capacity did not vary significantly across tree populations of *E. grandiflora* growing in different habitats but did vary among populations of *P. hebetatum*. Although it is known that the isoprene trait is conserved within plant species, emission quantities may vary significantly among photosynthetic capacity, carbon and nutrient investment trade-offs, habitat and the environment (Harrison *et al.* 2013). The species investigated here occur in forest types that vary in edaphic properties, soil waterholding capacity, species richness and below- and aboveground biomass (Andreae *et al.* 2015). These changes in soil and vegetation attributes can influence plant performance and, in intraspecific processes, it is common to observe increases in both plant growth and defence secondary metabolites as

resource availability increases (*e.g.* increased nutrient availability in uplands) (Agrawal 2020). Yet, although we observed the highest isoprene emission from *P. hebetatum* in upland forest, this was not observed in *E. grandiflora*, probably because of large variability within individuals in the same forest type.

The plant intraspecific variability was even more pronounced within emissions of monoterpenes – either in diversity of chemical compounds or in total amount – when comparing individuals found in the different forest types. This group of compounds is known to have two different processes of emission. After being synthesized, many monoterpenes are stored in leaves and their inducible emission results mostly from biotic stress; nonetheless, when plant species lack storage structures, most hydrophobic monoterpenes that were synthesized can accumulate in the leaf lipid phase and be constitutively emitted to the atmosphere (Ormeño *et al.* 2011). Although the functional role of the constitutive emission of monoterpenes has been reported as being similar to that of isoprene emission (Loreto *et al.* 1996) – namely, leaf thermal protection and leaf excess energy dissipation (Rosenstiel *et al.* 2004; Sanadze 2004; Sharkey & Monson 2017) – the main functional role of monoterpenes is attributed to plant defence against pathogens and herbivores (Fineschi & Loreto 2012), which could result in increased success in plant competition and colonization (Salazar *et al.* 2018). Thus, the high variability of monoterpene emission within species may be related to a plant defence strategy.

In contrast to isoprene and monoterpenes, sesquiterpene emission was only observed from *P. hebetatum*, in trees of all three forest types. Although ambient air concentrations of sesquiterpenes have been reported in central Amazonia (Jardine *et al.* 2011; Alves *et al.* 2016), to the best of our knowledge, this is the first time that constitutive emission of sesquiterpenes has been observed for an Amazonian tree species. *P. hebetatum* was measured for isoprenoid emission in another Amazonian Forest site, but the authors only found emission of isoprene and the monoterpene cis-β-ocimene (Jardine *et al.* 2020); however, it is important to note that, in our study, constitutive sesquiterpene emission was only observed in the dry season (see below) and Jardine *et al.* (2020) did not specify the season when their measurements were performed. In addition, it is hypothesized that the abundance of *Protium* species across the whole Amazon Basin is related to high diversity of chemical defences in these species, being a strategy against the large number of enemies that consistently attack plants (Salazar *et al.* 2018). This hypothesis is indeed reinforced by the fact that *P. hebetatum* occurs in all three forest types examined here, in contrast to the other two hyperdominant species, which occurred in only one or two of the forest types. Furthermore, given that the upland forest has the highest plant species richness in our study site (Andreae *et al.* 2015), high demand for chemical compounds for herbivory defence is expected in this environment. Habitats with high plant richness commonly also have increased richness of herbivores; hence, constant and high potential plant losses to herbivore attack are diminished through high investments in plant defence (Bixenmann *et al.* 2016). This could explain why sesquiterpene emission rates and their chemical diversity (Table 3) as well as leaf stored sesquiterpenes (Figure S4) peaked in the upland forest.

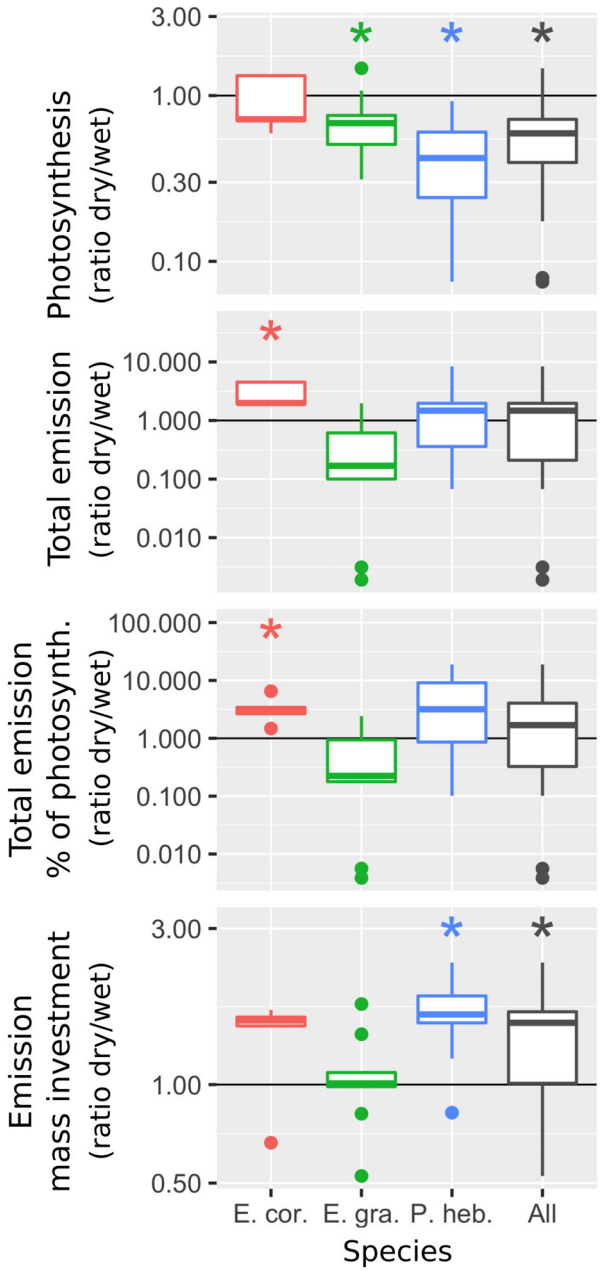

Fig. 4. Seasonal variation in photosynthesis, total emissions and metrics of carbon investment, grouped by plant species and all trees combined. Data are plotted as dry season values as a factor of wet season values, on a $\log_{10}$ scale, with the bold line at 1 indicating no seasonal difference. Stars indicate significant differences between seasons, determined by paired *t*-test on wet and dry season values measured from the same individuals (alpha = 0.05). Boxes show the median and first and third quartiles, with whiskers and points distinguished at 1.5 times the interquartile range.

Investment of C in isoprenoid emissions shifts to heavier compounds when photosynthesis is reduced in the dry season

We found a general trend of decreasing photosynthesis rates from the wet to the dry season, coupled with relatively constant total isoprenoid emission rates (Fig. 4). This combination led to a three-fold average increase in C allocation to isoprenoid

emissions relative to photosynthesis (although this was variable and not significant; Fig. 4). Nevertheless, the C sink to isoprenoid emissions was less than 2% of photosynthesis in most plants, except in strongly sesquiterpene-emitting *P. hebetatum*, whose emissions averaged 6.1% of photosynthesis (occasionally >10%) in the uplands in the dry season. The surprisingly high C investment in sesquiterpene emissions is corroborated our observations of high concentrations of stored sesquiterpenes in the wet season (Figure S4), and similar storage observations in many species of *Protium* (Salazar *et al.* 2018). Associated with this increasing investment in emissions, plants also allocated more C toward heavier isoprenoid compounds (Fig. 4). Increasing 'isoprenoid mass investment' was a result of reduced isoprene emissions and increased monoterpene and sesquiterpene emissions in the dry season (Figure S2).

Seasonal shifts in isoprenoid emission profiles may be attributable to leaf phenology and changing environmental stress conditions. Leaf age is a well-known driver of seasonal variation in both photosynthesis and isoprenoid emissions in the Amazon, at the leaf (Kuhn *et al.* 2004b; Alves *et al.* 2014; Albert *et al.* 2018) and ecosystem (Alves *et al.* 2016, 2018; Wu *et al.* 2016) scales. As we lack data on leaf age and phenological patterns in our studied trees, we cannot entirely discount their influence on our measured emissions; however, we were careful in all seasons to measure only leaves in a broadly 'mature' phase, *i.e.* fully expanded, lignified and healthy in appearance. Substantial environmental seasonality in the central Amazon also drives variation in leaf gas exchange. Photosynthesis is light-limited in the wet season, and limited in the dry season by drought-like conditions of reduced soil water and increased temperatures and vapor pressure deficit (Wu *et al.* 2017; Smith *et al.* 2020). During the dry season, reduced transpiration to conserve water reduces evaporative cooling and further elevates leaf temperatures in high sunlight (Fontes *et al.* 2018), driving high isoprenoid emission rates (Alves *et al.* 2016). These drought-like conditions are mediated by a gradient of soil water availability, which decreases from groundwater-subsidized white-sand valleys to the clay uplands (Garcia *et al.* 2021), where we observed generally higher emissions in the dry season (Fig. 2). Previous work showed high prevalence of isoprene emitting species among hygrophytic plants, to monoterpene emitters among xerophytic plants (Loreto *et al.* 2013), which may be analogous to the shift in emissions we observed from isoprene in wet conditions to heavier compounds in the dry season.

We hypothesize that shifting C investment toward heavier compounds during the dry season is a consequence of changing leaf metabolic status induced by drought conditions. Reduced photosynthesis reduces the rate of production of the primary isoprenoid building block, dimethylallyl diphosphate (DMADP) (Lantz *et al.* 2019). Both 5C isoprene and 10C monoterpenes are produced in the chloroplast from DMADP, but monoterpene emissions require less DMADP due to the much higher reaction affinity of monoterpene synthase enzymes compared to isoprene synthase (Harrison *et al.* 2013). This mechanism has been previously hypothesized to explain a shift from monoterpene emissions in developing leaves with low photosynthetic capacity, to isoprene emissions as leaves matured in the tropical tree *Hymenaea courbaril* (Kuhn *et al.* 2004b). Synthesis of 15C sesquiterpenes is still less dependent on photosynthetic rates as it takes place *via* a distinct metabolic pathway in the cytosol instead of in the chloroplast (Sallaud *et al.* 2009). It has been proposed that all three classes of isoprenoids play similar roles in the leaf, as antioxidants or signalling molecules for stress response (Vickers *et al.* 2009; Harrison *et al.* 2013; Riedlmeier *et al.* 2017; Zuo *et al.* 2019; Frank *et al.* 2021; Monson *et al.* 2021). Therefore, it is plausible that our observations reflect plant strategies to shift emission profiles in order to accomplish the same protective role under different metabolic conditions as the environment changes. We encourage further work to explore this hypothesis.

Implications for forest emissions and modelling

Although there is variability within and among the tree species studied here, and it is not possible to generalize results from three species to a whole plant community, in this paper we present the results for species that are widespread in the central Amazon and a make meaningful contribution to plant biomass and productivity (Fauset *et al.* 2015). Understanding mechanisms of seasonal variation in plant emissions of isoprenoids is important for predicting their influence on atmospheric chemical–physical processes. For example, each class of isoprenoid contributes differently to secondary organic aerosol (SOA) formation. Laboratory-determined SOA yield from isoprene has been reported as <6% (Kroll *et al.* 2005; Xu *et al.* 2014) or higher over forested regions when isoprene is emitted in much larger quantities relative to other compounds (Carlton *et al.* 2009). Yield rates tend to be higher (~5–10%) for monoterpenes (Griffin *et al.* 1999a, 1999b) and higher still (~20–70%) for sesquiterpenes (Hoffmann *et al.* 1997; Griffin *et al.* 1999b; Lee *et al.* 2006a,b; Chen *et al.* 2012; Jaoui *et al.* 2013). While emission models incorporate photosynthetic and temperature effects on emission rates (*e.g.* MEGAN; Guenther *et al.* 2012), our study highlights the importance of understanding drought effects on isoprenoid fractionation in order to capture seasonal shifts in emission compositions in models.

In this light, it is important for future studies to consider a wider range of volatile organic compounds together with their synergetic importance in plant ecophysiological processes and subsequent impact on the atmosphere. Our results suggest that emissions of monoterpenes and sesquiterpenes might be higher than anticipated and indicate a seasonal change in the composition of the emitted isoprenoids. In fact, seasonal shifts in monoterpene composition have already been reported in ambient air (Jardine *et al.* 2015; Yáñez-Serrano *et al.* 2018); but sesquiterpenes might have been underestimated, given their high reactivity with ozone and OH and thereby the difficulty to detect them in ambient air (Jardine *et al.* 2011; Yee *et al.* 2018), indicating that only leaf-level measurements are likely to give us a true measure of forest sesquiterpene emissions. This opens more questions in order to understand what processes regulate isoprenoid emission capacities of Amazonian trees, and the need to consider seasonal shifts in isoprenoid composition in emission modelling.

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AUTHOR CONTRIBUTIONS

Eliane Gomes Alves, Tyeen Taylor, Michelle Robin and Débora Pinheiro de Oliveira contributed to the development and sampling design of the study, the collection and the chemical analysis of isoprenoid samples, and to the statistical analysis of datasets. Juliana Schietti contributed to the development and sampling design of the study, and to the statistical analysis of datasets. Sérgio Duvoisin Júnior, Nora Zannoni, Jonathan Williams and Christoph Hartmann contributed to the chemical analysis of isoprenoid samples. José Francisco C. Gonçalves contributed to the collection of isoprenoid data. Jochen Schöngart, Florian Wittmann and Maria T. F. Piedade contributed the dataset for the initial selection of species. All authors contributed to writing of the manuscript.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Table S1. Compounds detected in blank samples for each field campaign. Values are means (SD) of mixing ratios (ppt) of all blanks in which each compound was detected.

Figure S1. Seasonal variation in isoprene and monoterpenes, grouped by plant species and all trees combined. Data is plotted as dry season values as a factor of wet season values, on a $\log_{10}$ scale, with the bold line at 1 indicating no seasonal difference. Stars indicate significant differences between seasons, determined by subtracting wet from paired dry season values and comparing the distribution to 0 (*t*-test, alpha = 0.05). Boxes show the median and first and third quartiles, with whiskers and points distinguished at 1.5 times the interquartile range.

Figure S2. Seasonal variation in isoprenoid emission and photosynthetic capacities for the subset of trees sampled during the dry-to-wet season transition (n = 5 for *E. coriacea*; n = 3 for *P. hebetatum*). Letters denote significant differences between seasons, within species, by Tukey HSD test (alpha = 0.05).

Figure S3. Relationship between total isoprenoid emission rate and photosynthetic rate among all measurements from each species. A significant relationship was detected only in *E. grandiflora* (linear regression, $P < 0.01$, $r = 0.37$).

Figure S4. Leaf concentration of monoterpenes (a) and sesquiterpenes (b) for *P. hebetatum* across all forest types.

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