



Chiral Volatile Organic Compound Fluxes from Soil in the Amazon Rainforest across seasons

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Abstract. The rainforest floor is an underexplored source and sink of biogenic volatile organic compounds (BVOC), and its contribution to the ecosystem BVOC budget remains poorly understood. We performed multi-seasonal measurements in the Amazon rainforest on the soil-atmosphere exchange of enantiomer-resolved monoterpenes (C₁₀H₁₆) and sesquiterpenes (C₁₅H₂₄), isoprene, and two isoprene oxidation products: methacrolein and methyl vinyl ketone. Soil uptake of isoprene and isoprene oxidation products was stronger during dry seasons than wet seasons and peaked in the afternoon hours. Sesquiterpene emission was highest during the El Niño- influenced dry season. Monoterpene fluxes showed changes in speciation across seasons. The presence or removal of the litter layer strongly altered the speciation of the monoterpene and sesquiterpene fluxes, partly shifting from emission with the litter layer to uptake without it. At the same time, the litter had no significant effect on isoprene. Enantiomeric ratios of α -pinene, limonene, β -pinene, and camphene differed between soil emissions and ambient air and shifted seasonally, suggesting distinct soil sources and processes. For each sesquiterpene only one enantiomer was detected. Although soil BVOC fluxes contribute little to the overall atmospheric budget in rainforests dominated by the plant canopy, they may affect near-surface chemistry and play important roles in soil ecology.

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1 Introduction

The Amazon rainforest, Earth's largest tropical forest, releases a significant portion of carbon as biogenic volatile organic compounds (BVOC) to the atmosphere (~300 Tg C yr⁻¹ (Guenther et al., 2012)). These BVOCs serve crucial ecological functions in vegetation response to abiotic (e.g., heat, drought, and oxidation) and biotic stress (e.g., pathogens and herbivores) as well as in the interactions between plants, animals, and microbes for communication (Kesselmeier and Staudt, 1999; Guenther et al., 2006; Gill and Tuteja, 2010; Ueda et al., 2012; Peñuelas et al., 2014; Staudt et al., 2017; Huang et al., 2019; Yáñez-Serrano et al., 2019, 2020; Honeker et al., 2023). Once emitted into the atmosphere, BVOCs rapidly react with oxidants such as ozone and hydroxyl radicals, thereby modulating oxidant levels and contributing to secondary organic aerosols (SOA) formation (Tripathi et al., 2025). SOA can grow to become cloud condensation nuclei (CCN) and, in turn, affect the Earth's radiative balance and climate (Andreae and Crutzen, 1997; Atkinson, 2000; Lelieveld et al., 2008; Williams, 2004). Among BVOCs, isoprene (150 Tg yr⁻¹) and monoterpenes (MTs 60 Tg yr⁻¹) dominate emissions, while sesquiterpenes (SQTs), although less abundant, are highly reactive with ozone making them important for atmospheric chemistry processes (Bonn and Moortgat, 2003; Bourtsoukidis et al., 2012; Horváth et al., 2012; Yee et al., 2018; Barreira et al., 2021; Dada et al., 2023; Isaacman-VanWertz et al., 2024; Bourtsoukidis et al., 2025a). Moreover, most MTs and SQTs are chiral, existing in two mirror-image forms known as enantiomers. These enantiomers can have distinct biological impacts and their emissions may be linked to different biological processes making enantiomer-resolved studies increasingly important (Williams et al., 2007; Yassaa and Williams, 2007; Song et al., 2014; Staudt et al., 2019; Zannoni et al., 2020;

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Byron et al., 2021, 2025; Daber et al., 2025). For instance, abiotic stress has been shown to alter the chiral ratio of the plant emitted monoterpene α -pinene (Byron et al., 2021, 2025), yet enantiomer-resolved soil fluxes have not been reported. Soils are recognized as both a source and sink of BVOCs, however, compared to canopy BVOC, understanding on soil BVOC fluxes seasonal and diurnal dynamic, enantiomeric resolution, and the environmental thresholds controlling flux direction and speciation remain poorly constrained. Flux magnitudes and speciation vary with vegetation, litter, soil properties, and available ambient VOCs (Kivimäenpää et al., 2018; Mäki et al., 2019b; Tang et al., 2019; Rinnan and Albers, 2020; Ghirardo et al., 2020; Llusà et al., 2022; Mu et al., 2023). Across ecosystems, soil BVOC fluxes are typically one to two orders of magnitude lower than canopy emissions, partly due to concurrent microbial uptake (Cleveland and Yavitt, 1997; Owen et al., 2007; Peñuelas et al., 2014; Drewer et al., 2021). Microbes can consume isoprene using it as an energy source, and may emit it at low rates (Cleveland and Yavitt, 1997; Gray et al., 2015). In tropical forests, MTs are uptaken or emitted depending on the environmental conditions such as the soil water content, nutrient composition in soil, temperature, season, and vegetation (Bourtsoukidis et al., 2018; Llusà et al., 2022). Amazonian soils are reported to act as a strong source of SQTs under certain conditions (Bourtsoukidis et al., 2018). SQT emissions are associated with plant roots (Mäki et al., 2017; Tsuruta et al., 2018), soil fungi, and microbes (Asensio et al., 2008b; Horváth et al., 2012; Weigl et al., 2016). Soil BVOC fluxes in an artificial tropical forest have been reported to alter strongly under drought conditions (Pugliese et al., 2023).

El Niño climate events which occur semi-periodically (every 2-7 years) impact the Amazon rainforest by decreasing rainfall and elevating temperatures. The 2023-24 El Niño event caused a record drought in the Amazon rainforest (Espinoza et al., 2024). Climate projections indicate that the frequency and intensity of El Niño events are likely to increase under continued greenhouse gas emissions, with potentially profound effects on the Amazon and its BVOC dynamics (Geng et al., 2024).

In this study we measured soil BVOC fluxes in the Amazon rainforest across four seasons, including the El Niño drought period in the dry season 2023. Soil fluxes of isoprene, two of isoprene's oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR), and enantiomer-resolved MTs and SQTs were quantified using thermal desorption-chiral gas chromatography-time of flight mass spectrometry (TD-GC-ToF-MS). The measurements were conducted at the Amazon Tall Tower Observatory (ATTO) research station (Andreae et al., 2015) located 150 km north east of Manaus (Brazil). The effect of temperature, soil moisture, soil properties, litter content and terpenoid ambient concentrations on soil terpenoid fluxes in terms of magnitude, flux direction (emission and/or uptake), and chemical composition, including chiral speciation was investigated.

2 Methods

2.1 Study site and sampling set-up

The experiments were conducted at the Amazon Tall Tower Observatory (ATTO) research facility in 2023 and 2024 across four seasons: from January 22-26, 2023 during the dry-to-wet transition season (dry-to-wet 2023), from October 1-14, 2023 during the dry season (dry 2023), from April 24 to May 2, 2024 during the wet season (Wet 2024), and from October 11-20, 2024 during the dry season (dry 2024). The ATTO site is a long-term measuring station in the Amazon Basin implemented to better the understanding of biosphere – atmosphere interactions (Andreae et al., 2015). The predominant wind direction from the northwest brings air masses from pristine rainforest with minimal human perturbation (Pöhlker et al., 2019). In the Amazon Basin the dry season with the lowest rainfall usually lasts from June to September and the wet season from January to April (Biscaro et al., 2021). The data presented here was taken at the end of each wet and dry season. The dry season in 2023 was influenced by an El Niño event with the result of a prolonged drought and higher than usual temperatures (Espinoza et al., 2024).



Soil VOC fluxes were measured from three manually operated soil chambers at six different times of the day: 5 am, 8 am, 11 am, 2pm, 5 pm, and 8 pm local time. The three manual chambers were made from polyvinyl chloride (PVC), had a volume of 3.5 L, and consisted of a collar (ID: 19.4 cm, Area: 0.0295 m²) and a lid equipped with a Teflon inlet and outlet (Fig. 1). The three PVC collars were installed at three different locations in close proximity to each other near the 325 m tall tower.

85 To avoid cutting roots, the collars were gently placed on the soil and sealed from the outside with soil taken from the area surrounding the collars. In January 2023 (dry-to-wet season 2023), the three chambers were installed on spot 1, spot 2, and spot 3 (Table 1). To investigate the effect of litter content on soil fluxes, the litter layer was removed from spot 3. Spot 1 was located near a termite nest. In October 2023 (dry season 2023), the chambers in spot 2 and 3 were moved to spot 4 and 5, where their litter layers were kept intact. Additional soil flux measurements without litter were performed from spot 5 in

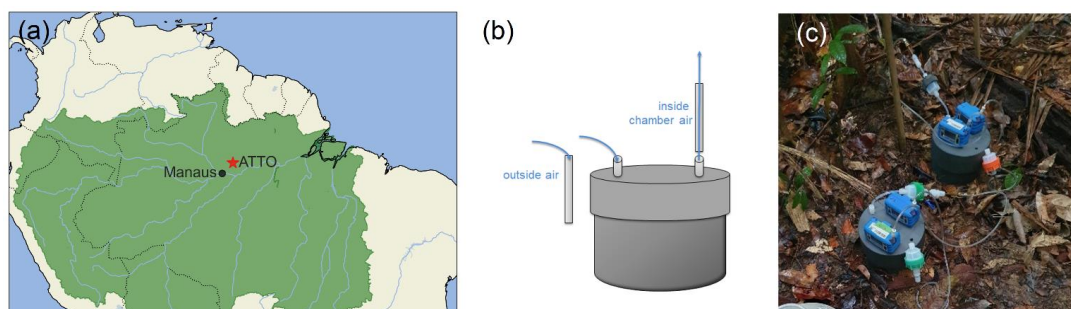
90 October 2024 (Table 1). Spot 4 and 5 were located within 15 m of spot 2 and 3. For soil flux measurements, the chamber lids were kept closed for 15 minutes before collecting samples, following a method used for cartridge measurements from a steady-state chamber within a study by Pugliese et al., (2023). Air was sampled on two sorbent cartridges in parallel: one connected at the outlet of the chamber; and one sampling the incoming ambient air near the chamber's inlet. The air volume was taken using a handheld pump (GilAir plus, Gilian) for 30 minutes at a flow rate of 200 mL min⁻¹, resulting in a total of 6

95 L of air collected. To prevent ozone from affecting the sampled VOCs, an ozone scrubber, consisting of a dried quartz filter soaked with a 10% sodium thiosulfate solution, was placed in front of each cartridge during sampling. The ozone scrubbers were replaced after a maximum time of two weeks, as this time interval has been tested to be their minimum durability (Ernle et al., 2023). The sorbent cartridges were made of silica-coated stainless-steel tubes (89 mm x 5.33 mm I.D., SilcoNert 2000, SilcoTek) containing 150 mg of Tenax ® TA mesh range 80/100 (Supelco) and Carbograph ® 5 TD mesh range 40/60

100 (Lara srl.). The sorbents were sealed with quartz wool and stainless-steel tension springs (Sigma Aldrich).

Prior to use, the cartridges were conditioned at 300 °C for 1 hour while being flushed with pure nitrogen at 2 bar pressures (TC-20, Markes International). After sampling, the cartridges were stored in a freezer at -20 °C and analyzed within 60 days at the Max Planck Institute for Chemistry in Mainz, Germany.

105 To assess the effect of the chamber material on artifacts of the investigated soil BVOC fluxes, measurements were taken from a clean blank chamber. It was placed close to the other chambers on a soil spot where the bottom was covered in Teflon foil. 23 replicates were measured from the blank chamber distributed across all seasons, and the mean blank fluxes and the standard deviation median are reported in Table A2 in Appendix A.



110 **Figure 1** (a) Map of the measurement location with the Amazon Basin watershed region overlaid. (Lehner and Grill, 2013) (b) Schematic and (c) photo of the soil measurement set-up.

Table 1 Overview of measurement campaigns with attributed season, start date, end date, measured chambers and the number of flux data points



Name in plots	Season	Start Date	End Date	Number of flux data points	Chambers Measured
Jan 2023	Dry-to-wet	2023-01-22	2023-01-26	20	Spot 1, Spot 2, Spot 3 without litter
Oct 2023	Dry	2023-10-01	2023-10-14	39	Spot 1, Spot 4, Spot 5
Apr-May 2024	Wet	2024-04-24	2024-05-02	35	Spot 1, Spot 4, Spot 5
Oct 2024	Dry	2024-10-11	2024-10-20	43	Spot 1, Spot 4, Spot 5, Spot 5 without litter

115 2.2 BVOC analysis - Thermal Desorption - Gas Chromatography - Time of Flight Mass Spectrometer (TD-GC-TOF)

Sampled cartridges were desorbed using a thermal desorption unit (TD100-xr and UNITY xr, Markes International). The thermal desorption process consisted of two stages. In the first stage, the cartridges were dry-purged for 5 min and then desorbed for 10 min at 250 °C. The desorbed sample was pre-concentrated onto a cold trap (Material Emissions, Markes International). In the second stage, the cold trap was first purged for 1 min at 30 °C and then injected at 250 °C for 5 min into the gas chromatograph (GC, Agilent Technologies 7890B) equipped with a 60 m long chiral β -DEX™ 120 capillary column (Sigma Aldrich) with an inner diameter of 250 μ m and a film thickness of 0.25 μ m. Helium 5.0 was used as a carrier gas at 1.2 ml min⁻¹ flow rate. The GC oven temperature was initially held at 50 °C for 5 min, then ramped at 1.5°C min⁻¹ to 110 °C, followed by a ramp at 10°C min⁻¹ to 220 °C, where it was held for 10 minutes.

125 Detection was performed using a Time-of-Flight-Mass Spectrometer (TOF-MS, BenchTOF, MARKES International Ltd., U.K.). The mass range that is recorded by the TOF-MS was set from 40 to 600 m/z. The filament voltage was set between 1.7 V and 1.8 V.

The GC-TOF-MS peaks were integrated using chromatography analysis software PARADISE (v 6.1.7 dev) and IDL (Obersteiner et al., 2015). Compounds were quantified using a gas standard calibration mixture and liquid standards injected at 1, 2, 4, 6, 8, and 10 μ L in methanol-diluted compound mixtures with a syringe directly onto the sorbent cartridge. The gas standard mixture contained isoprene, MVK, MACR, tricyclene, (–) and (+)- α -pinene, (–)- β -pinene, (+) and (–)-camphene, sabinene, β -myrcene, (–)- α -phellandrene, (–)-3-carene, α -terpinene, (+)-limonene, γ -terpinene, terpinolene, m- p- and o-cymene, (+) and (–)-linalool, and β -caryophyllene (Apel-Riemer International, USA). For compounds without available gas or liquid standards, quantification was based on the response factor of a compound with the closest mass spectra resemblance. Identifying various SQTs and MTs without standards can be challenging due to their structural similarities, leading to increased uncertainty. β -caryophyllene was used for quantifying uncharacterized SQTs (SQT_unknown), while (–)- β -pinene and (+)-limonene were used for (+)- β -pinene and (–)-limonene, respectively. (+)-camphene and (–)-camphene were used for both detected α -fenchene enantiomers due to their similar structures. Compounds in the sample chromatogram were identified by matching retention times with those of the standards, and enantiomers were confirmed by spiking with pure standards. Compounds lacking standards were identified by comparing their mass spectra with those in the NIST library. Peak areas were used to quantify concentrations, and measurement variability was assessed by the deviation in measurements from at least five samples with the same concentration of standard calibration gas or liquid standard injection.



2.3 Flux calculations

145 The VOC fluxes were calculated according to the following formula:

$$F = Q * \frac{C_t - C_0}{A}$$

where F is the flux rate ($\mu\text{mol m}^{-2} \text{h}^{-1}$), Q is the flow rate (200 mL min^{-1} equals $0.012 \text{ m}^3 \text{ h}^{-1}$), A is the chamber area (0.02956 m^2), C_t is the BVOC concentration in the chamber, and C_0 is the BVOC concentration outside the chamber (both in pptv).

150 The flux error was calculated by the variability of the BVOC concentration derived from repeated measurements of a known concentration of analyte and ranged between 3% for α -pinene and up to 20% for sabinene as this peak was not separated well. The calibration gas mixture is contributing a systematic error of up to 5% (as stated by the supplier Apel-Riemer International, USA).

2.4 Soil properties and soil respiration

155 Soil samples were collected in June 2023 near spots 1, 2, and 3, where VOCs had been measured in January 2023. Samples were taken using a metal core, and the top 5 cm was retained for analysis. After removing larger roots manually, samples were sieved and stored in plastic bags prior to analysis.

Physicochemical analyses were performed by the Departamento de Ciência do Solo, University of São Paulo. Soil microbial biomass carbon was determined following Vance et al. (1987). Particle density was measured using a pycnometer according to EMBRAPA's Manual de Métodos de Análise de Solo (3rd edition, 2017). Soil texture was assessed using the Bouyoucos
 160 hydrometer method (SSSA Book Series 5, 1996). Total nitrogen was extracted by the Kjeldahl method, with electrical conductivity measured via a conductivity meter. Ammonium (N-NH_4^+) and nitrate (N-NO_3^-) concentrations were determined by steam distillation (EMBRAPA, 2009). All procedures followed standard protocols detailed in EMBRAPA manuals.

165 The chambers contained litter as found at the site, except for one experimental chamber in the dry-to-wet season 2023 and the dry season 2024, where fluxes without litter were investigated and the litter was actively removed. To measure the litter density at the site, litter samples were collected from six spots arranged in a circle of approximately 5 m in the same area as the sampling chambers, ensuring that ongoing flux measurements were not disturbed. The litter was dried in an oven at 60°C and weighed until no weight change was observable to determine the sample dry weight.

170 Soil respiration, i.e., soil CO_2 emission flux, was measured using an automated closed dynamic soil flux measuring system consisting of an infrared gas analyzer (LI-870, Licor Inc., Lincoln, NA, USA), an 8-port multiplexer (LI-8250, Licor Inc., Lincoln, NA, USA), and three dynamic soil flux chambers (LI 8200-104 Long-Term Chambers with opaque lids, Licor Inc., Lincoln, NA, USA). The soil flux chambers were placed on PVC collars (ID: 19.4 cm) installed close to spot 1, spot 2, and spot 3 during dry-to-wet season 2023, and close to spot 4 and 5 during dry 2023 and wet season 2024. As done for the
 175 manual chamber, the litter layer was removed from spot 3 (Table 1). The soil flux measurement is based on the gas concentration development in the recirculated ambient air within the closed dynamic system once the chamber lid is closed. Each measurement consisted of: 90 s of pre-purge (chamber lid open) to flush the lines with the ambient air; 390 s (240 s in January 2023) of closure time; 60 s of post-purge. The soil CO_2 flux was calculated by applying an exponential model to the CO_2 concentration change during chamber closure period (Pugliese et al. 2023). The first 30 s after the chamber closure were
 180 omitted due to possible perturbations induced by the chamber closure, and the exponential model was applied to the successive 240 s.



2.5 Meteorological and ozone data

The meteorological data, such as the relative humidity and temperature (measured by a termohygrometer, IAK I-Series (Galltec-Mela)) were taken at 26 m height within the canopy at 80 m walk-up INSTANT tower, which is also located at the ATTO site. Ozone data is from an inlet placed 50 cm above the soil. Ozone concentrations were computed by an Ozone Analyzer (Thermo Environmental Instruments 49i) located in a climatized container at the foot of the tower, that works by pumping air from the sample inlet, measuring O₃ concentration by a direct relationship with the absorption of UV light. The soil moisture was measured as soil water content at 10 cm depth close to the INSTANT tower at the ATTO site, at approximately 1 km distance from the measurement site. From the soil water content at 10 cm depth, the water-filled pore space (WFPS) was calculated using the formula $WFPS = \frac{\theta_v}{n}$ where θ_v represents the volumetric water content and n denotes the total porosity calculated as $n = 1 - \frac{\rho_b}{\rho_p}$. Here ρ_b is the bulk density, assumed to be at 1.18 g cm⁻³ as a mean value for Amazon rainforest soils with similar soil texture (Bernoux et al., 1998) and ρ_p is the particle density of the soil as the mean measured value for the analyzed soil samples.

2.6 Statistical analysis

Statistical analyses were performed using Python (version 3.12.4) with the following packages: numpy (v.2.0.0), pandas (v.2.2.2), matplotlib (v.3.9.1), seaborn (v.0.13.2), statsmodel (v.0.14.2), and scipy (v 1.16.0). Data visualization was conducted using matplotlib and seaborn. Statistical differences between soil fluxes measured in different seasons and from different soil plots were determined using the Tukey HSD (Honestly significant difference) test following a significant result from ANOVA. For comparisons of enantiomeric ratios, the non-parametric Mann-Whitney U test was used due to non-normality of the data. For correlations between the fluxes and environmental parameter Pearson coefficients were calculated. Statistical significance was accepted if $p < 0.05$.

3 Results

3.1 Soil properties

In this study, three separate chambers were set up and sampled in each measured season. Each chamber was placed over soil with distinct characteristics, representing the extremes of soil type and litter coverage in the vicinity of the tower. This strategy allowed us to gauge the range of possible soil fluxes and their drivers, which can be combined with subsequent soil surveys over wider areas to provide realistic regional soil flux estimates. In the first measured season in January 2023, the first chamber (termed spot 1 with litter), was placed in vicinity to a termite nest, on relatively porous soil, with a high soil organic matter content, a natural litter covering, and a correspondingly high CO₂ respiration rate (Table 2). The CO₂ respiration did not show a pronounced diurnal cycle, therefore mean values with standard deviation are reported. In contrast to spot 1, spot 2 and spot 3 had very similar soil physiochemical properties and are more representative of the investigated area. These contrasting sites were deliberately chosen to represent the range of soil properties present in the rainforest. These two soil chambers were placed on less permeable soil, in one chamber the litter was left undisturbed (spot 2 with litter) and in the other the litter was removed (spot 3 without litter), so that the role of litter could be examined. The mean CO₂ flux was around three times lower in Spot 3 with the removed litter layer compared to spot 1 and 2. In contrast to that Spot 1 showed a marked difference in organic content compared to spot 2 and spot 3 (Table 2).

was more than three times higher in the chambers with litter content than in the chamber without litter in the dry-to-wet season 2023. Spots 4 and 5, measured in October 2023 and April-May 2023 had similar CO₂ fluxes. Following the dry-to-wet season 2023, the chambers from Spots 1-3 were relocated to new sites to ensure undisturbed soil conditions after sampling for analysis of physicochemical properties (Table 2). During the following three measured seasons, dry 2023, wet



2024, and dry 2024, the chambers were kept at the same locations with spot 1 remaining very close to the same location as before (approximately 0.5 m distance to spot 1 in the dry-to-wet season) and the other two chambers were moved approximately 4–5 m and therefore given the new names spot 4 and spot 5. It is worth noting that the spot 1 chamber was located close (approximately 1 m) to a termite nest in all measured seasons, whose processed wood residues likely contributed to the higher organic content.

Soil physicochemical properties for the three chambers as measured in the dry-to-wet season 2023 are shown in Table 2. At all three spots, the soil was clay-based. The microbial biomass and organic matter content were higher in the spot 1 than in the other two chambers. The removal of litter did not have an impact on the measured soil physicochemical properties.

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The dry weight of litter samples taken at five positions around the areas sampled in the dry-to-wet season 2023 had an average of 9.5 g per chamber area. The five litter samples ranged from 6.1 to 15.2 g, showing significant variability even within a few meters. Nonetheless, based on our visual inspections, we believe the litter amounts contained within the chambers were representative of the location throughout all the sampling periods. When scaled to 1 m², the mean litter weights were 322 (207–515) g m⁻².

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Table 2 Soil CO₂ respiration rate with standard deviation and physiochemical parameters from the three soil chambers measured in January 2023; soil samples were taken in June 2023.

		Spot 1 with litter	Spot 2 with litter	Spot 3 without litter
CO₂ respiration	[μmol m ⁻² s ⁻¹]	8.7±0.7	7±1	2.4±0.5
Organic Matter	[g kg ⁻¹]	105.7	74.3	69.9
Colometric Organic Matter				
Matter	[g dm ⁻³]	63.3	47.7	44.7
Organic Carbon	[g kg ⁻¹]	61.3	43.1	40.5
Microbial Biomass				
Carbon	[mg C g ⁻¹ of dry soil]	1.76	1.49	1.57
N total	[mg kg ⁻¹]	4123	3437	3395
pH	CaCl ₂	3.53	3.75	3.82
	KCl	3.6	3.78	3.88
Particle Density	[g cm ⁻³]	2.54	2.58	2.61
Soil texture	Coarse Sand [%]	7	9	9
	Fine Sand [%]	6	3	2
	Total Sand [%]	13	11	11
	Silt [%]	14	23	19
	Clay [%]	73	65	70
Texture Class		clay	clay	clay

240 3.2 Meteorological conditions

At the ATTO site, the mean monthly rainfall during the years 2023–2024 was 59 mm, with the highest rainfall occurring in March 2023 (410 mm) during the wet season and the lowest in August 2023 (23 mm) during the dry season (not shown here). The mean air temperature is higher in the dry seasons, with the highest temperatures in October 2023 reaching up to



37 °C during daytime and dropping to 26 °C at night. Relative humidity in the dry seasons varied from between 80-90% (peaking at 05:00 am) to 45-50% around midday (Fig. 3 c). In the wet season 2024 and dry-to-wet 2023, temperatures were cooler and relative humidity (RH) higher; with midday temperature maxima between 28-30°C (80% RH) and night time temperature minima between 23-24°C (100% RH). Generally, soil temperature peaks later in the day and was less variable spanning from 24 – 28°C at 10 cm depth. The soil water content did not show a diel cycle, but rather changed seasonally between 0.17-0.3 m³m⁻³. The calculated water-filled pore space at 10 cm depth was 46±2% in the dry-to-wet transition season 2023, 28.5±0.4% in the dry season 2023, 56±4% in the wet season 2024 and 32.3±0.2% in the dry season 2024. Photosynthetically active radiation (PAR) (Fig. 3 e) is slightly higher during the dry seasons than during wet season. Figure 2 shows the mean diurnal meteorological values of air temperature, soil temperature, relative humidity, soil water content and photosynthetically active radiation (PAR) for the four measurement periods.

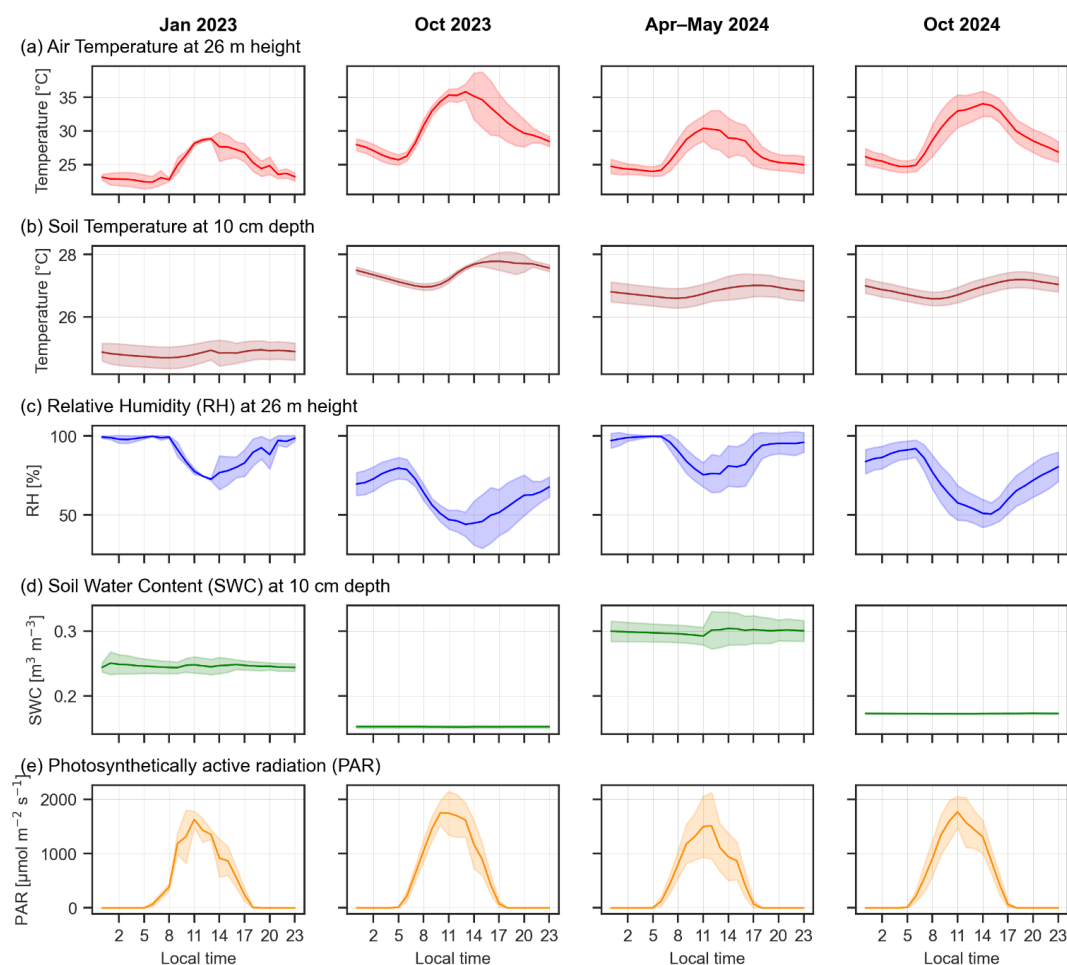


Figure 2 Meteorological data during the measured seasons with (a) temperature (red) and (c) relative humidity (blue) measured at 26 m at the Instant tower, (b) soil temperature (orange) and (d) soil water-content (green) measured at 10 cm depth and (e) photosynthetically active radiation (PAR) incoming at 81m at the Instant tower across the four measurement periods in the different seasons. The line represents the mean and shaded area is the standard deviation.



3.3 Diurnal and seasonal dynamics of soil terpene exchanges

The cartridge measurements taken outside of the chambers were used to determine the ambient mixing ratios of the terpenoids at soil level (15 cm above the ground), while those taken from the chambers were used to derive BVOC soil fluxes. Our measurements revealed distinct patterns in BVOC concentrations and fluxes from the Amazon rainforest soils. Figure 3 summarizes the mean measured mixing ratios for terpenoids (isoprene, total monoterpenes, and total sesquiterpenes), methacrolein (MACR) and methyl vinyl ketone (MVK), at the soil level (outside of the chambers) over the four seasons sampled. The BVOC measurements at soil level showed higher mixing ratios for all terpenoids in the dry seasons (dry 2023 and dry 2024) than in the wet seasons (dry-to-wet 2023 and wet 2024). Isoprene exhibited the largest seasonal change, increasing by almost an order of magnitude from 0.1-1.6 ppbv (wet season) to over 4 ppbv (dry seasons) (Table A1 with mean seasonal values in Appendix A). While isoprene peaked around noon, MTs and SQTs at soil level peaked later in the day in the dry seasons.

Soil level MT and SQT mixing ratios were equivalent to 33% of the isoprene mixing ratio in the dry season 2023 and 2024, and even at times exceeded isoprene mixing ratio levels in the wet season. SQTs were generally elevated during the dry season 2023; and in both dry season 2023 and dry season 2024, a maximum in SQTs was observed later in the day at 5 pm. Diurnal cycles in SQTs were less pronounced in the dry-to-wet and wet seasons.

The net soil fluxes of isoprene and two of its oxidation products methacrolein (MACR) and methyl vinyl ketone (MVK) (Fig. 3) were negative in all four measured seasons, indicating that these species were consistently taken up by the soil. The fluxes showed strong seasonal variation, with higher uptake fluxes in the dry season 2023 and 2024 compared to the dry-to-wet and wet seasons (Tukey test: $p < 0.001$).

Unlike isoprene, which was taken up by the soil, MTs and SQTs show remarkable variation between seasons and even between years (Fig. 3). Notably, MTs and SQTs did not display as clear a diurnal cycle as isoprene (Fig. 4 and 5). While MTs and SQTs were predominantly emitted, they were also taken up in many samples in 2024. The emission or uptake is highly seasonal, time-of-day dependent and specific to soil conditions. Interestingly, the SQT emission was significantly higher in the dry season 2023 compared to the other measured seasons.

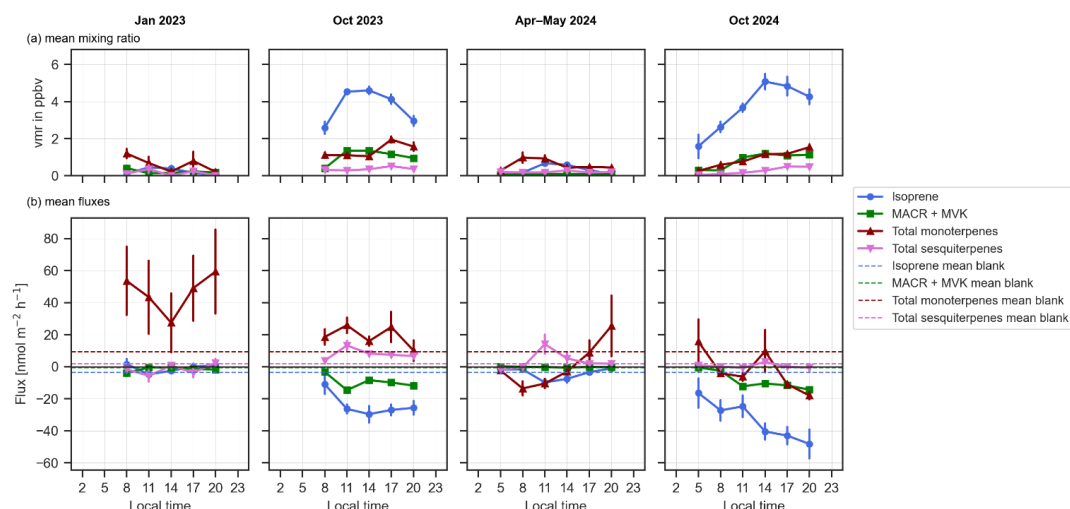


Figure 3 Diurnal curves of the (a) mean mixing ratios in ppbv at the soil level and (b) mean calculated fluxes in $\text{nmol m}^{-2} \text{h}^{-1}$ from the soil chambers of isoprene (blue), isoprene oxidation products methacrolein (MACR) and methyl vinyl ketone (MVK), the total monoterpenes (red) and the total sesquiterpenes (pink) over the four measured seasons dry-to-wet 2023, dry 2023, wet 2024 and dry 2024 in the course of a day from 5 am to 8 pm. Error bars indicate the standard error. Dotted lines represent the mean blank chamber measurements.



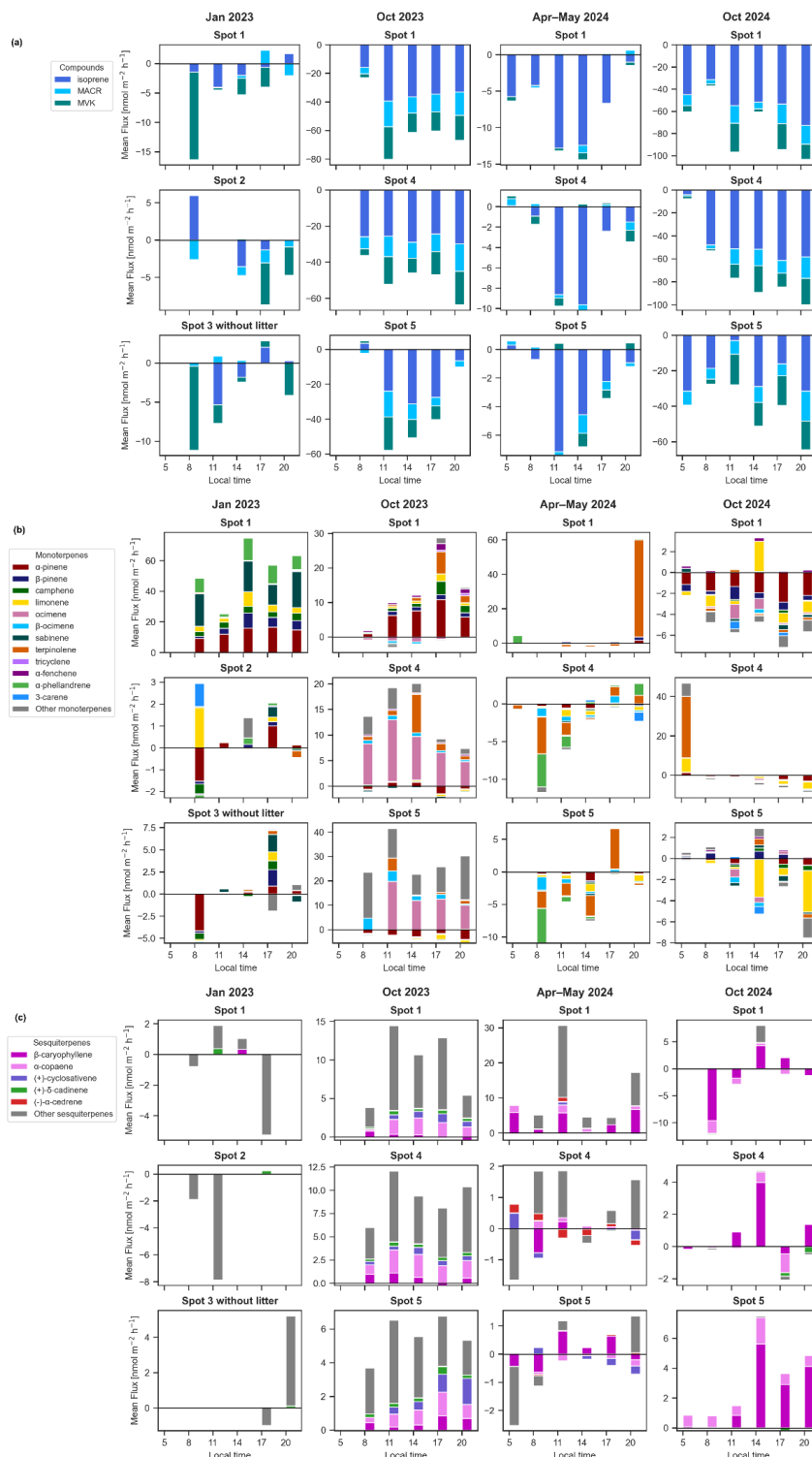
3.4 Effects of the soil properties on terpenoid soil fluxes

290 In this section we examined how the chamber location and associated soil properties (soil spots) influenced the various compounds fluxes over the four seasons. The results are summarized in Fig. 4.

For isoprene, in the dry-to-wet season 2023 no significant differences in fluxes were found ($p > 0.05$) (Fig. 4a) between the measured soil chambers. However, in the other three seasons there was a showed significantly higher isoprene uptake by spot 1 than spot 5 ($p < 0.01$ for all) and in the dry season 2024 also in spot 5 than spot 4 ($p < 0.001$).

295 Comparing fluxes of MTs from different soil spots, we note clear monoterpene speciation differences (Fig. 4b). The highest emission rates were observed for soil spot 1 in the dry-to-wet transition season 2023. Here, the flux was significantly higher compared to the other two spots ($p < 0.0001$). The flux in spot 1 in both seasons in 2023 was dominated by α -pinene emission, while in the dry season 2024 it was uptaken in the same soil spot. In the other chambers in the dry-to-wet and dry season 2023 α -pinene was uptaken, and ocimene dominated the emission in the dry season 2023. In the wet season 2024 the uptake rates for terpinolene and limonene exceeded those for α -pinene, while in the dry season 2024 α -pinene and limonene dominated the MT uptake fluxes.

300 The total SQTs flux is dominated by β -caryophyllene and α -copaene, followed by $(-)$ - α -cedrene, $(+)$ -cyclosativene and $(+)$ - δ -cadinene. Some other SQTs could not be identified as no standard was available and the matching factor with the NIST library was high for several different possible SQTs. They are shown as “other sesquiterpenes” (Fig. 4c) The highest observed emission was in the dry season 2023 with values of mean total SQTs emission of $8 \pm 2 \text{ nmol m}^{-2} \text{ h}^{-1}$. In the wet season 2024 and dry season 2024, the mean emission rates were lower at 4 ± 4 and $0.4 \pm 0.5 \text{ nmol m}^{-2} \text{ h}^{-1}$, respectively, and even negative in the dry-to-wet season 2023 at $-0.9 \pm 0.3 \text{ nmol m}^{-2} \text{ h}^{-1}$. In the wet and dry season 2024, SQT flux changed between uptake und emission during the day and was soil spot dependent.



310 **Figure 4** Stacked plots of the mean flux values of the compounds (a) isoprene and its oxidation products methacrolein (MACR) and methyl vinyl ketone (MVK), (b) monoterpenes and (c) sesquiterpenes from the measured chamber spots across seasons except the spots with removed litter layer. Note different y-axis dimensions.



3.4.1 Effect of litter removal

When litter was removed from the soil plot, in the two seasons dry-to-wet season 2023 and dry season 2024, no significant difference was found in the fluxes for isoprene and total MTs ($p > 0.05$). However, there was a notable shift in the terpenoid speciation between the soil chambers with and without litter (Fig. 5). In the dry season 2024, there was an emission of β -pinene, α -copaene and β -caryophyllene in spot 5 with litter and an uptake of those terpenoids when the litter was removed. In contrast, limonene was taken up in both cases, but less with the litter layer intact. Similarly in the dry-to-wet season 2023, β -pinene, α -terpinene, and 3-carene emissions declined with litter removal and α -pinene even shifted from emission to uptake.

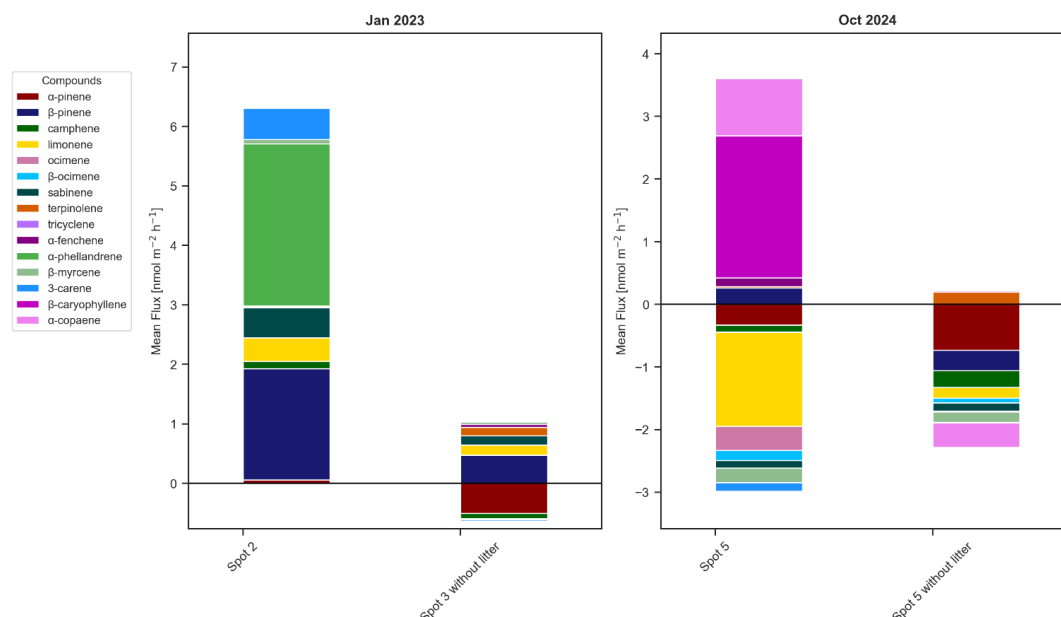


Figure 5 Stacked plots of the mean flux values of monoterpenes and sesquiterpenes showing the difference between the litter layer removed (“without litter”) to the one with intact litter layer in the dry-to wet season 2023 for two different spots at the same time and in the dry season 2024 for the same spot before and after litter removal.

3.4.2 Soil fluxes VS environmental conditions

Isoprene, MVK and MACR have a strong negative correlation (Fig. 6) with their ambient atmospheric concentration indicating the uptake rates were higher when the available concentrations in the air above the soil were higher. Different MT species like α -phellandrene, 3-carene, γ -terpinene, limonene, and β -ocimene, also show negative correlation with their mixing ratios (-0.21 to -0.82 ; $p < 0.001$), while β -myrcene had positive correlation with the ambient concentration (0.54 ; $p < 0.001$). In general, the correlations with the environmental conditions like air and soil temperature and soil water content were stronger for isoprene and its oxidation products. The correlation with the photosynthetic active radiation (PAR) was highest for ocimene (0.29 ; $p < 0.01$) and the total SQTs, as well as α -copaene (0.26 and 0.24 ; $p < 0.001$).



	ambient VMR	air temperature	PAR	soil temperature	soil water content	ozone
isoprene	-0.74 ***	-0.48 ***	-0.076	-0.39 ***	0.54 ***	-0.43 ***
MVK	-0.78 ***	-0.56 ***	-0.11 *	-0.27 ***	0.59 ***	-0.6 ***
MACR	-0.81 ***	-0.52 ***	-0.085	-0.38 ***	0.63 ***	-0.65 ***
Total Monoterpenes	-0.12 *	-0.11 *	-0.08	-0.27 ***	-0.048	0.02
α-pinene	-0.03	0.0022	-0.0093	-0.2 ***	-0.078 *	0.077 *
β-pinene	-0.16 ***	-0.062	-0.042	-0.28 ***	0.024	-0.0042
camphene	0.082 *	-0.073 *	-0.11 **	-0.21 ***	-0.1 **	0.013
limonene	-0.24 ***	-0.07 *	0.012	-0.23 ***	-0.025	-0.061
ocimene	0.29 **	0.21 *	0.29 **	0.14	-0.49 ***	0.55 ***
β-ocimene	-0.21 ***	0.12 *	0.08	0.071	-0.23 ***	0.21 ***
sabinene	0.11 *	-0.22 ***	-0.11 *	-0.47 ***	0.11 *	-0.13 *
terpinolene	0.017	-0.17 **	-0.14 **	0.027	0.081	-0.051
tricyclene	0.14 **	0.0052	-0.081	-0.028	-0.12 *	0.017
γ-terpinene	-0.52 ***	-0.12 *	-0.15 **	-0.16 ***	-0.15 **	0.11 *
α-terpinene	-0.15 **	-0.07	-0.041	-0.089	-0.071	0.087
α-fenchene	-0.073	0.091 *	-0.09 *	0.18 ***	-0.23 ***	0.11 *
(-)-α-phellandrene	-0.82 ***	-0.25 **	-0.22 *	-0.32 ***	-0.049	0.069
β-myrcene	0.54 ***	-0.077	-0.12 *	-0.0029	-0.13 **	0.048
3-carene	-0.72 ***	-0.037	0.028	-0.19 *	0.016	-0.091
Total Sesquiterpenes	0.11 *	0.26 ***	0.26 ***	0.26 ***	-0.11 *	0.16 **
β-caryophyllene	-0.15 **	0.0036	-0.044	0.1 *	0.065	0.043
α-copaene	-0.21 ***	0.32 ***	0.24 ***	0.28 ***	-0.24 ***	0.4 ***
(+)-cyclosativene	-0.54 ***	0.5 ***	0.13 *	0.48 ***	-0.55 ***	0.53 ***

Figure 6 Heatmap of correlations between the flux of measured compounds and various environmental variables: ambient mixing ratio (VMR) of each compound, air temperature at 26 m, incoming photosynthetically active radiation (PAR) at 81 m, soil temperature and soil water content at 10 cm depth. Statistical significance of the Pearson correlation is indicated by asterisks: (*) for $p < 0.05$, () for $p < 0.01$ and (***) for $p < 0.001$.**

3.5 Atmospheric implications

The emission fluxes from the soil ($\text{Flux} > 0$) were analyzed alongside their lifetimes for the reaction with the hydroxyl radical (OH) and ozone for substances with established reaction constants in the literature (Table B1 in Appendix B shows the used reaction coefficients). The lifetime of each substance emission was calculated with an OH concentration of $1.0 \cdot 10^6 \text{ molecules cm}^{-3}$ based on estimations of previous studies (Pfannerstill et al., 2021; Ringsdorf et al., 2024) and the measured ozone at 50 cm above the soil, which was in the range of 1.2– 23.5 ppbv.

The mean MT and SQT emission fluxes are shown as measured in Fig. 7, along with the emission fluxes weighted according to their reactivity to OH and O_3 . This serves to highlight emissions with greater atmospheric chemistry impact. The



importance of the mean emission composition of α -pinene was 28% in January 2023, but when weighted by its contribution to OH reactivity it was only 16% and further decreased to 6% when weighted by its contribution to ozone reactivity. Opposed to this the importance of β -caryophyllene as a reactive sesquiterpene increased from 4% of total emissions in October 2023, to 5% contribution to OH reactivity and 52% responsible for ozone reactivity. The other seasons show similar trends.

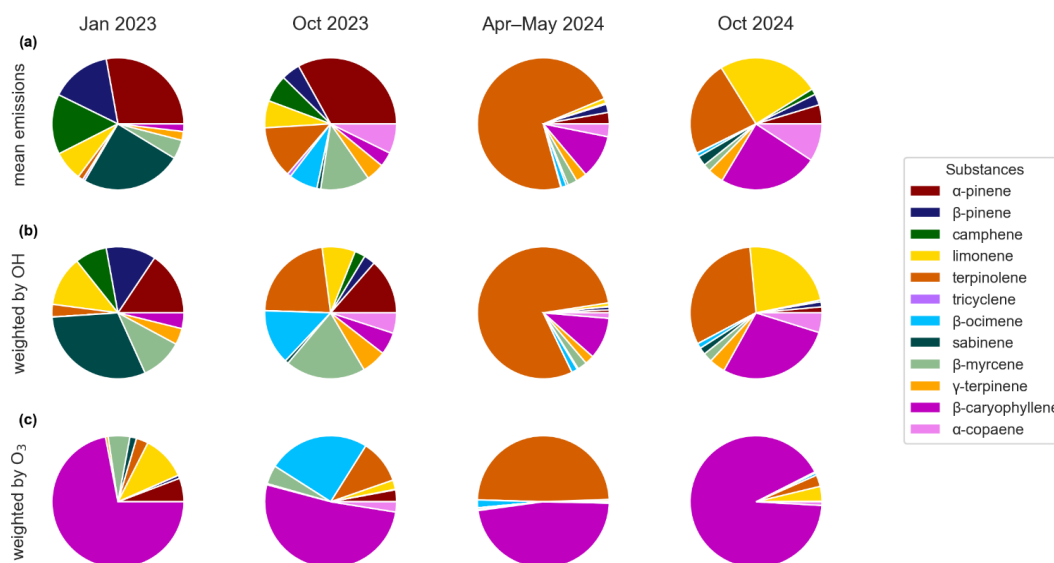


Figure 7 (a) Pie charts representing the mean emission fluxes composition. Reactivity impact on atmospheric chemistry towards (b) OH radicals and (c) Ozone (O_3).

3.6 Chirality

The chiral composition of the sampled MTs and SQTs was investigated. Interestingly, for the SQTs found here, only one enantiomer was detected, while for many MTs, both enantiomers were present in the samples.

The (–)- α -pinene was significantly more enriched ($p < 0.05$) inside the soil chamber than in the ambient air in the dry-to-wet season 2023, dry season 2023, and in the wet season 2024 (Fig. 8). The ratio of (+)-to (–)-limonene and the ratio of (+)- to (–)-camphene was significantly different in the soil than in the ambient air during the dry 2023, wet 2024, and dry season 2024. The ratio of (+) to (–)- β -pinene was higher in the ambient air than inside the soil chambers in the dry-to-wet 2023, dry 2023, and dry season 2024.

When only comparing the ambient enantiomeric ratios across the season, they are in most cases significantly different from each other (Fig. 8 e-h)), especially when comparing wet season 2024 with the dry season 2023 it was significantly different for all chiral MTs.

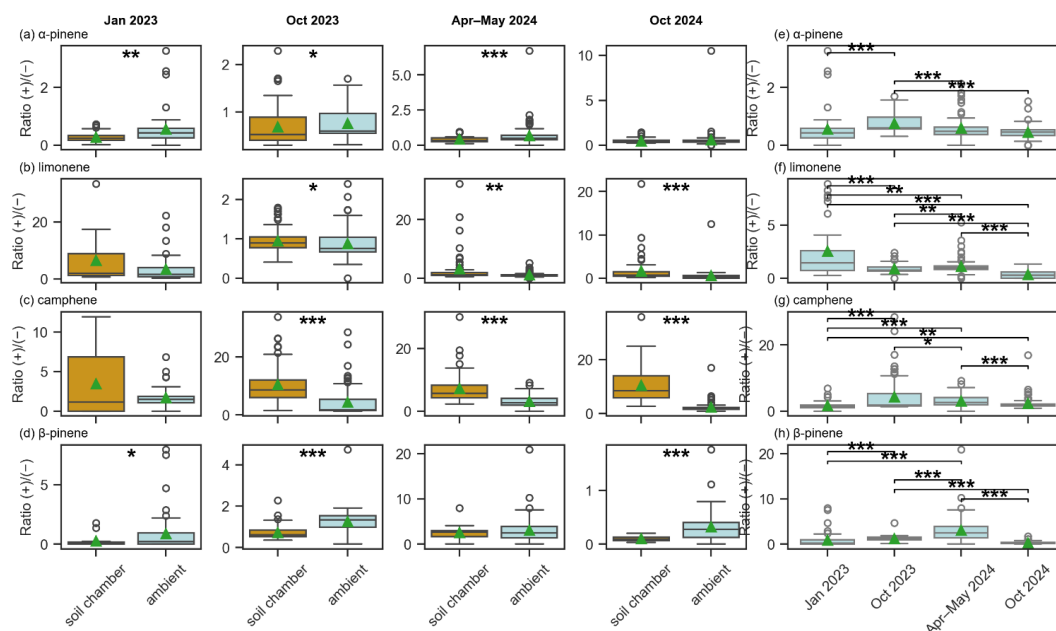


Figure 8 Boxplots show the ratio of the (+)- to (-)-enantiomers for (a) α -pinene, (b) limonene, (c) camphene and (d) β -pinene in both ambient air (light blue) and soil chamber air (dark orange) across different seasons. The rightmost panels display the seasonal distribution of ambient air enantiomeric ratios for (e) α -pinene, (f) limonene, (g) camphene and (h) β -pinene. The boxes represent 25% to 75% of the dataset. Mean values are indicated by green triangles, while the median values are indicated by the central lines. Whiskers indicate the minimum and maximum data points at 1.5 times the interquartile range. Circles represent the outliers. A single asterisk (*) denotes statistically significant differences between groups ($p < 0.05$), double asterisks (**) indicate highly significant differences ($p < 0.01$), and (***) indicate very high significant differences ($p < 0.001$). For improved visualization, in plot (e), two outliers with a ratio of (+)/(-) greater than 5 and in plot (f) one outlier with the ratio greater than 10 are not displayed. They are still included in the statistical analysis.

4 Discussion

Our data demonstrate that Amazonian Forest soils act as a sink and source of isoprenoid BVOCs. Isoprene is uptaken in the dry seasons, MTs and SQTs are emitted and uptaken, dependent on season and the local soil spot. Notably, under extreme drought conditions such as those during the 2023 El Niño event, these soils can become sources of highly reactive SQTs.

4.1 Drivers of variation in soil isoprenoid fluxes

4.1.1 Isoprene and the oxidation products MACR and MVK

As shown in Fig. 4, the isoprene mixing ratios follow diurnal cycles with peak levels around noon, which is consistent with light and temperature driven *de novo* emissions from the canopy above (Guenther et al., 1996; Crutzen et al., 2000; Yáñez-Serrano et al., 2015; Alves et al., 2016; Jardine et al., 2017; Gomes Alves et al., 2023). In the dry seasons, the soil uptake of isoprene mirrors the ambient diurnal concentration, suggesting it is a key factor in determining the flux. However, no night-time sampling after 8 pm or before 5 am was performed which could bias the estimates of diel patterns. For isoprene, MACR, and MVK, strong correlations between soil fluxes and both ambient mixing ratios (-0.74 to -0.81 ; $p < 0.001$) and key environmental parameters such as soil water content (0.54 to 0.63 ; $p < 0.001$) and temperature (-0.48 to -0.56 ; $p < 0.001$) (Fig. 7) are found. The correlation with the environmental parameters like temperature hint either to the higher ambient concentrations of isoprene at higher temperatures (Alves et al., 2016) or to more efficient uptake rates at higher temperatures. Jiao et al., (2023) found that the size of the BVOC sink in soils was proportional to the atmospheric availability of the compound, indicating that higher uptake rates are driven by higher ambient concentrations.



Laboratory *in vitro* studies suggest that soil microorganisms like bacterial and fungal taxa consume isoprene (Cleveland and Yavitt, 1997; Gray et al., 2015) and use it as a carbon source. At the same time, bacteria can also be emitters of isoprene (Fall and Copley, 2000). Experiments with glass beads and sterilized soils suggest abiotic factors like adsorption and solubility in soil water are playing only a minor role in BVOC fluxes from soil (Cleveland and Yavitt, 1997). Cleveland and Yavitt (1998) reported optimal temperature and soil humidity thresholds for isoprene uptake in temperate forest soils. Accordingly, the pronounced seasonal differences in isoprene uptake observed here likely reflect shifting conditions for the microbial communities which is likely responsible for these processes.

MACR and MVK are the dominant first-generation oxidation products of isoprene (Pierotti et al., 1990), but they can also be directly emitted by plants (Jardine et al., 2012). MACR and MVK have been reported to have a bidirectional flux in and from trees (Fares et al., 2015) and can be absorbed by tree saplings (Tani et al., 2010). Therefore, a consumption of these compounds by roots and/or microorganisms in the soil is a possible explanation for the observed uptake rates. The processes for the uptake of MACR and MVK may be similar to those of isoprene.

4.1.2 Monoterpenes and sesquiterpenes

Different MTs correlated negatively or positively with ambient concentrations (Fig. 7), indicating there are different processes responsible for the soil fluxes of each MT. During different seasons, daytime and soil spots, different MT species fluxes were observed (Fig. 5), suggesting very local and seasonally changing processes are at play. The seasonal differences were likely caused by a shift in the microbiome during the transition of an El Niño-influenced year 2023 to the year thereafter, and the different conditions across the different seasons. Roots have also been implicated as sources of MTs from soils (Asensio et al., 2008a), and both plant roots and microbial communities are responsive to climatic variation and drought stress (Bourtsoukidis et al., 2014; Byron et al., 2021; Honeker et al., 2023; Pugliese et al., 2023). So, the roots, as well as the microbiome, could have contributed to the different MT species fluxes.

Soil microorganisms, particularly fungi, are known to be significant sources of SQTs (Horváth et al., 2012; Ditengou et al., 2015; Gfeller et al., 2019). A study by Bourtsoukidis et al. (2018a) has shown that Amazonian soils can emit SQTs at rates comparable to the plant canopy during the dry season conditions. In contrast, our study did not observe consistent SQT emissions during the two dry seasons of 2023 and 2024. Only in the El Niño-influenced dry season 2023 was an emission pattern of SQT evident. In the subsequent dry season 2024, SQTs were even partly uptaken by the same soil spots. The extreme dry season in 2023 was characterized by particularly low soil water-filled pore space (WFPS), reaching $30.32 \pm 1.27\%$ at 10 cm depth, closely matching the optimum for SQT emission reported by Bourtsoukidis et al. (2018a) at $31.3 \pm 6.3\%$. In contrast, WFPS in the dry season 2024 was higher at $33.64 \pm 1.51\%$

4.2 Effect of litter

The removal of litter during the dry-to-wet season 2023 and the dry season 2024 did not significantly affect the flux of isoprene. This suggests that microorganisms residing in the soil layer beneath the litter are primarily responsible for metabolizing these compounds. In contrast, the removal of litter did decrease the flux of certain compounds like α -pinene, β -pinene, limonene, camphene, α -copaene and β -caryophyllene. Although this result was not statistically significant (ANOVA t-test $p > 0.05$, sample size with litter $n=23$, without litter $n=8$) it gives directional evidence towards the role of litter on total soil terpenoid fluxes. The alteration could be attributed to the abiotic degradation of storage pools within the litter material or to the activity of microorganisms inhabiting the litter surfaces. Previous studies have shown that biotic VOC emissions from litter can be 5 to 10 times higher compared to abiotic processes (Gray et al., 2010), indicating that the microbial community on the litter surfaces plays a significant role in VOC fluxes. Similar findings have been reported in soil terpenoid VOC flux shifts following litter removal in other ecosystems, such as an eucalyptus plantation (Mu et al., 2023), in Boreal forests (Mäki et al., 2017, 2019a), and in a Mediterranean forest (Yang et al., 2024). Litter VOCs were found to have an influence in



microbial community structures (McBride et al., 2020) and are known to mediate many microbe–microbe, microbe–plant, and microbe–animal interactions (Bitas et al., 2013; Schmidt et al., 2015; Schulz-Bohm et al., 2017). So, the very local litter structure could be responsible for the different MT and SQTs in the studied soil spots. The highest litter fall rates are usually observed at the end of the dry season and can be increased during an El Niño dry season (Martius et al., 2004; Barlow et al., 2007; Brando et al., 2008), so also the seasonal differences observed for MTs and SQTs could be partly attributed to the litter layer.

4.3 Chirality

In tropical rainforests, the most abundant monoterpene in ambient air is α -pinene, with the (–)-enantiomer usually dominating over the (+)-enantiomer (Williams et al., 2007; Zannoni et al., 2020; Byron et al., 2021). Recently, experiments using isotopically labelled CO_2 within an enclosed rainforest biome revealed that (–)- α -pinene and (–)-limonene are, like isoprene, emitted *de novo*, but also emitted from storage pools, whereas (+)- α -pinene and (+)-limonene are solely emitted from storage pools (Byron et al., 2021). During the dry-to-wet season 2023, dry season 2023, and the wet season 2024, elevated ratios of (–)- α -pinene to (+)- α -pinene in soil compared to ambient air suggest a preferential uptake of (+)- α -pinene or a preferential emission of (–)- α -pinene by the soils. It could be that (–)- α -pinene is synthesized *de novo* by roots or microorganisms in the soil. For β -pinene there seems to be a mechanism at play altering the ratio coming from soils only during the dry seasons and dry-to-wet season, possibly a response to the lower water content in the soil. Camphene and limonene seem to behave similarly to each other and the ratio between soil and ambient is present in all measured seasons except for the dry-to-wet transition season, indicating a consistent difference between the soil enantiomeric fingerprint and the ambient air. So, for these different chiral MT different variables seem to have an influence on the enantiomeric ratio. Chiral monoterpene emissions from plants are known to be tissue-specific, meaning leaves, stem, and belowground emission of enantiomer ratios often differ (Staudt et al., 2019; Daber et al., 2025). So, the roots could be altering the ratio of the chiral enantiomers from the soil, but it is unclear if microbes and fungi also take part. As chiral enantiomers share identical physicochemical properties, abiotic processes cannot explain the discrimination between soil chamber and ambient air ratios. Litter degradation mechanisms could also influence chiral ratios at the soil, as litter fall rates change between seasons (Martius et al., 2004; Barlow et al., 2007; Brando et al., 2008).

As the chiral ratios also change between seasons, but not always between the soil chamber and ambient air, soils are not the only influence on chiral ratios of MTs, above-ground plants must also play an important role. It is known that drought and recovery phases change the chiral ratio of MTs (Byron et al., 2021, 2025), but also mechanical stress or herbivory could impact the ratios, as it is known to alter terpenoid VOC emissions (Holopainen and Gershenzon, 2010; Midzi et al., 2022; Bourtsoukidis et al., 2024).

4.4 Comparison with isoprenoid flux data

4.4.1 Soil fluxes

Here we compare the found soil fluxes with literature values. Very few studies have reported BVOC soil fluxes in tropical rainforests.

Isoprene

The values determined for the uptake flux for isoprene in this study (mean flux of $-19 \pm 7 \text{ nmol m}^{-2} \text{ h}^{-1}$ across all seasons) differ from those found in other studies conducted in different ecosystems or an enclosed artificial rainforest environment.

For instance, the drought study in an experimental rainforest by Pugliese et al. (2023) and the earlier one by Pegoraro et al. (2006) reported isoprene uptake flux values that are a factor of 1000 higher. We have to note that those studies were carried out in an artificial enclosed rainforest “Biosphere” with no oxidation by OH or O_3 occurring and therefore ambient concentrations of isoprene reach over 200 ppbv, 10 times those found in the natural Amazon ecosystem. This will favor soil



bacteria that use ambient isoprene and therefore influence the measured uptake rates. Similarly, a study in an Eucalyptus urophylla plantation forest in subtropical China (Mu et al., 2023) found values for isoprene uptake differing by a factor of 500 to the here found values. Eucalyptus trees are known for their high isoprene emission (Benjamin et al., 1996), and the available isoprene in such plantations makes an increase in isoprene uptake likely. So, these discrepancies can be attributed to the vastly different ecosystem with different conditions than those studied here.

Monoterpenes

The mean flux of total MTs found in this study was $10 \pm 20 \text{ nmol m}^{-2} \text{ h}^{-1}$ across all seasons. Other soil flux studies reported values between $174\text{--}734 \text{ nmol m}^{-2} \text{ h}^{-1}$ for Malaysian Borneo rainforest soil (Drewer et al., 2021) and $76 \text{ nmol m}^{-2} \text{ h}^{-1}$ in (unfertilized) soil spots in a tropical rainforest in Guiana (Llusà et al., 2022). Boreal forest showed higher fluxes for MTs from soil in the range of $145\text{--}454 \text{ nmol m}^{-2} \text{ h}^{-1}$, probably because of storage pool emissions from needle leaf litter (Mäki et al., 2017, 2019a).

Conversely, an uptake of MTs of $-73 \text{ nmol m}^{-2} \text{ h}^{-1}$ was found in an Eucalyptus urophylla plantation forest in subtropical China (Mu et al., 2023) and a mean uptake rate of $-3 \text{ nmol m}^{-2} \text{ h}^{-1}$ in a Mediterranean shrubland (Asensio et al., 2008a). MTs are likely taken up by microorganisms as an energy source and emitted by others and from roots. All of these processes are likely influenced by temperature and soil water content, with each community strain having its optimal conditions for emission or uptake processes.

Sesquiterpenes

The overall low mean emission flux for SQTs found here is $4 \pm 2 \text{ nmol m}^{-2} \text{ h}^{-1}$. In comparison to another study conducted with soil from the same measurement site but mostly under laboratory conditions (Bourtsoukidis et al., 2018), the fluxes for SQTs identified here are lower by a factor of 10 to 10,000. However, this data was derived from a study where BVOC-free air was cycled into the chambers and onto soil at laboratory conditions, generating a maximum potential flux. The air was partially enriched with VOCs from a calibration mixture, which cannot reflect natural conditions with their greater chemical diversity and simultaneous soil uptake and emission.

The higher emission rates of SQT during the dry season 2023 are consistent with the high abundance of sesquiterpenoids measured within the rainforest canopy during the same and similar time periods, which was influenced by El Niño and resulted in severe drought conditions in plants (Pfannerstill et al., 2018; Byron et al., 2025). The largest emissions of SQTs from the soil were noted at the optimal water-filled pore space (WFPS) of approximately 35% as determined by the model developed by Bourtsoukidis et al., (2018b), with a similar value occurring during the extremely dry season 2023.

In other soil studies, SQT fluxes were also low, ranging between values for uptake in the range of $-32\text{--}-44 \text{ nmol m}^{-2} \text{ h}^{-1}$ (Llusà et al., 2022; Mu et al., 2023) and emission of $3\text{--}121 \text{ nmol m}^{-2} \text{ h}^{-1}$ (Mäki et al., 2019a; Llusà et al., 2022).

The fluxes measured in this study are generally lower than those reported in the literature, which can be attributed to differences in environmental conditions.

4.4.2 Context of soil fluxes with canopy and plants fluxes in tropical rainforests

When comparing the uptake rates of isoprene by the soil to the estimated canopy fluxes, they appear rather small. The mean isoprene uptake rate of $-19 \text{ nmol m}^{-2} \text{ h}^{-1}$ across all seasons is less than 0.1% of any reported canopy isoprene flux from tropical rainforests, which are in the range of $11\text{--}1007 \text{ } \mu\text{mol m}^{-2} \text{ h}^{-1}$ (Sarkar et al., 2020; Rizzo et al., 2010; Müller et al., 2008; Karl et al., 2007; Kuhn et al., 2007; Greenberg et al., 2004; Karl et al., 2004; Rinne et al., 2002). However, the isoprene uptake may sustain soil microbes and perform multiple other functions within the soil ecosystem. The actual isoprene used up in soils might be larger when taking into account in the soil produced and emitted isoprene.

The MTs and SQTs fluxes from the soil are also smaller by several orders of magnitude than those reported for the forest canopy. The mean SQT flux of $4 \pm 2 \text{ nmol m}^{-2} \text{ h}^{-1}$ found here makes up only a fraction of the estimated SQT canopy flux of $1.7\text{--}3.8 \text{ } \mu\text{mol m}^{-2} \text{ h}^{-1}$ at the site (Alves et al., 2016). However, SQT fluxes are scarce as their lifetimes and concentrations are



low, and measurements remain difficult. It likely exerts a disproportionate influence given the high reactivity of SQTs in the atmospheric boundary layer.

The SQT soil flux is also 6 to 500 times smaller compared to cryptogamic species emission rates at the same measurement site that were evaluated per tree surface area: 0.025 to almost 1.96 $\mu\text{mol m}^{-2}_{\text{tree}} \text{h}^{-1}$ (Edtbauer et al., 2021).

520 4.5 Impact on air chemistry

The uptake flux of isoprene by soil is very small compared to the sink via reaction with OH, so it contributes very little to the overall isoprene budget dominated by plants. Also, the emission fluxes of MTs and SQTs from soil are small compared to the canopy fluxes, but the emission of highly reactive species, such as β -caryophyllene, can have an impact on local, near-surface atmospheric chemistry, particularly in relation to particle formation. Our findings indicate that ozone reactivity at the soil level is predominantly driven by emissions of β -caryophyllene (Fig. 8) while α -pinene is less important although it is emitted in higher quantities. Soil emissions could influence the atmospheric oxidative capacity by suppressing oxidants through their reactivity (Dada et al., 2023). This in turn can affect the formation of secondary organic aerosols (SOAs), a fraction of which will grow to become cloud condensation nuclei and thus impact clouds, weather patterns and climate (Dada et al., 2023; Tripathi et al., 2025). Changes in land use or climate conditions that alter these emissions could, in turn, influence atmospheric composition and climate dynamics. Nevertheless, it is still unclear if these below-canopy emissions have an effect beyond the near-surface processes.

4.6 Limitations of this study and future directions

The study was conducted at three locations on a Terra Firme rainforest plateau, and the samples exhibited significant variability between soil spots. Expanding the spatial resolution could provide deeper insights into the overall fluxes of terpenoids at the soil-atmosphere interface in the Amazon rainforest. Measurements were paused during rain to protect the equipment, and while some samples were collected shortly before or after rain events, this may have introduced some bias. Furthermore, logistical constraints limited measurements to between 5 am and 8 pm potentially omitting nocturnal microbial and abiotic processes.

In the future, actual microbial taxa responsible for certain compounds should be identified. Additionally, isotopic labelling and on-line measurements with a greater time resolution between samples, could further strengthen the understanding of soil BVOC exchange processes.

5 Conclusion

This study highlights the Amazon soil as a dynamic, context-sensitive participant in the regional BVOC budget. The soil-atmosphere exchange of terpenoids and their enantiomers in the Amazon rainforest is strongly connected to season and environmental conditions like temperature and soil moisture. For the uptake of isoprene, MACR, and MVK ambient concentrations and temperature seem to be the primary drivers. MT and SQT emissions and uptake showed to be governed on the litter layer and season, as well as showing very local differences from spot to spot in the composition of the total flux. An El Niño drought period caused enhanced SQT emissions from soil.

Chiral analysis revealed distinct patterns in the emission and uptake of monoterpene enantiomers, like α -pinene, limonene, camphene and β -pinene, indicating shifts in source contributions, *de novo* synthesis or possible preferential uptake of one enantiomer over the other. Elevated ratios of (+)- β -pinene to (–)- β -pinene in soils during the dry season, hint towards a response in the soil to lower soil moisture. Soil processes are influencing the chiral ratio of MTs in the Amazon, but are not the only determining factor as differences in the ratio were also observed in ambient air across seasons.



While soil fluxes of terpenoids are generally much lower than those from the forest canopy, the emission of highly reactive
555 compounds such as SQTs and their oxidation products can impact local atmospheric chemistry and SOA formation (Andreae
and Crutzen, 1997; Atkinson, 2000; Williams, 2004; Lelieveld et al., 2008; Tripathi et al., 2025; Bourtsoukidis et al., 2025b).
These findings underscore the importance of considering soil processes in models of rainforest BVOC emissions, especially
in the context of ongoing climate change and increasing frequency of extreme weather events which could enhance SQT
emission from soils. By taking up isoprene and emitting MTs and SQTs the soil will exert partial control over near-surface
560 ambient atmospheric ozone and OH.
Future research should expand spatial and temporal coverage, integrate microbial community analyses, and further resolve
the mechanisms underlying chiral BVOC fluxes. Such efforts are essential for a comprehensive understanding of the
Amazon's role in regional and global atmospheric chemistry, especially in the face of climate warming.

Appendix A

565 **Table A1 Mean Retention times, mean measured flux in nmol m⁻² h⁻¹ with standard deviation and mean ambient ratio in pptv with
standard deviation of all measured terpenoid substances in each season.**

Number of data points	mean RT [min]	mean flux [nmol m ⁻² h ⁻¹]				ambient vmr [pptv]			
		31	70	58	55	33	81	58	54
Substance		Jan 2023	Oct 2023	Apr-May 2024	Oct 2024	Jan 2023	Oct 2023	Apr-May 2024	Oct 2024
isoprene	5.50	-1.46 ± 4.72	-27.18 ± 21.82	-5.00 ± 7.06	-35.33 ± 26.32	220.66 ± 262.27	3829.13 ± 1462.75	356.48 ± 448.87	3977.21 ± 1922.10
MACR	8.04	-0.58 ± 1.25	-10.84 ± 7.43	-0.23 ± 0.92	-8.63 ± 7.07	92.74 ± 78.31	974.02 ± 506.21	69.94 ± 41.23	820.60 ± 476.11
MVK	8.55	-2.94 ± 4.68	-11.48 ± 8.83	-0.33 ± 1.18	-11.34 ± 10.30	303.22 ± 291.41	1168.65 ± 713.21	95.35 ± 53.64	1049.95 ± 688.54
sabinene	32.82	2.69 ± 6.70	-0.31 ± 0.14	-0.14 ± 0.21	-0.15 ± 0.42	15.71 ± 17.54	30.86 ± 9.65	11.81 ± 8.42	25.48 ± 15.92
tricyclene	33.42	0.09 ± 0.21	0.14 ± 0.44	0.00 ± 0.06	-0.01 ± 0.02	2.88 ± 3.10	2.74 ± 1.82	1.30 ± 0.69	2.24 ± 1.28
(-)-α-pinene	33.95	5.63 ± 9.86	3.35 ± 8.11	-0.30 ± 1.56	-1.46 ± 1.95	42.20 ± 52.10	312.59 ± 144.49	62.43 ± 42.52	230.42 ± 124.94
(+)-α-pinene	34.44	3.50 ± 6.54	1.91 ± 5.15	0.05 ± 0.61	-0.60 ± 1.01	38.61 ± 106.25	222.45 ± 168.90	21.48 ± 11.59	101.49 ± 74.42
3-carene	35.70	0.06 ± 0.32	-0.00 ± 0.14	-0.19 ± 0.64	-0.12 ± 0.38	2.54 ± 4.57	2.11 ± 6.50	22.85 ± 41.13	10.87 ± 19.46
(+)-α-fenchene	36.93	0.26 ± 0.35	0.88 ± 1.86	-0.07 ± 0.13	0.19 ± 0.19	0.00 ± 0.00	15.07 ± 20.76	10.28 ± 4.33	2.22 ± 3.94
(-)-α-fenchene	37.22	0.17 ± 0.13	0.45 ± 0.99	-0.01 ± 0.04	0.10 ± 0.13	0.00 ± 0.00	3.42 ± 8.69	3.88 ± 1.89	0.85 ± 1.08
(+)-camphene	37.63	1.94 ± 3.01	0.77 ± 2.76	-0.22 ± 0.16	-0.35 ± 0.55	10.24 ± 22.46	68.85 ± 24.63	19.55 ± 9.66	55.73 ± 23.17
(-)-camphene	38.28	1.49 ± 2.63	0.99 ± 2.27	-0.00 ± 0.08	0.07 ± 0.18	9.86 ± 21.10	10.88 ± 15.89	3.41 ± 2.37	7.44 ± 4.91
(+)-β-pinene	39.61	3.33 ± 7.38	0.58 ± 0.93	0.22 ± 1.59	0.12 ± 0.24	2.08 ± 4.78	27.08 ± 22.66	23.51 ± 15.27	14.18 ± 8.61
(-)-β-pinene	40.02	1.70 ± 2.07	0.41 ± 1.18	-0.00 ± 0.33	-0.47 ± 0.90	3.95 ± 7.88	35.95 ± 14.49	11.78 ± 14.15	117.78 ± 50.05
ocimene	40.91		6.62 ± 7.22		-0.36 ± 0.41		105.92 ± 99.78		29.31 ± 25.42
(-)-limonene	41.48	1.39 ± 2.31	0.27 ± 2.38	-0.25 ± 0.45	-0.30 ± 3.19	7.07 ± 5.79	98.56 ± 110.33	27.36 ± 24.79	59.94 ± 67.64
(+)-limonene	41.87	1.36 ± 3.46	0.11 ± 1.31	-0.71 ± 1.15	-1.18 ± 3.98	10.21 ± 8.20	84.53 ± 66.76	57.35 ± 54.25	91.84 ± 212.67
terpinolene	45.32	0.17 ± 0.29	2.36 ± 6.76	4.13 ± 27.40	0.68 ± 4.73	8.72 ± 8.41	28.18 ± 29.79	91.87 ± 102.60	14.46 ± 9.11
α-copaene	57.04	0.00 ± 0.00	1.54 ± 0.89	0.38 ± 1.18	-0.06 ± 1.59	0.00 ± 0.00	63.81 ± 30.85	26.27 ± 22.84	115.55 ± 116.90
β-caryophyllene	60.78	0.04 ± 0.13	0.33 ± 0.75	1.90 ± 4.82	0.94 ± 4.29	0.00 ± 0.00	42.06 ± 31.43	24.34 ± 51.74	136.66 ± 210.52



(+)-cyclosativene	62.65		0.66 ± 0.50	-0.02 ± 0.39	0.00 ± 0.00		3.41 ± 6.67	36.40 ± 24.52	0.00 ± 0.00
(-)-α-cedrene	63.79	0.00 ± 0.01	0.04 ± 0.07	0.04 ± 0.45	0.00 ± 0.00	0.00 ± 0.00	1.51 ± 2.20	27.88 ± 17.12	0.00 ± 0.00
(+)-δ-cadinene	66.24	0.05 ± 0.14	0.33 ± 0.21	0.01 ± 0.05	-0.04 ± 0.15	1.04 ± 3.20	14.26 ± 6.60	1.96 ± 1.31	6.77 ± 9.71

Table A2 Mean blank measurements of each substance of the flux in nmol m⁻² h⁻¹ with standard deviation in each season.

	Jan 2023	Oct 2023	Apr-May 2024	Oct 2024
Number of blank datapoints	2	4	4	11
Substance	flux [nmol m⁻² h⁻¹]			
isoprene	-6.56 ± 4.30	-0.06 ± 2.33	1.91 ± 9.39	-8.52 ± 15.47
MACR	-1.35 ± 2.16	0.11 ± 3.40	0.03 ± 0.50	-0.66 ± 4.42
MVK	-0.20 ± 0.90	-2.81 ± 6.64	0.28 ± 1.13	0.31 ± 6.47
tricyclene	nan ± nan	0.16 ± 0.13	0.02 ± 0.00	-0.06 ± 0.07
(-)-α-pinene	-0.01 ± 0.00	0.03 ± 0.04	0.01 ± 0.02	-0.01 ± 0.02
sabinene	0.17 ± 0.02	1.70 ± 1.66	0.33 ± 1.26	-0.35 ± 1.07
(+)-α-pinene	0.05 ± 0.00	10.85 ± 8.72	-0.01 ± 0.18	-0.38 ± 0.53
α-phellandrene	0.00 ± nan	-0.00 ± 0.00	nan ± nan	-0.10 ± 0.23
(+)-α-fenchene		0.10 ± 0.09	0.08 ± nan	0.07 ± 0.09
(-)-α-fenchene		0.01 ± 0.01		0.01 ± 0.01
(+)-camphene	0.00 ± 0.00	0.18 ± 0.21	0.37 ± 0.30	0.01 ± 0.09
3-carene	0.00 ± 0.00	0.28 ± 0.40	0.03 ± 0.05	0.03 ± 0.08
(-)-camphene	0.02 ± 0.02	0.24 ± 0.14	-0.44 ± nan	0.01 ± 0.11
(+)-β-pinene		0.09 ± 0.08	0.01 ± 0.18	-0.13 ± 0.30
(-)-β-pinene		5.56 ± 4.78		-0.14 ± 0.02
ocimene	0.02 ± 0.01	0.15 ± 0.00	0.08 ± 0.28	0.09 ± 0.55
(-)-limonene	0.02 ± 0.01	3.92 ± 2.80	0.50 ± 0.32	-1.87 ± 5.07
(+)-limonene	0.00 ± nan	0.19 ± 0.30	-0.19 ± 0.06	-0.02 ± 0.05
terpinolene	0.00 ± 0.00	0.90 ± 0.95	0.14 ± 0.39	0.19 ± 0.42
α-copaene	0.00 ± 0.00	0.25 ± 0.36	0.15 ± 0.55	0.06 ± 0.65
(+)-cyclosativene		0.07 ± 0.08	0.30 ± 0.20	0.00 ± 0.00
β-caryophyllene		0.01 ± 0.00	0.21 ± 1.04	0.00 ± 0.00
(-)-α-cedrene		0.18 ± 0.18	-0.01 ± 0.00	0.01 ± 0.04
(+)-δ-cadinene	-6.56 ± 4.30	-0.06 ± 2.33	1.91 ± 9.39	-8.52 ± 15.47

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Appendix B

Table B1 Rate coefficients used for lifetime calculations.

Substance	CAS Number	Rate Coefficient OH ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference	Rate Coefficient Ozone ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference
isoprene	78-79-5	1.01E-10	(Atkinson et al., 2006)	1.29E-17	(Grosjean and Grosjean, 1996) (Atkinson et al., 1992)
MACR	78-85-3	5.00E-11	(Atkinson, 1986)	1.00E-20	(Atkinson et al., 1990)
MVK	78-94-4	1.78E-11	(Chuang and Stevens, 2004)	5.40E-18	(Neeb et al., 1998)
α -pinene	80-56-8	5.37E-11	(Atkinson et al., 2006)	9.00E-17	(Atkinson et al., 2006)
β -pinene	127-91-3	7.89E-11	(Atkinson and Arey, 2003)	2.10E-17	(Atkinson and Arey, 2003)
limonene	5989-27-5	1.61E-10	(Gill and Hites, 2002)	6.40E-16	(Atkinson and Arey, 2003)
camphene	201-234-8	5.10E-11	(Gaona-Colmán et al., 2017)	5.10E-19	(Gaona-Colmán et al., 2017)
β -myrcene	123-35-3	2.13E-10	(Atkinson, 1986)	4.90E-16	(Atkinson et al., 1990)
β -ocimene	3338-55-4	2.50E-10	(Atkinson, 1986)	3.15E-15	(Kim et al., 2011)
γ -terpinene	99-85-4	1.77E-10	(Atkinson and Arey, 2003)	1.40E-16	(Atkinson and Arey, 2003)
α -terpinene	99-86-5	3.60E-10	(Atkinson, 1986)	2.10E-14	(Atkinson and Arey, 2003)
sabinene	3387-41-5	1.19E-10	(Pang et al., 2023)	3.40E-17	(Pang et al., 2023)
terpinolene	586-62-9	2.30E-10	(Atkinson and Arey, 2003)	1.40E-15	(Atkinson et al., 1990)
p-cymene	99-87-6	1.57E-11	(Alarcón et al., 2013)	5.00E-20	(Atkinson et al., 1990)
α -copaene	3856-25-5	9.00E-11	(Atkinson, 1986)	2.90E-16	Estimated (Pollmann et al., 2005)
β -caryophyllene	87-44-5	2.00E-10	(Axel Clausen and Wolkoff, 1997)	1.15E-14	(Axel Clausen and Wolkoff, 1997; Richters et al., 2015)



575 **Data availability:** The data used to support the findings in this study are publicly available on the ATTO data portal and can be accessed with the following DOI: <https://doi.org/10.17871/ATTO.612.7.2472> (Schüttler et al., 2025)

Author contributions:

580 **JS:** Conceptualization, Methodology, Investigation, Visualization, Data curation, Formal analysis, Project administration, Writing – original draft

GP: Conceptualization, Methodology, Investigation, Project administration

JB: Conceptualization, Methodology, Investigation, Project administration

CM: Investigation, Data curation

CQDJ: Investigation, Project administration

585 **HH:** Project administration, Supervision

JL: Funding acquisition

JW: Conceptualization, Methodology, Investigation, Funding acquisition, Project administration, Supervision

All authors: Writing – review & editing

590 **Competing interests:** The authors declare that they have no conflict of interest.

Acknowledgements: For the operation of the ATTO site, we acknowledge the support by the Instituto Nacional de Pesquisas da Amazônia (INPA), the Amazon State University (UEA), the Large-Scale Biosphere-Atmosphere Experiment (LBA), FAPEAM, the Reserva de Desenvolvimento Sustentável do Uatumã (SDS/CEUC/RDS- Uatumã), and the Max Planck Society. Particularly, we would like to thank all colleagues involved in the technical, logistical, and scientific support of the ATTO project. We acknowledge the support by the University of São Paulo (USP) and the Instituto Nacional de Pesquisas da Amazônia (INPA).

During the preparation of this work, the author used perplexity and ChatGPT to improve the readability and language. After using this service, the author reviewed and edited the content as needed and takes full responsibility for the content of the published article.

Financial support: The ATTO project is supported by the Max Planck Society (MPG), the Bundesministerium für Bildung und Forschung (01LB1001A, 01LK1602B, and 01LK2101B), and the Brazilian Ministério da Ciência, Tecnologia e Inovação (01.11.0248.00).

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