Science of the Total Environment 802 (2022) 149769

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Contrasting nitrogen and phosphorus fertilization effects on soil terpene exchanges in a tropical forest

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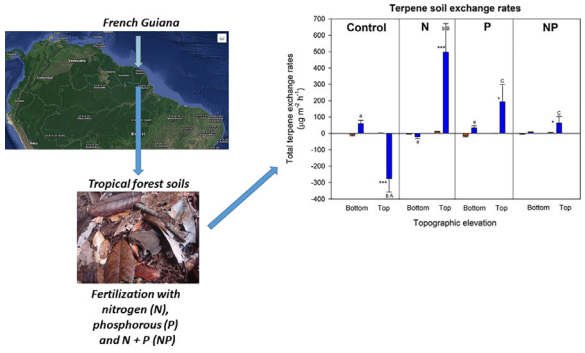
HIGHLIGHTS

- We report on the dynamics of soil BVOCs in French Guiana forests.
- We analyze the exchanges of terpenes after applications of N, P and N + P fertilizers.
- Soils changed from sinks (up to 276 μg m^{-2} h^{-1}) to sources (up to 497 μg m^{-2} h^{-1}).
- The highest rates of emissions occurred at higher elevations during the wet season.
- These changes have potential impacts on atmospheric chemistry and ecosystem function.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 May 2021
Received in revised form 9 August 2021
Accepted 16 August 2021
Available online 24 August 2021

Editor: Elena Paoletti

Keywords:
French Guyana
Monoterpenes
Sesquiterpenes
Nutrients
Topographic elevation
Season

ABSTRACT

Production, emission, and absorption of biogenic volatile organic compounds (BVOCs) in ecosystem soils and associated impacts of nutrient availability are unclear; thus, predictions of effects of global change on source-sink dynamic under increased atmospheric N deposition and nutrition imbalances are limited. Here, we report the dynamics of soil BVOCs under field conditions from two undisturbed tropical rainforests from French Guiana. We analyzed effects of experimental soil applications of nitrogen (N), phosphorus (P), and N + P on soil BVOC exchanges (in particular of total terpenes, monoterpenes, and sesquiterpenes), to determine source and sink dynamics between seasons (dry and wet) and elevations (upper and lower elevations corresponding to top of the hills (30 m high) and bottom of the valley). We identified 45 soil terpenoids compounds emitted to the atmosphere, comprising 26 monoterpenes and 19 sesquiterpenes; of these, it was possible to identify 13 and 7 compounds, respectively. Under ambient conditions, soils acted as sinks of these BVOCs, with greatest soil uptake recorded for sesquiterpenes at upper elevations during the wet season (-282 μg m^{-2} h^{-1}). Fertilization shifted soils from a sink to source, with greatest levels of terpene emissions recorded at upper elevations during the wet season, following the addition of N (monoterpenes: 406 μg m^{-2} h^{-1}) and P (sesquiterpenes: 210 μg m^{-2} h^{-1}). Total soil terpene emission rates were negatively correlated with total atmospheric terpene concentrations. These results indicate likely shifts in tropical soils from sink to source of atmospheric terpenes under projected increases

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https://doi.org/10.1016/j.scitotenv.2021.149769

in N deposition under global change, with potential impacts on regional-scale atmospheric chemistry balance and ecosystem function.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are a complex family of molecules, comprising isoprene, methylbutenol (MBO), terpenes (mainly mono- and sesquiterpenes), alkanes, alkenes, alcohols, esters, carbonyls, and acids (Schade et al., 2000; Peñuelas and Llusià, 2001), that are widely emitted by plants from a range of tissue types and under diverse physiological processes (Lerdau et al., 1997; Seufert, 1997; Baldwin, 2010). Some compounds, such as methyl salicylate, hexenal, and terpenes, are triggered as defense responses to pathogen and herbivore attack (Llusià and Peñuelas, 2001), while others, such as methyl jasmonate, alkenes, (E)-3-hexen-1-ol, and also terpenes, act as infochemicals within and between plant organs (Landi, 2020), and between plants and animals (Brilli et al., 2009; Trowbridge and Stoy, 2013) and micro-organisms (del Rosario Cappellari et al., 2019; Guo et al., 2021).

While the composition and emission of BVOCs produced by aboveground plant parts have been studied extensively (Peñuelas and Llusià, 2004; Peñuelas and Staudt, 2010), studies from soils are less common, but have shown they derive from decomposing litter and organic matter (e.g. Valolahti et al., 2015; Bachy et al., 2016; Isidorov et al., 2016; Svendsen et al., 2018; Staudt et al., 2019) and vary with litter composition (Schade and Goldstein, 2001; Kainulainen and Holopainen, 2002; Leff and Fierer, 2008), presence of tree roots (Aaltonen et al., 2011, 2013) and its exudates (Lin et al., 2007), and damaged roots (Hayward et al., 2001; Greenberg et al., 2012; Rinnan et al., 2013; Gray et al., 2015; Mäki et al., 2017), understory vegetation type (grass, shrub, moss, lichen) (Mäki et al., 2017), and plant organ and tissue type (Lin et al., 2007; Asensio et al., 2008b; Delory et al., 2016), mycorrhizal interactions (Sun and Tang, 2013; Trowbridge et al., 2020), invertebrate activity (Peñuelas et al., 2014), etc. Studies have also shown that micro-organisms (Schulz and Dickschat, 2007; Korpi et al., 2009) and the root (Aaltonen et al., 2011, 2013) and rhizosphere system (Lin et al., 2007; Owen et al., 2007; Massalha et al., 2017; Schulz-Bohm et al., 2017; Bourtsoukidis et al., 2018) are major sources of soil BVOCs, including fungi (Werner et al., 2016; Dickschat, 2016; Raza et al., 2017; Schmidt et al., 2018), actinomycetes bacteria (Ramirez et al., 2009; Insam and Seewald, 2010; Yamada et al., 2012, 2015; Dickschat, 2016) and protists (Rinkel et al., 2019).

Emissions of BVOCs contribute to atmospheric hydrocarbon loads, affecting atmospheric chemistry and climate through ozone and aerosol formation, methane oxidation, and the carbon monoxide budget (Chameides et al., 1988; Guenther et al., 1995; Andreae and Crutzen, 1997; Lerdau et al., 1997; Kavouras et al., 1999). CO is identified as an important indirect greenhouse gas. An addition of CO to the atmosphere perturbs the OH-CH_4-O_3 chemistry. Model calculations indicate that the emission of 100Mt of CO stimulates an atmospheric chemistry perturbation that is equivalent to direct emission of about 5 Mt. of CH_4 (Dentener et al., 2018). Thus, BVOCs play a key role in the balance of multiple atmospheric and climate chemical reactions (Riipinen et al., 2012; Bonn and Moortgat, 2003; Peñuelas and Llusià, 2003) that may lead to global changes in biological (Gershenzon and Dudareva, 2007), ecological and climatic environmental conditions (Peñuelas and Staudt, 2010; Kesselmeier and Staudt, 1999; Copolovici and Niinemets, 2016).

Emissions of BVOCs from soil to the atmosphere tend to be one to two orders of magnitude lower than from aboveground vegetation (Peñuelas et al., 2014); however, recent research has shown that sesquiterpene emissions in tropical forest soils may equal those from the tree canopy, likely as a result of soil microorganism activity (Bourtsoukidis et al., 2018). Interactions between microbes and plant roots in the emission of BVOCs is unclear, although evidence from Mediterranean environments indicates that roots contribute to BVOC emissions and uptake through the production of sesquiterpenes and exudate stimulation of microbial BVOC absorption, respectively (Asensio et al., 2007a, 2007b, 2007c, 2008a, 2008b). Soil microorganism consumption of BVOCs would likely favor soil uptake (Wheatley et al., 1997; Paavolainen et al., 1998; Mackie and Wheatley, 1999; Vespermann et al., 2007a, 2007b) and it is likely that soils may act as a sink or a source of BVOCs, depending on their production and/or consumption by soil biota and environmental conditions (Vespermann et al., 2007a, 2007b; Ramirez et al., 2009; Insam and Seewald, 2010; Mäki et al., 2017; Tang et al., 2019). Furthermore, it has recently been shown that the structure of the soil microbial community and its diversity significantly influence the quantity and quality of BVOCs in the soil. This fact also has repercussions regarding the behavior of the soil as a source or sink of BVOCs (Abis et al., 2020).

Sources of BVOCs, including micro-organisms, are modulated by environmental factors, including soil temperature and water content (Asensio et al., 2008a, 2008b; Greenberg et al., 2012; Veres et al., 2014; Bourtsoukidis et al., 2018), and emission flow rates depend on compound (Asensio et al., 2007c, 2008a), where terpene emissions are known to vary with season (Asensio et al., 2007b). For example, rainfall increases BVOC emissions from litter, although litter moisture content plays only a minor role in emissions (Greenberg et al., 2012), while increases in temperature and decreases in soil moisture favor the volatilization of monoterpenes from the soil to the atmosphere (Van Roon et al., 2005); soil moisture content may be a greater driver of monoterpene emissions than of sesquiterpenes (Mäki et al., 2017).

Dynamics of BVOCs in ecosystems are driven by a number of factors. While effects of elevation on physico-chemical soil conditions, such as temperature and water content, may contribute to soil-atmosphere exchanges in BVOC, these associated factors to elevation have been considered very few times (Bourtsoukidis et al., 2018). Effects of nutrient fertilization on exchanges in BVOCs have been studied in aboveground plant organs (Blanch et al., 2007, 2009; Ormeño et al., 2009; Olivier et al., 2011a, 2011b), whereas little is known about effects on soil BVOC fluxes (Phoenix et al., 2006; Don et al., 2011; Smith et al., 2016; Pöyry et al., 2017; Raza et al., 2017), particularly in tropical soils, such as those in the Amazonian rainforests which as a whole represent a major global source of BVOCs (Yáñez-Serrano et al., 2020).

The nutrient content of the soil is also a factor to consider since, it directly conditions its biological activity and therefore the synthesis of BVOCs. In general, old tropical forests on ancient soils are limited in P (Bruijnzeel, 1991; Vitousek et al., 2010; Soong et al., 2020) because weathering causes primary minerals such as P to deplete, leaving fractions of P occluded as a dominant (Vitousek et al., 2010; Yang and Post, 2011; Fink et al., 2016; Urbina et al., 2021). This occurs when there is a high concentration of clay and ferric sesquioxides (1:1) that bind to P (Walker and Syers, 1976). Consequently, the N:P ratios of the soil (per unit mass) are also higher in Nouragues than in Paracou (Urbina et al., 2021) indicating a potential limitation of P as expected in this tropical region (Grau et al., 2017; Oliveira et al., 2015; Sayer and Banin, 2016; Vitousek and Farrington, 1997). In fact, Urbina et al. (2021) found that N:P ratios are much higher than the mean value of tropical forests growing in oxisols (23.5; Townsend et al., 2007), suggesting a clear P limitation (Mo et al., 2019). On the other hand, in these places it was found that there was more N in the soil than in the leaves themselves or in the leaf litter (Urbina et al., 2021), consistent

with several studies that clearly observed a stronger limitation by P than by N in tropical rainforest (Sayer and Banin, 2016; Turner and Condron, 2013; Vitousek et al., 2010). It was also seen that the total concentrations of K in the soil were surprisingly high and approximately equivalent to N, but in a form hardly assimilable by plants (Urbina et al., 2021).

Tropical ecosystems, especially humid ones, contain the greatest richness in biological species on the planet (Sodhi et al., 2010), they are a reservoir of more than 40% of carbon in the form of biomass (Brown and Lugo, 1982; Olson et al., 1983) and, among other services, they can regulate the Earth's climate (including the water cycle). Tropical and subtropical humid broadleaf forests cover only 14% of the Earth's land area, but they support at least half of all species and offer key ecosystem services, making them crucial to achieving conservation goals and the global climate. Furthermore, tropical ecosystems are considered to be some of the most fragile (Morris, 2010). These ecosystems are expected to be among the most sensitive to the direct effects of increased atmospheric carbon dioxide concentrations (Lugo and Brown, 1992), and it is unpredictable what the effects will be of one of the drivers of global change, such as the increase in eutrophication. Therefore, in this context of anthropogenic global change, it is of utmost importance to measure soil BVOCs exchanges in order to have a clearer vision of their ecological importance for maintening tropical ecosystems (Bawa et al., 2004; Hansen et al., 2020).

Here, we hypothesize that active soil-atmosphere exchanges in BVOCs in tropical forests would depend on climate and season conditions, elevation, and nutrient availability, as has been observed for soil CO_2 emissions (e.g. Epron et al., 2006; Jia et al., 2003; Souza et al., 2006; Silva et al., 2004; Risch and Frank, 2006). The aim of this study was to test this hypothesis analyzing terpenes, one of the main groups of BVOCs, and whiles doing so, to quantify seasonal and elevation (topographic) variations in terpene fluxes in tropical forest soils in French Guiana and their responses to nitrogen (N) and phosphorous (P) fertilization.

2. Methods

2.1. Study sites

The study was conducted at the Nouragues (Bongers, 2001) (04°05′ N, 52°40′W) and Paracou (Gourlet-Fleury et al., 2004) (05°18′N, 52°53′ W) research stations on the Guiana Shield, an old terrestrial craton in French Guiana, South America (Gibbs and Barron, 1993), (Fig. 1). The study sites lay within pristine tropical forest and have a mean annual air temperature of 26 °C (Bongers, 2001; Gourlet-Fleury et al., 2004), with similar amounts of rainfall at Paracou and Nouragues (mean annual averages of 2990 and 3100 mm, respectively; Bongers, 2001; Aguilos et al., 2019) (Fig. 1a and b). The tropical climate is characterized by a wet season from December to July and a dry season, with moderate rainfall (c. 100 mm month^{-1}; Aguilos et al., 2018) from August to November.

Soils at Nouragues are sandy (sand content ranged between 21.1 and 63.6% across the plots while clay content reached up to 42.9%; Table S1), with variable depth, originating from weathered granite (Van der Meer and Bongers, 1996), whereas those at Paracou are sandier than at Nouragues (ranging between 59.1 and 76.8% sand (by mass), and low in clay, not exceeding 20%; Table S1) (for more details see Van Langenhove, 2020), formed on shale floors, with pegmatite veins of the precambrian metamorphic Bonidoro series (Epron et al., 2006). The soils at both sites are characterized as nutrient-poor acrisols (FAO-ISRIC-ISSS, 1998; Nachtergaele et al., 2000; Urbina et al., 2021) and classified as Oxisols by the USDA soil classification (Anjos et al., 2015). Their pH values range between 3.7 and 4.5. Nouragues generally has a larger nutrient reserve than Paracou, but P was found to be the scarcest nutrient in the soil at both study sites (Urbina et al., 2021; Tables S2 and S3). Soil P stocks are similarly low between the two sites, while C, N, and K stocks are higher in Nouragues than in Paracou at the two sampled depths (in Nouragues, averages between 0 and 15 cm: P: 205; C: 50104; N: 3583; K: 2033; averages between 15 and 30 cm: P: 206; C: 28209; N: 2222.35; K: 2551; in Paracou, averages between 0 and 15 cm: P: 158; C: 36320; N: 2566; K: 1009, and averages between 15 and 30 cm: P: 142; C: 17172; N: 1361; K: 1265) (in kg/ha).

2.2. Experimental design

At each research station, four 50 × 50-m study plots were established adjacent to a creek at two elevations separated by about 30 m of altitude (T = top of the hill: upper elevation, and B = bottom of the hill: lower elevation, (Fig. 1c and d), to which one of four treatments was allocated (untreated control; addition of N; addition of P; addition of N + P). However, the sampling area was limited to a 20 × 20 m square inscribed in the largest. Within this last frame we established 5 sampling points, 3 of which were arbitrarily chosen in each sampling of the BVOCs (Fig. 1 c, d).

2.3. Fertilization treatments

Fertilization of the 50 × 50-m plots started in October 2016. Nitrogen was added as commercial urea ((NH2) 2CO) and P as triple superphosphate (Ca (H2PO4) 2). We add fertilizer by hand twice a year at a rate of 125 kg N ha-1 year-1 (N treatment) or 50 kg P ha-1 year-1 (P treatment), or both amounts together (N + P treatment).

The chemical composition of the applied fertilizers was analyzed to know the exact composition. The samples of both fertilizers were dried at 70 °C for 48 h, after which they were ground. These samples were analyzed in an ICP-AES to determine the content of K, Ca, Mg and Mn, as well as the content of heavy metals (As, Cd, Cr, Cu, Ni, Pb, Zn and Mo). The total N of the fertilizers was analyzed using a Dumas system. P2O5 and MgO in mineral acid were measured by inductively coupled plasma technique (ICP-OES).

2.4. Soil water content and soil temperature

We collected soil moisture and temperature data concurrently with BVOC sampling, at 10-cm depth from three positions around the external sides of each of the three chambers. Soil moisture was measured using an HH2 soil moisture meter connected to an ML2x soil moisture sensor (Delta-T Devices Ltd., Cambridge, England) and soil temperature was measured using a soil digital thermometer (TO 15, Jules Richard instruments, Argenteuil, France) (Table S4).

2.5. Soil and litter sampling

Soil was sampled at 0-15 cm depth using a corer auger and was a composite of three borings near (< 2 m apart) each other. Freshly fallen litter was collected at the same spots were the soil was sampled. Fresh subsamples of 2-mm sieved soil and litter samples were stored at 4 °C in zip-lock plastic bags until enzymatic analysis. For each sample one part was used for the analyses and the other part was dried 24 h at 105 °C for water content determination (soil) or dried 48 h at 70 °C (litter). The litter was collected throughout the surface layer until the soil with the superficial roots was visualized. In order to determine litter density, all the fresh litter within a 38 × 25 cm quadrat placed near the sampling point was collected in zip-lock bags and stored at 4 °C. Total fresh weight in each quadrat was measured and one subsample was used to determine litter water content; litter density was expressed as g litter DW per m^2.

2.6. Determination of enzymatic activity

Soil and litter samples were transported to the lab and stored in plastic zip bags at 4 °C until analysis. Fresh subsamples of 2-mm sieved soil and litter samples were stored at 4 °C in zip-lock plastic bags until

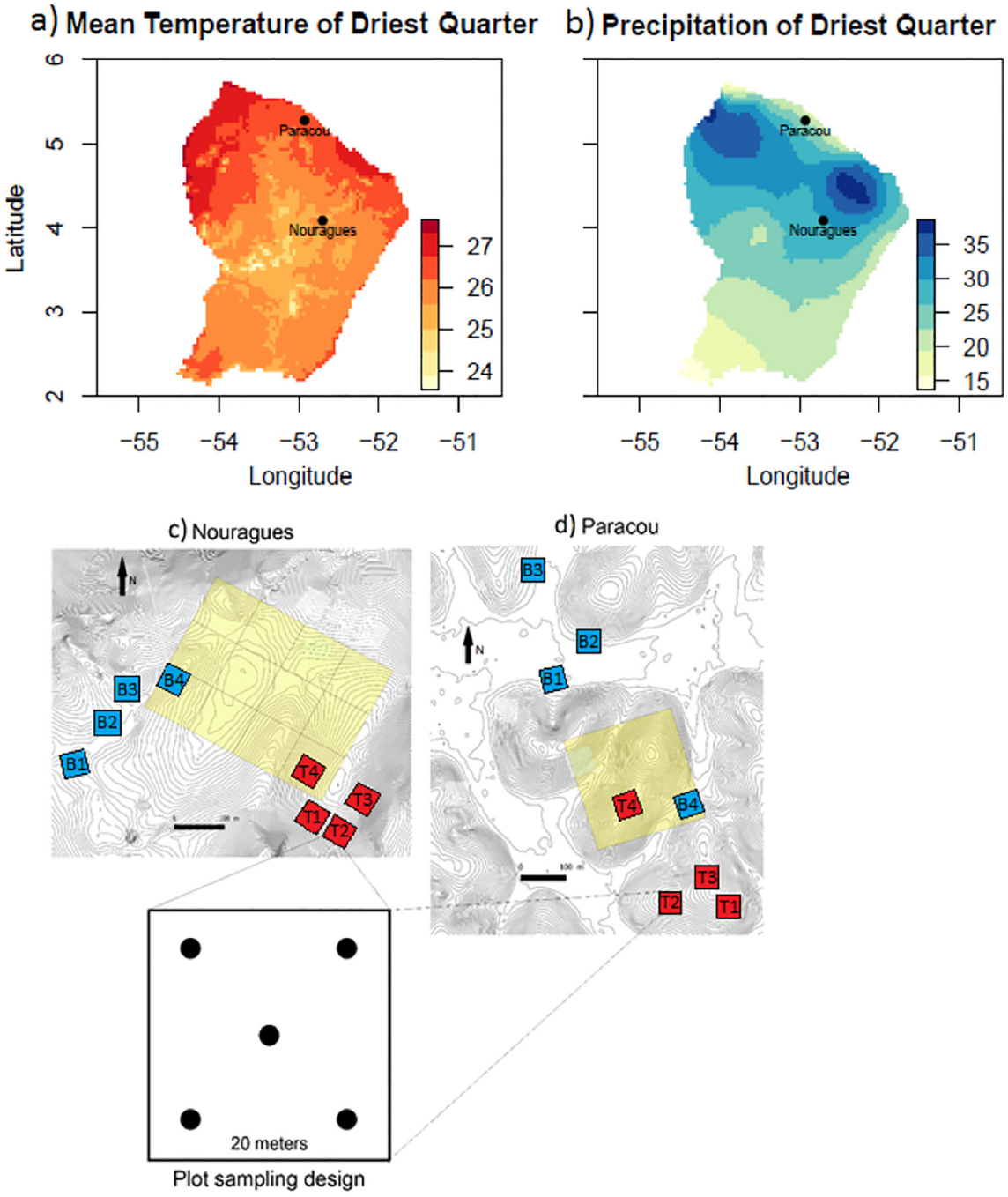

Fig. 1. a) Average temperature and **b)** rainfall during the driest quarter of the year in French Guiana, and sampling positions within experimental plots distributed across elevation levels upper-top of the hill and lower-bottom of the valley in Nouragues (**c**) and Paracou (**d**). Red squares: upper elevation; blue squares: lower elevation; treatment numbers 1-4 inside squares indicate addition of nitrogen, nitrogen + phosphorous, and phosphorous, and unfertilized control, respectively. Modified with permission from Courtois et al. 2018. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

enzymatic analysis. Fresh litter was cut in 1–2 cm pieces prior to enzyme analyses, one part was dried 48 h at 70 °C for water content determination.

We measured the maximum potential activity of acid phosphatase in the topsoil (0-15 cm) and the litter environment at each sampling point (enzyme referred as AcP hereinafter) by means of colorimetric assay techniques using *p*-Nitrophenylphosphate and *p*-Nitroaniline derivate chromogenic substrates (pNP and pNA, respectively) following Sinsabaugh et al. (1993), Popova and Deng (2010) and German et al. (2011) with some modifications.

For enzyme analyses, 2 g of soil or 1 g of litter were mixed with 60 μL of sodium acetate buffer (SA: 50 mM, pH 5) in a 125-mL glass jar for 10 min using a 2.5 cm magnetic stir bar at a maximum speed. Aliquots (100 μL each) of the soil suspension or litter homogenate were taken during continuous mixing using a 20–200 μL multi-channel pipette with wide orifice tips and were placed into 96 clear wells microplate (3 replicate wells per sample). Subsequently, 100 μL of respective substrate (5 mM) that was dissolved previously in its respective buffer was added to each microplate well. Plates were shaken 5 min in a microplate shaker at medium speed and incubated at 37 °C for 2 h. Soil/litter particles sank to the bottom of the wells during incubation. After incubation, 100 μL of the clean supernatant were transferred to a new microplate, where 5 μL of NaOH 1 M was previously added to each microplate well to terminate the enzymatic reaction. Absorbance of the clean

supernatant was measured at 405 nm using a microplate reader with an automixing feature (Tecan Sunrise, Tecan GmbH Grödig, Austria). The substrate controls (8 replicate wells) were performed using the same procedure but the mixture in each well was 100 μL substrate plus 100 μL of the corresponding buffer. The sample controls (3 replicate wells per sample) were assayed similarly in different plates, where the mixture in each well was 100 μL sample plus 100 μL of the corresponding buffer. The average absorbance of the eight substrate controls plus the average absorbance of the 3 sample controls was subtracted from the average absorbance of the 3 readings for each analysis. Negative potential activities were considered to indicate that no enzyme was present, and were converted to zero values before further analyses. Enzyme activity in reaction mixtures, expressed as μmol of pNP or pNA g^{-1} soil / litter DW h^{-1}, was calculated using the absorbance readings against a calibration curve that was constructed using pNP and pNA standards (Sigma-Aldrich, Darmstadt, Germany).

2.7. Soil BVOC sampling

In 2017, soil BVOCs were sampled during the wet and dry seasons, from 23 to 26 May and 9-12 October, respectively, at Paracou, and from 30 May-3 June and 17-22 October, respectively, at Nouragues. We collected two BVOC samples at three of the five points marked in each experimental plot (Fig. 1). In total there were 6 samplings of BVOCs per plot and one blank. At each sampling point of each plot, one of the two samples was without removing the litter, and then the next after removing the litter with great care not to break or injure the superficial roots.

Each sampled point was selected considering that there was an area as close as possible to the common sampling point that was covered with litter and with similar characteristics for the rest of the points of all the plots.

Given the logistical difficulties involved in going from one plot to another, the samplings were followed on the same plot until completion. At each point of each plot, the area of the chamber with litter was first sampled, and once the litter had been extracted from the sampling area, the second sampling was carried out.

The BVOCs were collected using an open sampling system comprising a Teflon chamber (internal diameter: 14 cm; thickness: 0.5 cm; height: 17 cm; volume: 2 L) containing two holes at different heights (at 5 and 13.5 cm from the ground); soil BVOCs were sampled through the upper hole, while the lower hole was connected to a Teflon tube, with the inlet located about 40 cm above the chamber, to balance the pressure generated by the sampling pump inside the chamber. A small fan placed inside the upper center of the chamber homogenized the air and prevented the accumulation of condensation. A band of soft silicone material covered with Teflon was fixed around the base of the chamber, to ensure contact with soil surface and to avoid causing damage to shallow roots.

Atmospheric BVOCs were collected prior to sampling the BVOCs from the soil, using the same approach, except that a Teflon film was placed between the soil and the chamber to avoid uptake or emission of BVOCs from the soil. The air was collected at 40 cm above the soil surface using a Teflon tube connected to the lower hole of the soil chamber; these samples were used as a blank for the calculation of soil-atmosphere exchange in BVOCs. As the adjustment between the chamber and the Teflon film were by contact, it could be considered that the terpene concentrations would be those in the area between the ground level and approximately 40 cm from it. Moreover, before taking a blank, we made sure that the chamber was free of any residue that could be adhered from a previous sampling. In addition, we exposed the chamber to the air for a few minutes before placing it in the sampling position.

Air exiting the soil chamber was pumped through a stainless steel tube (length: 89 mm; external diameter: 6.4 mm), which was manually filled with adsorbents (115 mg of Tenax TA and 230 mg of SulfiCarb, Markes International Inc. Wilmington, USA) separated by sorbent-retaining springs that were fixed using gauze-retaining springs and closed with air-tight caps (Markes International Inc. Wilmington, USA). The hydrophobic properties of activated adsorbents minimized sample displacement by water. Samples were collected for 20 min using a Q_{max} air-sampling pump (Supelco, Bellefonte, Pennsylvania); airflow was measured using a flowmeter (Bios Defender 510, Bios International Corporation, Butler, USA) and regulated using a valve to ensure similar flow rates among the sampling cartridges (297 ± 5 mL min^{-1} in the dry season; 319 ± 5 mL min^{-1} in the wet season). Immediately prior to sampling, blank soil BVOC measurements were performed using tubes that had been conditioned twice for 30 min at 350 °C using a stream of 100 mL min^{-1} of purified helium. Sampled terpenes were not chemically transformed in these tubes, as determined by reference to trapped standards (α-pinene, Δ^3-carene, limonene, α-humulene, and dodecane), and trapping and desorption efficiency of standards, such as α-pinene, β-pinene, and limonene, was 99%.

2.8. Soil BVOC analysis

Collected BVOCs in the stainless steel tubes were thermally desorbed using an automatic sample processor (TD Autosampler, Series 2 Ultra, Markes International Inc. Wilmington, USA), with a coupled injector (Unity, Series 2, Markes International Inc. Wilmington, USA), that was connected to a gas chromatograph (GC) (7890A, Agilent Technologies, Santa Clara, USA) with a mass spectrometer detector (5975C inert MSD with Triple-Axis Detector, Agilent Technologies). A full-scan (between 35 and 350 m z^{-1}) method was used in the chromatographic analyses.

Pre-desorption conditions consisted of a pre-purge time of 0.1 min, with a split of 20 mL min^{-1}, and a dry purge of 2 min. Then, BVOCs were desorbed with a flow path temperature of 200 °C, minimum carrier pressure of 0.5 KPa, and a GC cycle time of 30 min; the standby split was 25 mL min^{-1}. Sample desorption time was 30 min at 320 °C, and the trap was maintained in-line, with a flow rate of 50 mL min^{-1} and a split of 2 mL min^{-1}; cryotrap low temperature was -25 °C. *Prior* to heating, traps were held in a pre-cryotrap fire purge for 2 min. Cryotrap flow rate was 50 mL min^{-1}, with a split of 10 mL min^{-1}, and heating rate was 40 °C s^{-1} to cryotrap high of 320 °C that was maintained for 7 min, with a split of 5 mL min^{-1}.

Then, the cryofocused desorbed samples were injected into a GC column (HP 5MS, 30 m × 0.25 μm × 0.25 mm) using a transfer line at 250 °C. Following sample injection at 35 °C (initial time: 3 min), column temperature was increased stepwise by 15 °C min^{-1} to 150 °C, maintained for 5 min, then by 50 °C min^{-1} to 250 °C, maintained for 5 min, and finally by 30 °C min^{-1} to 280 °C for 5 min. Total run time was 30 min and the helium column flow rate was 1 mL min^{-1}; terpene emission rates were expressed as μg m^{-2} h^{-1}.

Terpene identification was performed through comparison of derived mass spectra with those published (Wiley275 and Nist05a libraries) and known standards such as those mentioned below for quantification. Quantification of peaks was conducted using the fragmentation product with mass 93 (Blanch et al., 2012; Llusià et al., 2012) and calibration curves were prepared using commercial standards of some of the most abundant compounds recorded, comprising four monoterpenes (α-pinene, sabinene, β-pinene, and limonene) and one sesquiterpene (α-caryophyllene) (Fluka Chemie AG, Buchs, Switzerland). These standards were adsorbed on cartridges similar to those of the samples by means of a valve coupled to the chromatograph and a flow of Helium 5.0 similar to that of the flows generated by the Qmax pump. They were then desorbed and analyzed following the same protocol that was used with the samples. Terpene calibration curves for signal and concentration were always highly correlated ($r^2 \geq 0.95$) and sensitivity of the most abundant terpenes were similar (differences were < 5%).

To carry out the standards, 3 different dilutions were made as follows: 1 μL of the pure standard was diluted in 1000 μL of pentane and 100 μL of this were taken and diluted in another 1000 μL of pentane. From this last dilution another 100 μL were taken and diluted in 1000 μL of pentane.

From the first dilution, 1 μL was injected into a BVOCs sampling tube. From the second also 1 μL, while from the third 2 μL.

In addition, we also prepared standards from a standard at 500 ppb of a 50 L bottle (Reimer Environmental, Inc., Miami, USA). From this pattern we injected 15, 25 and 35 mL into three sampling tubes respectively using the same valve mentioned above. In each sequence (of 30 tubes) of analysis, a series of three standards (one for each concentration) of the gas standard were added first, and at the end of series 3 (one for each concentration) of the liquid standard (previously gassed). To avoid interference with the samples due to contamination, the standards were placed from lowest to highest concentration. In addition, the analysis sequence was always started with an empty tube followed by a tube with the same adsorbents taken to the field and not sampled, to test for possible contamination throughout the process.

To calculate the μg of terpenes per m^2 and hour we apply the following formula:

$$[(AUs/svs)-(AUb/svb)] \times [(rf \times Chv \times 60\ min)/(AUrf \times Chs \times st)]$$

where:

AUs = Units of area of the soil air sample (arbitrary units)
svs = Volume of air sampled from the soil (mL)
AUb = Area units of the blank air sample (arbitrary units)
svb = Volume of air sampled as blank (mL)
rf = Response factor, calculated from the calibration curves (μg)
Chv = Volume of the sampling chamber (mL)
AUrf = Units of area corresponding to rf (arbitrary units)
Chs = Surface of the sampling chamber (m^2)
st = Sampling time (min)

2.9. Statistical analysis

Main effects of fertilization, season, elevation, enzymatic activity (AcP), … were tested using ANOVA, and Fisher's LSD post-hoc test was used to test for within-main effects differences among means ($P < 0.05$), and correlations between these variables and factors using STATISTICA v.6.0 for Windows (StatSoft, Inc. Tulsa, Oklahoma).

3. Results

3.1. Soil moisture and temperature

The average water content of the soil between the two sampling sites was analyzed in the range of 0 to 15 cm. There were significant differences between the two seasons (17.66 ± 0.88% and 34.71 ± 0.43% for the dry and wet season respectively; ANOVAs, $P < 0.001$, $N = 96$). There were also differences between the two topographic levels (24.10 ± 1.02% and 28.27 ± 1.16% bottom and top respectively; ANOVAs, $P < 0.001$, $N = 96$). Considering the season and the topographic level, there were only differences between the two topographic levels in the dry season (14.60 ± 0.43% and 20.73 ± 1.59% bottom and top respectively; ANOVAs, $P < 0.001$, $N = 48$).

The average soil temperature between the two sampling places was taken in the range of 0 to 15 cm. There were significant differences between the two seasons (25.25 ± 0.05 °C and 25.09 ± 0.02 °C for the dry and wet season respectively; ANOVAs, $P < 0.01$, $N = 96$). There were also differences between the two topographic levels (25.09 ± 0.04 °C and 25.24 ± 0.05 °C bottom and top respectively; ANOVAs, $P < 0.01$, $N = 96$). Considering the season and the topographic level, there were only differences between the two topographic levels in the dry season (25.16 ± 0.07 °C and 25.34 ± 0.08 °C bottom and top respectively; ANOVAs, $P < 0.01$, $N = 48$) (Table S4).

No significant differences were observed between soil moisture and temperature among the plots within the same sampling period.

3.2. Acid phosphatase (AcP) activity

3.2.1. AcP activity in soils

The average acid phosphatase activity of the soil between the two sampling sites was analyzed in the range of 0 to 15 cm and in the 2017 campaign. There were significant differences between the two seasons (44.66 ± 2.43 μmol pNP / g soil DW x h and 61.70 ± 3.70 μmol pNP / g soil DW x h for the dry and wet season respectively; ANOVAs, $P < 0.001$, $N = 80$) and for the two topographic levels (38.92 ± 1.74 μmol pNP / g soil DW x h and 67.44 ± 3.63 μmol pNP / g soil DW x h for the bottom and top elevations respectively; ANOVAs, $P < 0.001$, N = 80).

Considering the season and the topographic level, there were significant differences between the two seasons at each topographic level (34.43 ± 2.45 μmol pNP / g soil DW x h and 54.88 ± 3.53 μmol pNP / g soil DW x h dry in bottom and top plots respectively, ANOVAs, $P < 0.001$, $N = 40$, and 43.40 ± 2.30 and 80 ± 5.74 μmol pNP / g soil DW x h wet season in bottom and top plots respectively ANOVAs, $P < 0.001$, N = 40).

Fertilization as a whole did not affect AcP activity in soils except when fertilized with N (59.40 ± 4.62 μmol pNP / g soil DW x h and 47.20 ± 2.41 μmol pNP / g soil DW x h, N fertilized and control plots respectively, ANOVAs, $P < 0.01$, N = 40 for N fertilized and control plots).

Taking into account the treatment of each plot, no significant differences were seen between all treatments in soil AcP activity (Table S5).

3.2.2. AcP activity in litter

The average AcP activity of the litter between the two sampling sites was analyzed for 2017 campaign. There were significant differences between the two seasons (97.22 ± 9.96 μmol pNP / g soil DW x h and 510.80 ± 27.50 μmol pNP / g soil DW x h for the dry and wet season respectively; ANOVAs, $P < 0.001$, $N = 80$) but not for the two topographic levels.

Considering the season and the topographic level, there were significant differences only in dry seasons (142.18 ± 16.55 μmol pNP / g soil DW x h and 52.25 ± 4.93 μmol pNP / g soil DW x h, bottom and top plots respectively, ANOVAs, $P < 0.01$, $N = 40$).

Fertilization as a whole did affect AcP activity in litter (283.96 ± 23.51 μmol pNP / g soil DW x h and 364.06 ± 51.66 μmol pNP / g soil DW x h, fertilized and control plots respectively, ANOVAs, $P < 0.01$, $N = 120$ and 40 for fertilized and control respectively). For each fertilization treatment, the only treatment that seems to affect AcP activity is when fertilized with P (218.19 ± 27.94 μmol pNP / g soil DW x h and 364.06 ± 51.66 μmol pNP / g soil DW x h, P fertilized and control plots respectively, ANOVAs, $P < 0.01$, N = 40 for P fertilized and control plots).

Regarding the different fertilization treatments, there were only significant differences in the activity of the litter AcP in the Ns with respect Ps, and this versus NPs control plots in the wet season in the plots of the low level. Also of Ns with respect to P and controls, and Ps with respect to NPs and controls at the high level in the wet season (ANOVAs, $P < 0.001$, $N = 10$) (Table S5).

3.3. Soil terpene exchanges

Regardless of season, elevation, and fertilization, terpene exchanges were positive, with sesquiterpenes being the least emitted (total terpenes 34 ± 10.8 μg m^{-2} h^{-1}; monoterpenes 31.8 ± 6.26 μg m^{-2} h^{-1}; and, sesquiterpenes 2.19 ± 7.64 μg m^{-2} h^{-1}, $N = 320$). In unfertilized control plots, there were net soil uptakes of total terpenes (-55.66 ± 21.63 μg m^{-2} h^{-1}, $N = 80$) and sesquiterpenes (-65.97 ± 21.15 μg m^{-2} h^{-1}; N = 80) and

emissions of monoterpenes (10.4 ± 2.93 μg m^{-2} h^{-1}; N = 80), while in fertilized plots, terpenes were emitted (total terpenes: 63.9 ± 11.81 μg m^{-2} h^{-1}; monoterpenes: 39.0 ± 8.25 μg m^{-2} h^{-1}; and, sesquiterpenes: 24.9 ± 6.78 μg m^{-2} h^{-1}, $N = 240$).

We detected 45 terpenoid compounds (Fig. 2 and Table S6), 26 monoterpenes (13 unidentified), and 19 sesquiterpenes (12 unidentified). In the dry season, order of abundance of identified monoterpenes detected was α-pinene, terpinolene, α-phellandrene, camphene, verbenene, bornylene, trans-ocimene (with significant differences between control and N plots and N and P and NP plots), γ-terpinene, p-cymene, β-pinene, p-cymenene, camphor, and δ-limonene (with significant differences between N and P plots and P and NP plots), and of identified sesquiterpenes was α-cubebene, selinene, trans-caryophyllene, α-elemene, α-muurolene (with significant differences between N and P, NP and Control plots), δ-elemene, and α-copaene (with significant differences between control and N, P and NP plots) (Fig. 2 and Table S6). In the wet season, order of abundance of identified monoterpenes was verbenene (with significant differences between N and P, NP and control plots), γ-terpinene (with significant differences between N and P, NP and control plots), α-pinene (with significant differences between P and N, NP and control plots), β-pinene (with significant differences between N and P, NP and control plots), δ-limonene (with significant differences between N and control plots), camphene (with significant differences between N and NP and control plots), α-phellandrene (with significant differences between N and P, NP and control plots), p-cymenene (with significant differences between N and P, NP and control plots), p-cymene (with significant differences between N and P, NP and control plots and P and N, NP and control plots), terpinolene (with significant differences between N and P, NP and control plots), bornilene (with significant differences between N and P, NP and control plots), and camphor, and of sesquiterpenes was β-selinene (with significant differences between control and N, P, and NP and P and NP plots), α-elemene (with significant differences between N and control and P plots; P and N, NP and control plots; NP and control plots), trans-caryophyllene (with significant differences between control and P plots; P and NP plots), α-copaene (with significant differences between N and NP and control plots; control and N, P and NP plots; P and NP plots), α-cubebene (with significant differences between control and N plots; P and NP plots) and δ-elemene (Fig. 2 and Table S6). In the dry season we detected t-ocimene, α-muurolene, and four and eight unidentified mono- and sesquiterpenes respectively; none of these was detected in the wet season.

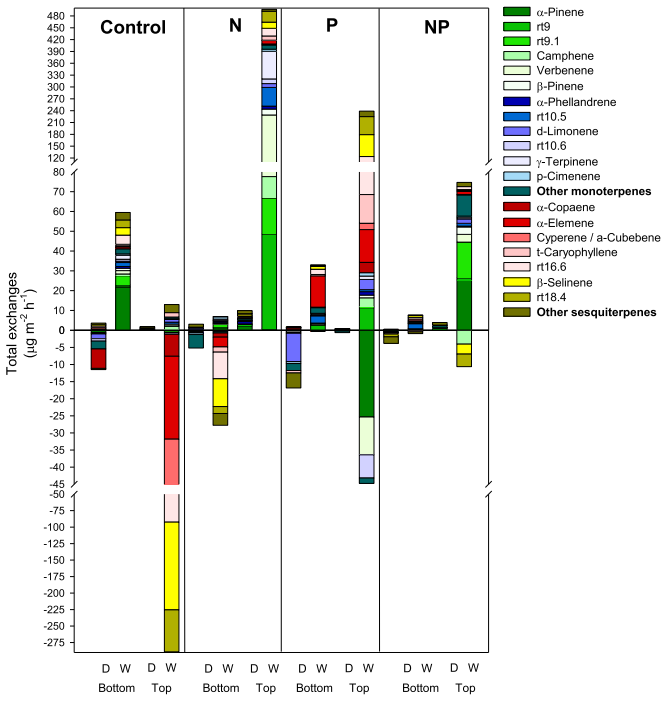

Fig. 2. Effects of fertilization on exchange rates μg m^{-2} h^{-1} of soil terpenes during wet W and dry D seasons at upper top of the hill and lower bottom of the valley elevations. Monoterpene $N = 26$, 13 identified; sesquiterpene $N = 14$, 7 identified; unidentified compounds are shown according to retention time rt. Negative values indicate soil uptake. Minority monoterpenes and minor sesquiterpenes were included in "Other monoterpenes" and "Other sesquiterpenes" respectively. N: addition of nitrogen; P; addition of phosphorous; NP: addition of nitrogen + phosphorous.

3.4. Litter terpene exchanges

Accumulated litter was measured during the wet and dry seasons of 2015 and 2016 (pretreatment), and 2017 (treatment). In general, we found that the presence of litter, season, and elevation did not affect terpene exchange; however, fertilization with P led to an increase in total terpene emissions when litter was removed (with litter: 9.6 ± 11 μg m^{-2} h^{-1}; post-removal of litter: 96.3 ± 38.4 μg m^{-2} h^{-1}, ANOVAs, $P < 0.05$, $N = 24$), particularly for sesquiterpenes (with litter: 19.9 ± 8.5 μg m^{-2} h^{-1}; ANOVAs, $P < 0.05$, N = 24 post-litter removal: 94.8 ± 36.5 μg m^{-2} h^{-1}) ANOVAs, $P < 0.001$, N = 24).

3.5. Main effects of soil moisture, soil temperature, AcP activity, fertilization, season, and elevation on soil terpene exchange rates

3.5.1. Soil moisture

In the control plots the exchanges of monoterpenes and sesquiterpenes were significantly correlated with soil moisture ($r = 0.45$, $P < 0.01$ and r = -0.38, $P < 0.01$, $N = 35$, respectively). In the plots fertilized with N, the total monoterpenes were significantly correlated with soil moisture ($r = 0.43$, $P < 0.01$, $N = 35$), not the sesquiterpenes. In the NP-fertilized plots and in the P fertilized plots both groups of terpenes were also significantly correlated (NP monoterpenes: $r = 0.63$, $P < 0.001$; NP sesquiterpenes: $r = 0.34$, $P < 0.05$, N = 35; P monoterpenes: r = 0.43, $P < 0.01$; P sesquiterpenes: $r = 0.53$, $P < 0.001$, N = 35) (Table S4).

3.5.2. Soil temperature

In the control plots, neither terpene group did significantly correlate with the soil temperature. In the plots fertilized with N, there were neither any significant correlation between any of the terpene groups and soil temperature. In the NP fertilized plots and the P fertilized plots, only sesquiterpenes had significant correlations with temperature ($r = 0.39$, $P < 0.01$, N = 35; $r = 0.85$, $P < 0.001$, N = 35) (Table S4).

3.5.3. AcP activity

In the control plots there was no significant correlation of ACP activity with any terpene group. In the plots fertilized with N, AcP was significantly correlated with monoterpenes ($r = 0.32$, $P < 0.05$, $N = 40$) and sesquiterpenes ($r = 0.58$, $P < 0.001$, N = 40). In the NP fertilized plots AcP was significantly correlated with sesquiterpenes ($r = 0.60$, $P < 0.001$, N = 40). In the plots fertilized with P, AcP activity was significantly correlated with total monoterpenes ($r = 0.35$, $P < 0.01$, N = 40) and total sesquiterpenes (r = 0.85, $P < 0.001$, N = 40) (Tables S4 and S5).

3.5.4. Fertilization

Fertilization transformed soils from a sink to a source of total terpenes (considering all the control plots, average exchange rate: -55.70 ± 21.62 μg m^{-2} h^{-1}; and fertilized plots: 63.90 ± 11.81 μg m^{-2} h^{-1}; ANOVAs, $P < 0.001$, $N = 48$ and 144 respectively; Fig. 3), mainly due to a shift from net uptake of sesquiterpenes to emissions (considering all the control plots, average exchange rate: -66 ± 21.14 μg m^{-2} h^{-1}; and fertilized plots: 24.91 ± 6.78 μg m^{-2} h^{-1}) (ANOVAs, $P < 0.001$, N = 48 and 144 respectively). There were no effects of fertilization on soil monoterpene

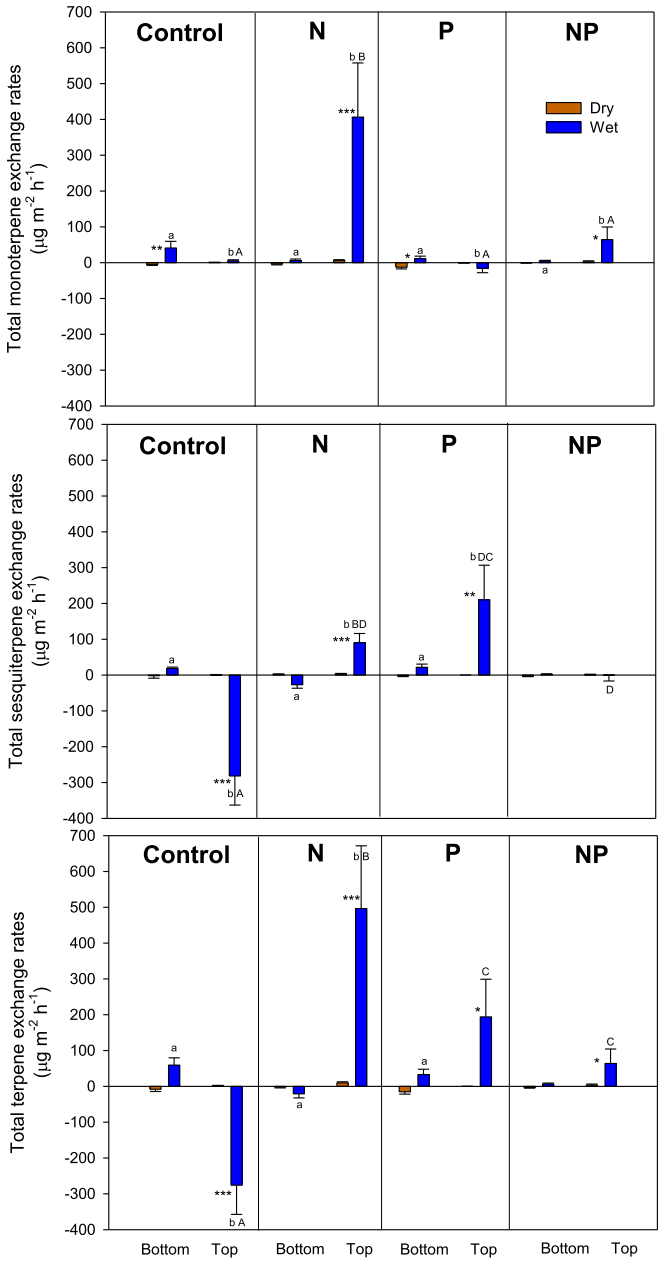

Fig. 3. Effects of elevation lower at bottom and upper at top of the hills, and fertilization on exchange rates μg m^{-2} h^{-1} of soil monoterpenes, sesquiterpenes, and total terpenes in wet W and dry D seasons. N: addition of nitrogen; P; addition of phosphorous; NP: addition of nitrogen + phosphorous; C: control. *$P < 0.01$; ** $P < 0.05$; ***$P < 0.001$. Lowercase letters indicate within season and fertilization differences in elevation effects and uppercase letters indicate within season and elevation differences in fertilization effects at $P < 0.01$.

exchange rates (control: 10.42 ± 2.93 μg m^{-2} h^{-1}; fertilized plots: 39 ± 8.25 μg m^{-2} h^{-1}) ($P < 0.05$; Fig. 3, Table S7).

Total terpene emissions were greatest in the N treatment (121 ± 38.3 μg m^{-2} h^{-1}), followed by the P (52.9 ± 20.7 μg m^{-2} h^{-1}) and NP treatments (17.8 ± 7.70 μg m^{-2} h^{-1}); the control acted as a sink (Fig. 3). Monoterpene emissions were greatest in the N treatment (104 ± 32.3 μg m^{-2} h^{-1}), followed by the NP treatment (17.8 ± 6.90 μg m^{-2} h^{-1}) and the control (10.40 ± 3.80 μg m^{-2} h^{-1}), whereas the P treatment was a sink (-4.30 ± 2.90 μg m^{-2} h^{-1}) (Fig. 3). Sesquiterpenes were emitted in all fertilized plots, and were greatest in the P treatment (57.4 ± 19.5 μg m^{-2} h^{-1}), followed by the N (17.3 ± 6.70 μg m^{-2} h^{-1}) and NP (0.04 ± 2.90 μg m^{-2} h^{-1}) treatments; the control was a sink (-66 ± 19.4 μg m^{-2} h^{-1}) (Fig. 3, Table S8).

3.5.5. Season

Averaged across fertilization treatments, there were huge seasonal differences in total terpene. In the dry season, terpene exchanges were only 2.3% of those measured in the wet season (dry season: -1.6 ± 1.1 μg m^{-2} h^{-1}; wet season: 69.6 ± 24.8 μg m^{-2} h^{-1}; ANOVAs, $P < 0.001$) and monoterpene (dry season: -1.7 ± 0.7 μg m^{-2} h^{-1}; wet season: 65.4 ± 16.9 μg m^{-2} h^{-1}; ANOVAs, $P < 0.001$) exchange rates; there were no effects on sesquiterpenes exchange rates.

In the unfertilized control plots, there were seasonal differences in mean uptake rates of total terpenes (dry season: -3.04 ± 2.4 μg m^{-2} h^{-1}; wet season: -108.3 ± 38.6 μg m^{-2} h^{-1}; ANOVAs, $P < 0.01$), emission/uptake rates of monoterpenes (dry season: -2.4 ± 0.8 μg m^{-2} h^{-1}; wet season: 23.3 ± 7.2 μg m^{-2} h^{-1}; ANOVAs, $P < 0.01$) and uptake rates of sesquiterpenes (dry season: -0.37 ± 2.4 μg m^{-2} h^{-1}; wet season: -131.6 ± 36.4 μg m^{-2} h^{-1}; ANOVAS, $P < 0.01$) (Table S7).

3.5.6. Elevation

In the unfertilized control, there were elevation (topographic) differences in terpene emission rates ($P < 0.001$), including total terpenes (lower elevation: 25.8 ± 12.9 μg m^{-2} h^{-1}; upper elevation: -137.1 ± 50.6 μg m^{-2} h^{-1}; ANOVAs, $P < 0.01$, $N = 24$) and sesquiterpenes (lower elevation: 8.3 ± 4.5 μg m^{-2} h^{-1}; upper elevation: -140.2 ± 50.9 μg m^{-2} h^{-1}; $P < 0.001$, N = 24) (Table S7).

Across all fertilization treatments, there elevation differences in terpene emission rates ($P < 0.001$), where they were greater at upper elevations than lower elevations for total terpenes (128.1 ± 40.8 μg m^{-2} h^{-1} and -0.33 ± 3.9 μg m^{-2} h^{-1}, respectively; ANOVAs, $P < 0.001$, $N = 72$) and total monoterpenes (77.2 ± 31.61 μg m^{-2} h^{-1} and 0.77 ± 1.9 μg m^{-2} h^{-1}, respectively; ANOVAs, $P < 0.01$, N = 72); and total sesquiterpenes (50.9 ± 19.4 μg m^{-2} h^{-1} and -1.04 ± 2.9 μg m^{-2} h^{-1}, respectively; ANOVAs, $P < 0.001$, N = 72) (Table S8).

3.6. Interactive effects of season, topographic elevation and fertilization on terpene exchange rates

Across the fertilization treatments, total terpene and monoterpene exchange rates varied with elevation in the wet season, and there were no elevation differences with season in sesquiterpenes exchange rates (Table S7).

There were between and within season effects on terpene exchange rates that varied with elevation and fertilization. So, where maximum exchange rates occurred in the wet season at upper elevations (Table S7). In the wet season, there were contrasting effects of fertilization on terpene exchange at upper elevations, where fertilizer application led to emissions (251.58 ± 37.98 μg m^{-2} h^{-1}) and non-application of fertilizer led to uptakes (-276.05 ± 64.33 μg m^{-2} h^{-1}) (Table S7). At upper elevations, fertilizer application led to greater emissions of monoterpenes (151.64 ± 28.48 μg m^{-2} h^{-1}) than untreated plots (5.46 ± 10 μg m^{-2} h^{-1}) and fertilized plots at lower elevations (7.25 ± 0.99 μg m^{-2} h^{-1}) (Table S7). There were no fertilization or elevation effects on terpene exchange rates in the dry season.

The total terpenes in the wet season in the control plots were emitted in greater quantity in the lower elevations while immissions were produced mostly in the top (higher elevations). However, more total terpenes were emitted in the top fertilized plots than in the bottom in wet season. In contrast, in the dry season there were no significant differences (Table S7).

In the wet season, the plots fertilized at lower elevations emitted less monoterpenes than those fertilized at higher elevations. And in the top plots, in general, there were more emissions of monoterpenes in the fertilized ones than in the control ones. In contrast, in the dry season there were no significant differences. Sesquiterpenes in the wet season in the control plots were emitted in greater quantity in the bottom plots while in the top, immissions were mainly produced. On the other hand, in the bottom fertilized plots, immissions were mainly produced. In contrast, in the dry season there were no significant differences (Table S7).

Total terpene exchanges were higher in N, P and NP top plots than control in top plots in wet season and in bottom plots in wet season (Fig. 3 and Table S8). Total monoterpenes exchanges were higher in N top plots in wet season versus control plots (Fig. 3 and Table S8). Total sesquiterpenes were higher in P and N top plots in wet season versus controls (Fig. 3 and Table S8).

3.7. Atmospheric terpene concentrations

Average ground-level concentrations of total terpenes, monoterpenes, and sesquiterpenes were 17.4 ± 3.68, 4.14 ± 0.92, and 13.3 ± 3.52 ppbv respectively. Atmospheric concentrations of total terpenes were higher in the wet (32.2 ± 7.05 ppbv) than the dry season (2.60 ± 0.38 ppbv) (ANOVAs, $P < 0.001$, $N = 96$) and tended to be higher at the upper (29.1 ± 7.14 ppbv) than lower elevation (5.67 ± 0.84 ppbv) (ANOVAS, $P < 0.001$, N = 96) (Fig. 4).

During the dry season there were no elevation differences in BVOC concentrations, whereas during the wet season, concentrations of total terpenes, monoterpenes, and sesquiterpenes were greater at upper elevations (57.6 ± 13.10, 12.2 ± 3.40, and 45.4 ± 13.1 ppbv, respectively) than at lower elevations (6.80 ± 1.53, 1.16 ± 0.24, and 5.64 ± 1.33 ppbv, respectively) (ANOVAs, $P < 0.001$, $N = 48$).

Addition of fertilizer resulted in lower concentrations of total terpenes (10.41 ± 1.70 ppbv) and sesquiterpenes (5.42 ± 0.80 ppbv) than in the untreated controls (38.36 ± 13.49 and 36.80 ± 13.43 ppbv, respectively) (ANOVAs, $P < 0.001$, $N = 144$ and 48 for fertilized and control plots respectively) (Fig. 4).

Exchange of total terpenes in soils was negatively correlated with atmospheric concentrations ($r = -0.14$, $P < 0.05$); this relationship was particularly strong for sesquiterpenes ($r = -0.62$, $P < 0.05$, $N = 192$) during the wet season (Fig. 4).

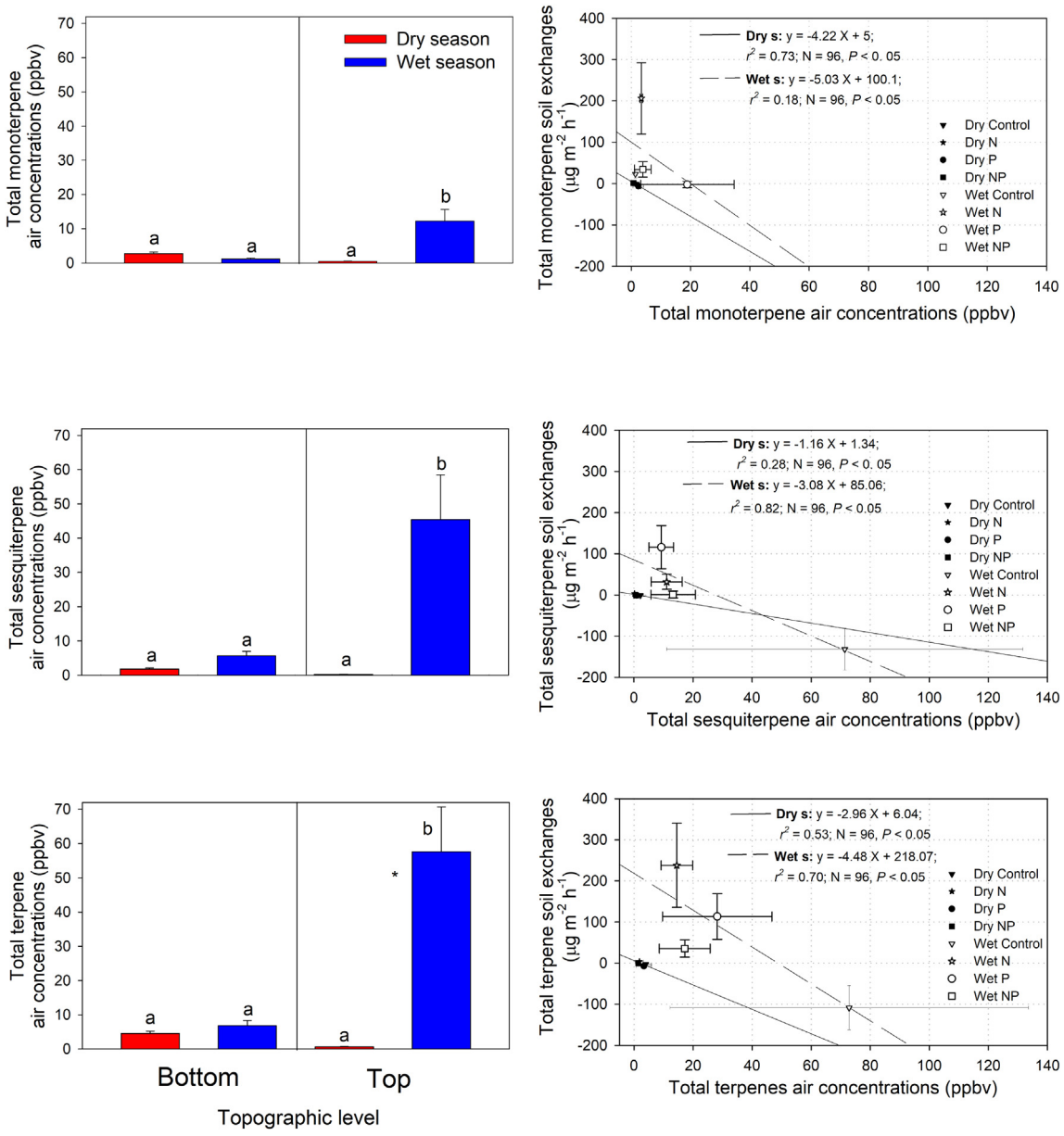

Fig. 4. Effects of fertilization, season, and elevation lower at bottom and upper at top of the hills on average ± SE atmospheric concentrations ppbv of monoterpenes, sesquiterpenes, and total terpenes, and correlations between soil total terpene exchanges and total atmospheric terpene concentrations in the dry solid symbols and wet open symbols seasons. Fertilization treatments are control triangle; N: addition of nitrogen star; P: addition of phosphorous circle; NP: addition of nitrogen + phosphorous square. The letters indicate significant differences in terpene concentrations between different topographic levels of the same season ($P < 0.01$), and the asterisk indicates significant differences in terpene concentrations between season ($P < 0.01$).

4. Discussion

4.1. Terpene exchanges

The range of terpenes emissions recorded in this study was within that reported from other forest biomes, such as 936 μg m^{-2} h^{-1} (Aaltonen et al., 2013) and 5 μg m^{-2} h^{-1} (Aaltonen et al., 2011) in a Scots pine forest and 20 μg m^{-2} h^{-1} in a holm oak forest (Asensio et al., 2007b, 2007c), where emissions of monoterpenes were greater than those of sesquiterpenes. Atmospheric concentrations of total terpenes were a key determinant of the direction of soil fluxes, where total soil terpene exchange rates were negative (uptakes) when atmospheric concentrations of terpenes were greatest across all treatments (Fig. 4). In general, we found that atmospheric concentrations of terpenes were greater than those observed by other authors (Yáñez-Serrano et al., 2015, 2018, 2020). In the unfertilized plots, high uptake of terpenes could, in part, be a result of an atmosphere-soil sesquiterpenes concentration gradient that generated an influx of volatiles to the soil. Field chamber and continuous-flow studies have demonstrated that soil is a biological sink (uptake) for BVOCs at environmentally relevant concentrations, because many microorganisms use VOCs as sources of C and energy (Albers et al., 2018; McGenity et al., 2018; Zhang et al., 2018), as indicated by uptake of monoterpenes by soil and microorganisms (Aaltonen et al., 2013; Spielmann et al., 2017; Puentes-Cala et al., 2018; Staudt et al., 2019). In this sense, the compensation point of reactive gases with their exchanges with leaves (Niinemets et al., 2014) could be used homologously in soils.

Most of the terpenes recorded in this study have also recently been reported from tropical forest soils (Bourtsoukidis et al., 2018), albeit at lower exchange rates of total terpenes and monoterpenes than we found. The substantial emissions of sesquiterpenes recorded from these tropical soils may be of comparable magnitude to canopy emissions and confirm an important ecological relation between soil microbes (Bourtsoukidis et al., 2018) root exudation, mycorrhizal interactions, invertebrate activity, litter decomposition or disturbance, fresh leaf fall, etc., and atmospheric BVOCs.

4.2. Main selected drivers of variation in soil terpene exchange rates

4.2.1. Fertilization

We found that fertilization with N alone led to greatest increases in emissions, as would be expected in a P-limited system, because excess N contributes to the activity of enzymes that synthesize terpenes, whereas under the addition of P, a proportion of N is assigned to functions, other than terpene synthesis. In contrast, the high levels of terpene uptake in the unfertilized control plots may be explained by increases in microbial activity consuming the volatiles as a C source, creating a BVOC gradient towards the soil (Ramirez et al., 2009; Fanin, 2012; Asensio et al., 2012), while the lower terpene emissions in the NP and P plots than in the N plots may reflect the use of these nutrients for plant growth. The greater levels of terpene emissions in the NP, P and specially in N fertilized plots may be explained by greater BVOC production as a result of increased microbial activity and/or changes in microbe community composition (Liu et al., 2013), as well as interactions between microbes that cause feedback effects on soil C pools and CO_2 fluxes (Ramirez et al., 2009; Asensio et al., 2012; Liu et al., 2013). In tropical soils, addition of N leads to short term decreases in soil microbe biomass (Liu et al., 2013), while long term addition of N (>8 years) alters the microbe community structure, by decreasing activity of gram-negative bacteria, including that of nitrifying species, and increasing fungi/bacteria ratios (Balser, 2001). In contrast, we found that addition of P increased soil microbe biomass, indicating that P availability is a limiting factor for microbe growth in this old-growth tropical forest; this stimulating effect of P on microbe biomass may be temporary (Liu et al., 2012), although long term addition of P (> 4 years) increases soil respiration (Liu et al., 2013).

A fertilization experiment carried out in this study forest, in which C (as cellulose), N (as urea), and P (as phosphate) were added, revealed that litter C quality and P content explained more than 50% of the variability in soil microbial respiration, indicating co-limitation by C and P, while in the litter layer, microbial respiration was co-limited by N and P as a result of differences in the microbe community, including the ratios of fungi/bacteria and copiotrophic/oligotrophic bacteria (Fanin, 2012). These effects of fertilization increase decomposition rates of soil organic matter, leading to a higher production of terpenes in soils, as was recorded in our study, most notably for sesquiterpenes (Figs. 2 and 3; Tables S7 and S8).

Differences in soil BVOC exchanges with and without the addition of N have been reported in a subtropical pine forest, where the addition of N resulted in a change of soils acting as a source of alkanes and a sink for alkenes (Zhang et al., 2017). Here, we observed that the addition of N only led to larger increases in terpene emissions from the soil. Addition of N, without the limiting nutrient P, may stimulate production of anti-stress compounds and/or biosynthesis of C-rich compounds, as a result of the prevention by lack of P of N investment in functions related to growth, drought response, and energy use in soil micro-organisms and plant roots. Given P is important for cell growth (Oliveiro et al., 2020), a sudden increase in reactive available N may promote the synthesis of enzymes related to terpene production, as indicated by the lower level of soil terpene emissions in this study under N + P addition than with the addition of N alone. In contrast, we found that emissions of sesquiterpenes were higher in P fertilized soils.

4.2.2. Season

Seasonal variation in soil temperature and moisture content drives rates of change in soil BVOC, where it has been shown that, in general, increases in soil temperature and increases in soil moisture (negative correlation, except in wet season at bottom elevation, but not significant correlated, Table S4) promote the volatilization of monoterpenes from the soil to the atmosphere (Van Roon et al., 2005), probably due to the variation in the biological activity of the soil and physical factors such as diffusion.

Our results support the findings that higher BVOC emissions, due to higher levels of soil enzyme activity, occur under higher soil moisture content (Sardans and Peñuelas, 2005) during the wet season. While the low availability of water in the soil tends to increase the emission rates of COVB (Asensio et al., 2007b, 2007c) in the highest plots, decreasing the absorption of compounds by the soil (Pegoraro et al., 2005). On the other hand, although it has been seen that higher soil temperatures increase monoterpene immissions (Asensio et al., 2007b, 2007c, 2008b), it has not been observed in the present work in the dry season, probably because it is not It is a determining factor between stations due to its low variability. For example, temperature regulates isoprenoid emissions through physical processes (volatility and diffusion) and the activity of enzymes related to BVOC synthesis in plants and microorganisms (Peñuelas and Staudt, 2010), while isoprenoid flux in soils increase after rain events (Greenberg et al., 2012). In addition, we found evidence of variation in seasonal effects on emission rates between compounds (Fig. 2 and Table S6) (Van Roon et al., 2005; Asensio et al., 2007b, 2007c), where some compounds were detected in the dry season but not in the wet season (t-ocimene, plus four other unidentified monoterpenes, and α-muurolene, plus eight other unidentified sesquiterpenes) and vice versa (three unidentified monoterpenes) (Fig. 2 and Table S6), probably as result of the variation in the soil of the water content (and not so much by the temperature in this case) (Asensio et al., 2007c, 2008a; Raza et al., 2017), the variation in the composition and quantity of the litter (Isidorov and Jdanova, 2002; Leff and Fierer, 2008) and by the alteration of microbial processes (Rinnan et al., 2007, 2008).

Our results showed that seasonal variation in atmospheric terpene concentrations correlated with soil BVOC fluxes, where soil absorption fluxes were particularly high for sesquiterpenes during the wet season

and at higher elevations (Fig. 3). On the other hand, the highest atmospheric concentrations of total terpenes during the same season are supported by previous studies in tropical systems (Langford et al., 2010; Yáñez-Serrano et al., 2015).

This evidence of soils acting as sinks for COVB, as indicated by negative exchange rates (Figs. 2, 3 and 4) (Cleveland and Yavitt, 1998), is supported by a limited number of studies in tropical ecosystems (Raza et al., 2017; Bourtsoukidis et al., 2018), where the function of the soil as a regulator of BVOC exchanges with the atmosphere may differ from that of temperate climates due to its greater biodiversity, dynamism and biological activity (Trumbore, 1993; Gershenzon and Dudareva, 2007; Šimpraga et al., 2019; Tang et al., 2019).

Another aspect to consider that can vary seasonally and that influences BVOCs exchanges is litter. The emission of BVOCs by litter has been found to be significant (Leff and Fierer, 2008). And, in addition, it has been shown that up to 80% of BVOC derived from litter can be consumed by microbes as a source of C (Ramirez et al., 2009). Soil microorganisms are key drivers of BVOC production and consumption in soils (Gans et al., 2005; Lin et al., 2007; Yamada et al., 2012; Schulz-Bohm et al., 2017; Bourtsoukidis et al., 2018). For example, soil microbes degrade isoprene and monoterpenes (Cleveland and Yavitt, 1997; Khawand et al., 2016; Albers et al., 2018) In studies in which soils have been sterilized, leaving minimal microbial activity, they have shown a reduced or null capacity for BVOC mineralization (Gray et al., 2015; Albers et al., 2018; Kramshoj et al., 2018; Li et al., 2019). However, some studies consider that litter is a minor source of VOCs released into the atmosphere (Faubert et al., 2010; Greenberg et al., 2012). So much so that the litter, together with the organic matter below it, can retain monoterpenes and, in this way, reduce their volatilization, which would result in a lower emission of BVOCs (Van Roon et al., 2005). And, in fact, a trend in this sense was seen in the present work (data not shown).

Therefore, seasonal variation in litter accumulation can affect the type and rates of change of soil BVOCs (Isidorov and Jdanova, 2002; Faubert et al., 2010). We observed the highest litter accumulations during the dry season in 2015 and 2016 and during the wet season of 2017, when we recorded higher levels of microbial activity and terpene exchange (Fig. 3 and Tables S4 and S5). Laboratory studies have shown that litter quality and incubation temperature and duration affect the composition and concentrations of COVB derived from litter, probably as a result of decomposition activity (Gray et al., 2010; Svendsen et al., 2018).

4.2.3. Topographic elevation

Spatial and temporal variations in soil BVOC production, diffusion, and emissions are driven by soil characteristics; however, effects of elevation-topography have been little studied, particularly in tropical forests. Thus, elevation-topography may be an additional factor for inclusion in models of soil exchanges in BVOCs (Meixner and Eugster, 1999), but could mask the influence of a range of drivers. For example, we found that the greatest exchanges in soil BVOCs, which occurred in plots at high elevations (top of the hills), were related to enzyme activity, litter, soil moisture, soil temperature, and fertilization (Table S4); it is likely that these exchanges may have also been related to other soil factors that vary with elevation, including nutrient content, pH, cation exchange capacity, iron oxide content, density and porosity (Fang et al., 1998; La Scala Júnior et al., 2000; Xu and Qi, 2001; Epron et al., 2006; Yoo et al., 2006), and CO_2 exchange (Brito et al., 2009).

In the unfertilized control plots, total terpenes were emitted in greatest rates at lower elevations (bottom of the valleys), while at upper elevations, they were taken up (mainly sesquiterpenes); across all treatments, total terpenes (mainly monoterpenes) tended to be emitted at upper elevations. These contrasting results may be explained by differences in microbial activity, as indicated by soil AcP content that was marginally lower ($P < 0.05$) at upper elevations, and the positive effects of fertilization on emissions, particularly during the wet season at upper elevations (Fig. 3; Tables S6-S8). There were seasonal differences in total terpene exchanges at upper elevations, where exchange levels were higher during the wet than the dry season.

5. Conclusions

We characterized the spatio-temporal differences in the soil terpene exchanges of tropical forests under the effects of fertilization with N and P. Overall, effects of fertilization with N and P alone on terpene emissions varied with compound, where N fertilization favored monoterpene emissions, P fertilization favored sesquiterpenes emissions, and there was an antagonistic effect of the addition of N + P resulting in much lower overall effect on terpene fluxes. Our study also confirmed temperature and moisture as drivers of terpene contributions to the atmosphere and the capacity of tropical soils to absorb them, indicating the interest of including such data in models for the prediction of climate change effects on tropical soil dynamics.

The tropical soils in this study were a net sink of terpenes under ambient conditions, particularly for sesquiterpenes at upper elevations (top of the hills) during the wet season, likely as a result of biological and physical factors, such as microbial consumption of soil-litter volatiles and high concentrations of atmospheric terpenes that favored soil uptake of terpenes.

We found previously undescribed terpenic compounds in this tropical forest. We also found high levels of heterogeneity and magnitudes in soil emissions of terpenes that were similar to those of foliar surfaces, confirming the need for further study of implications of global change on soil BVOC fluxes in tropical ecosystems, due to their crucial role in ecosystem function and atmospheric chemistry.

Meanwhile, these results indicate likely shifts in tropical soils from sink to source of atmospheric terpenes under projected increases in N deposition under global change, with potential impacts on regional-scale atmospheric chemistry and climate, and ecosystem function. This merits further attempting and research initiatives because it can have implications in the future projections of functioning and carbon balances of the tropical rainforests, and can improve the modelling performance.

CRediT authorship contribution statement

Joan Llusia: Collection of samples of BVOCs and their analysis and writing of the document. **Dolores Asensio:** She was part of the litter and soil sampling group. She also participated in the analysis of the enzymatic activity of soils and litter. Manuscript review. **Jordi Sardans:** Planning and development of the experiment, supervision of the collection of the samples. Manuscript review. **Iolanda Filella:** Planning and development of the experiment. Manuscript review. **Guille Peguero:** Support in field work and manuscript review. **Oriol Grau:** Support in field work and manuscript review. **Romà Ogaya:** Support in field work and manuscript review. **Albert Gargallo-Garriga:** He participated in the analysis of the enzymatic activity of soils and litter. Manuscript review. **Lore T. Verryckt:** Support in field and laboratory work and manuscript review. **Leandro Van Langenhove:** Support in field work and analyses of soil properties. Manuscript review. **Ivan A. Janssens:** Planning and development of the experiment, supervision of the collection of the samples and manuscript review. **Laëtitia Brechet:** Support in field work and manuscript review. **Elodie Courtois:** Support in field work and manuscript review. **Clément Stahl:** Support in field work and manuscript review. **Josep Peñuelas:** Planning and development of the experiment, supervision of the collection of the samples and manuscript review.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the Spanish Government project PID2019-110521GB-I00, Fundación Areces Elemental-Climate-2021, the Catalan Government project SGR2017-1005, and the ERC Synergy project SyG-2013-610028 IMBALANCE-P. We thank staff at the Nouragues research station, managed by USR mixte LEEISA (CNRS; Cayenne), and the Paracou research station, managed by UMR Ecofog (CIRAD, INRA; Kourou); both research stations receive support from Investissement d'Avenir grants managed by Agence Nationale de la Recherche (CEBA: ANR-10-LABX-25-01, ANAEE-France: ANR-11-INBS-0001). We also thank Anna Escolà and Pere-Roc Fernández for dedicated assistance as field and laboratory technicians in French Guiana.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.149769.

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