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Intermediate-scale horizontal isoprene concentrations in the near-canopy forest atmosphere and implications for emission heterogeneity

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Significance

Unquantified intermediate-scale heterogeneity in VOC emissions over Amazonia may be a key contributor to the observed discrepancy between measured and modeled VOC concentrations, but in situ measurements for investigating the possibility have been lacking. The measurements presented herein quantify horizontal VOC concentration gradients over different forest subtypes at intermediate scales of several hundred meters. The results suggest that there are biases in both top-down estimates based on satellite or aircraft measurements and bottom-up approaches based on leaf or tower measurements. The results demonstrate how observations collected by UAV-enabled technologies fill a missing niche among leaf-level, tower, aircraft, and satellite scales. Information at this previously unavailable scale is needed for accurate understanding and predictions related to changing forests under climate stress.

Abstract

The emissions, deposition, and chemistry of volatile organic compounds (VOCs) are thought to be influenced by underlying landscape heterogeneity at intermediate horizontal scales of several hundred meters across different

forest subtypes within a tropical forest. Quantitative observations and scientific understanding at these scales, however, remain lacking, in large part due to a historical absence of canopy access and suitable observational approaches. Herein, horizontal heterogeneity in VOC concentrations in the near-canopy atmosphere was examined by sampling from an unmanned aerial vehicle (UAV) flown horizontally several hundred meters over the plateau and slope forests in central Amazonia during the morning and early afternoon periods of the wet season of 2018. Unlike terpene concentrations, the isoprene concentrations in the near-canopy atmosphere over the plateau forest were 60% greater than those over the slope forest. A gradient transport model constrained by the data suggests that isoprene emissions differed by 220 to 330% from these forest subtypes, which is in contrast to a 0% difference implemented in most present-day biosphere emissions models (i.e., homogeneous emissions). Quantifying VOC concentrations, emissions, and other processes at intermediate horizontal scales is essential for understanding the ecological and Earth system roles of VOCs and representing them in climate and air quality models.

Keywords: isoprene emissions | landscape heterogeneity | intermediate horizontal scales | Amazon tropical forest | UAV measurements

Introduction

Volatile organic compounds (VOCs) emitted from forests have important roles in signaling among plants, animals, insects, and microbes; ecosystem functioning and health; and atmospheric chemistry and climate (1, 2). Tropical forests are the major global VOC source but are comparatively less studied and understood than their temperate and boreal counterparts (3). Tropical forest landscapes can have great heterogeneity and many forest subtypes at scales of hundreds of meters (i.e., intermediate horizontal scales) (4, 5). In central Amazonia, rolling hills underlying the tropical forest north of the Amazon River give rise to plateaus interspersed by waterlogged valleys, all dissected by streams and rivers and joined by sloped regions, at scales of hundreds of meters. Myriad forest subtypes and biodiversity result across this intermediate scale for reasons of water, sunlight, and soil, among other factors and variations (6, 7).

The landscape variability at intermediate scales is thought to be associated with variability in VOC emissions at the same scale (8). For any VOC, some tropical forest subtypes can have high emissions of that VOC, whereas other subtypes can exhibit low emissions or pockets of net deposition, even as the forest as a whole emits in net. This emerging view of a heterogeneous patchwork of VOC emissions and deposition has important implications for interpreting results of earlier studies that have largely reported VOC observations from single locations, such as tower sites, with no information on the surrounding horizontal heterogeneity in VOC emissions and deposition. Atmospheric chemical transport models also do not accurately simulate VOC oxidation over tropical forests (9), and process-level models

such as large-eddy simulations suggest that nonuniform VOC emissions from different forest subtypes can be one possible explanation (10–12).

Measurements of VOC variability over the forest subtypes are needed to investigate this possibility as well as to improve predictive capabilities for models of emissions and reactive chemistry over these landscapes.

Topography is often a first surrogate of landscape variability and thus also of VOC emissions, especially in Amazonia (13, 14). Contributing factors tying topography to forest subtype are variations in elevation, slope, aspect, drainage, soil type, and microclimate, among others, that determine forest species composition and diversity. Flood-free plateau forest grows on the tops of rolling hills, and over 200 species are routinely identified in inventories (15). The soils are strongly leached, with low natural fertility and high acidity. By comparison, valley forests are populated by plants adapted to richer, waterlogged soils and wetlands. More than 100 species are typically identified in inventories (15). Slope forests have a mix of valley and plateau plant families. Estimates are on the order of 10,000 distinct tree species across Amazonia (5, 16).

Herein, results are reported for investigating the heterogeneity of isoprene concentrations in the near-canopy atmosphere over plateau, slope, and valley forest subtypes in the central Amazonian forest during the wet season of 2018. Isoprene is the nonmethane VOC emitted in greatest quantity by land surfaces on Earth, as represented in the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (3). One estimate is that isoprene emissions alone represent 70% of total VOCs emitted by plants globally into the atmosphere (17). Leading models such as MEGAN and others, however, are not presently able to predict emissions heterogeneity at the intermediate horizontal scales across forests, even as differences are thought to exist, in large part because of the absence of historical measurement platforms and datasets. For investigation of forest subtypes at intermediate scales without disturbance of the underlying landscape, chemical sampling and sensing by use of unmanned aerial vehicles (UAVs) represents an emerging frontier in atmospheric chemistry (18). In the present study, datasets of isoprene concentration were collected at intermediate scales by use of a UAV, and relative emission differences were inferred by use of a gradient transport model constrained to the measured heterogeneity in concentrations over the different forest subtypes.

Results

Different Forest Subtypes.

The UAV collected samples for 2 different locations above the Adolfo Ducke Forest Reserve (hereafter Ducke Reserve) in central Amazonia across 4 wk during the wet season from February 20 to March 15, 2018. The Ducke Reserve (10 km × 10 km) is located on the northern outskirts of Manaus, Brazil, in central Amazonia. Established in 1963, the reserve is recognized as a globally important site for the study of tropical forests (6, 14, 19). A tower

(MUSA tower) is located within the Manaus Botanical Gardens (MUSA) of the reserve (Fig. 1) (*Materials and Methods*). Valley and plateau regions in the tower vicinity are ~50 and 120 m above sea level (asl), respectively, and they are joined by sloped regions.

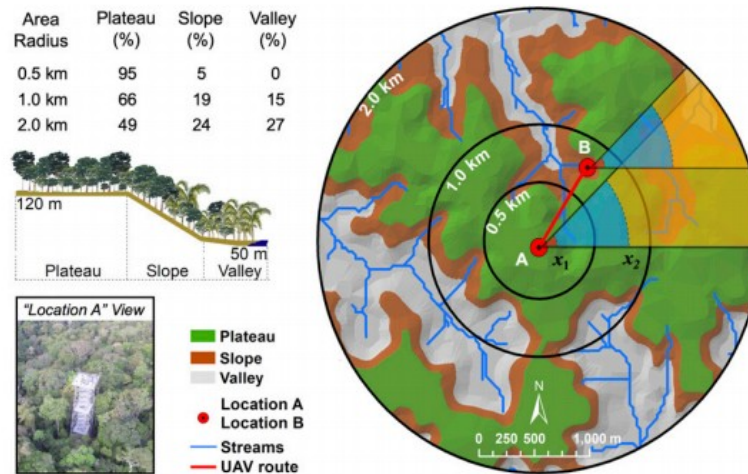


Fig. 1. Local topography surrounding the tower (location A) at the Manaus Botanical Gardens (MUSA) of the Adolfo Ducke Forest Reserve in the central Amazon, Brazil. The UAV flight route from location A over the plateau forest to location B over the slope forest is shown by the red line. Zones of influence are shown in translucent overlay on the forest subtypes surrounding locations A and B (see also *SI Appendix, Fig. S2*). The sector angle of each translucent overlay represents the variability of wind direction in the steady trade winds during the period of study. The dashed arc lines within a sector represent transitions from one zone of influence x_i to the next.

Biodiversity in Ducke Reserve is well characterized by tree inventory surveys. The plant species and occurrence in the reserve have 3 major forest classifications, described as valley, slope, and plateau forest subtypes (13↓–15, 20). These forest subtypes are represented in gray, brown, and green in Fig. 1. Valley forest occurs along the sandy banks of streams. Flooding is frequent, and the sediment mixes with the forest litter. Canopy height varies from 20 to 35 m. Plateau forest grows in the highest areas in well-drained yet nutrient-poor clay soil. Canopy height ranges from 25 to 35 m. Emergent trees can reach 45 m. Slope forest dissects the landscape, bridging between the valley and plateau forests. It is characterized by clay soils in the higher reaches of the slopes and sandy loam soils in the lower parts. Canopy height ranges from 25 to 35 m. Another important forest classification at Ducke Reserve, which is interspersed among these major topography-based classifications, is campinarana. It grows on extremely nutrient-poor, poorly drained, white quartz sandy regions. Canopy height varies between 15 and 25 m.

Ribeiro et al. (20) presented information on the prevalent plant species in each of the forest subtypes at Ducke Reserve, as summarized in *SI Appendix, Table S1*. The MUSA forestry staff inspected the actual plant species at locations A and B at the time of the UAV flights, and the species were identified as consistent with the inventory of Ribeiro et al. (20). Some important families include Arecaceae (commonly referred to as palm trees), Caryocaraceae, Clusiaceae, Fabaceae (legumes), Lecythidaceae, Meliaceae,

Mimosaceae (specialized legumes), Rapataceae, Solanaceae (nightshades), and Sapotaceae. The species that grow in abundance are distinct for each forest subtype. The photographs shown in Fig. 2 of the slope and plateau forests at locations A and B highlight differences in forest composition at the 2 locations.



Fig. 2. Photographs of the trees of the plateau forest (location A; *Top*) and the slope forest (location B; *Bottom*) of Fig. 1. (*Left*) The downward images of the top of the forest canopy were taken by a camera on the UAV. (*Right*) The upward images from the ground through the canopy were taken by a hiker at those locations.

Concentrations in Near-Canopy Atmosphere.

The UAV was launched and recovered from a platform atop the MUSA tower (3.003° S, 59.940° W; Fig. 1, Inset) (*Materials and Methods*). The longitude-latitude point of the MUSA tower is referred to as location A herein. The UAV flew 711 m to 2.997° S and 59.936° W. This longitude-latitude point is referred to as location B in the study. Locations A and B were located over plateau and slope forest subtypes, respectively. The UAV hovered over the canopy at location B and sampled VOCs. An automated sampler, mounted to the UAV, collected the VOC samples in cartridges (21). Simultaneous VOC sampling took place on the tower platform at location A. All samples were

analyzed offline by gas chromatography. For locations A and B, samples were collected cumulatively in 4 different cartridge tubes across a week for 20 min of sampling within each hour of 09:00 to 10:00, 10:10 to 11:10, 11:20 to 12:20, and 12:30 to 13:30 (local time; 4 h earlier relative to UTC). This approach captured daily trends while ensuring sufficient material for chemical analysis. Four composite samples were collected each week for a total of 4 wk over each location, resulting in a total of 32 samples.

Many compounds were identified in the collected samples, including isoprene, α -pinene, β -pinene, 9 other monoterpenes, β -caryophyllene, and 3 other sesquiterpenes, together representing a progressive set of C_5 , C_{10} , and C_{15} compounds (Fig. 3). After emitting into the atmosphere, these and other VOCs undergo atmospheric mixing and dilution as well as reactive chemical loss. An upward trend is common in the concentrations from morning to noon (3), which can be explained by increasing solar irradiance and temperature. Enzyme activity increases with temperature, and electron transport increases with sunlight until saturation, resulting in a tendency for increasing emissions of isoprene and many other terpenoid VOCs from plants and consequently for increasing near-canopy atmospheric concentrations, balanced against atmospheric dilution and chemical loss (22).

The isoprene concentrations were consistently higher over the plateau forest compared to those over the slope forest. The mean weekly isoprene concentrations above the slope forest ranged from 1.0 to 3.3 ppb (Fig. 3A and *SI Appendix*, Table S2). The mean concentrations above the plateau forest ranged from 2.9 to 4.9 ppb. The mean weekly differences for isoprene concentration over the slope compared to over the plateau forest ranged from 1.5 to 2.7 ppb. For the overall dataset, the mean isoprene concentration was 2.4 ppb over the slope forest, which can be compared to 4.4 ppb over the plateau forest, representing an increase of +80% for the latter. The calculated probability (P value) for a 2-way ANOVA analysis in location and time is <0.001 for the null hypothesis that the 2 sets of isoprene concentrations were the same over locations A and B (*SI Appendix*, Table S3). An implication is that measurements from a single tower placed at either location A or location B would have significant bias if taken as representative of the regional area of Ducke Reserve.

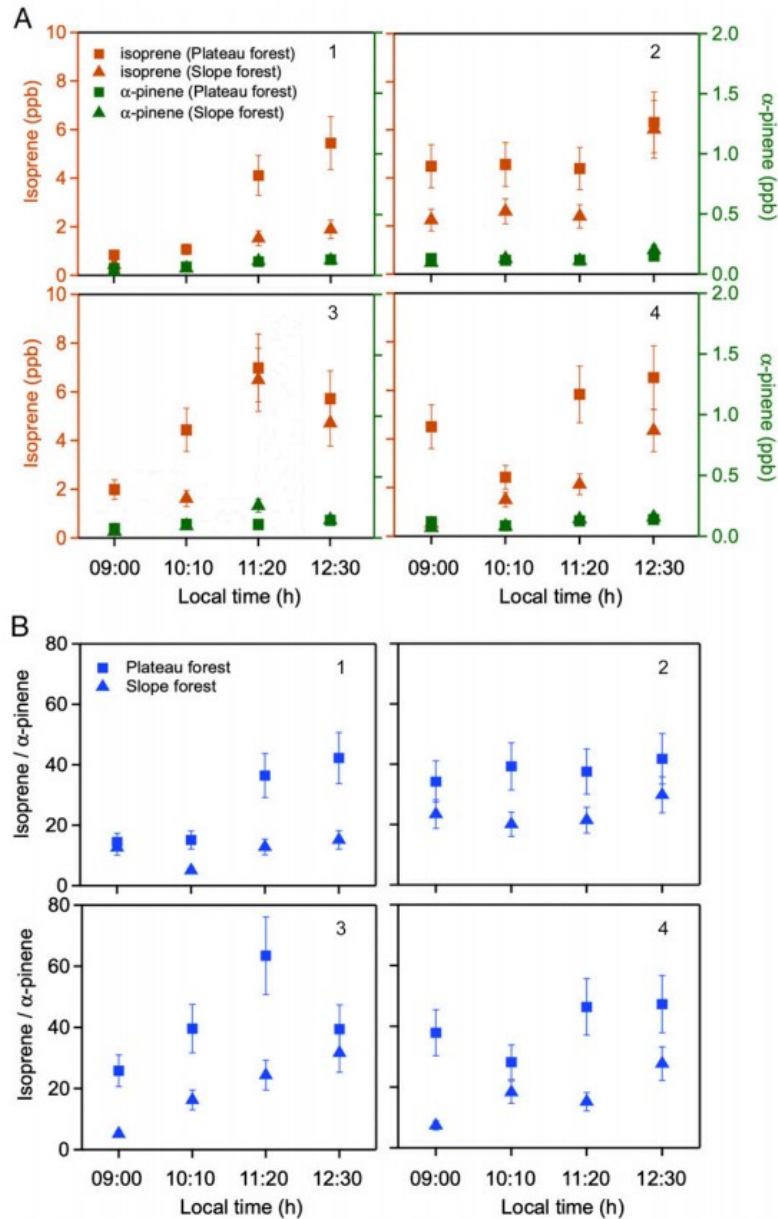


Fig. 3. (A) Isoprene (orange) and α -pinene (green) concentrations and (B) isoprene-to- α -pinene concentration ratios. The labels 1 to 4 indicate weeks 1 to 4, respectively, of the measurement period. Squares are over the plateau forest for 15 m above local canopy height at location A of Fig. 1. Triangles are over the slope forest for 47 m above local canopy height at location B of Fig. 1. The isoprene concentrations were consistently higher over the plateau forest compared to the slope forest. By comparison, no significant difference was observed for near-canopy α -pinene concentrations between the plateau forest and the slope forest. Data were collected and aggregated in intervals of 09:00 to 10:00 (local time), 10:10 to 11:10, 11:20 to 12:20, and 12:30 to 13:30 of the morning and early afternoon hours. Local time was UTC minus 4 h.

The observed isoprene concentrations can be compared to previous reports throughout Amazonia (*SI Appendix*, section S1 and Table S4). The reported concentrations range from <1 to 27 ppb, in part reflecting the heterogeneity of tropical forests. The mean observed concentrations of 2.4 and 4.4 ppb for locations A and B thus lie within the literature range reported for Amazonia.

Unlike isoprene concentrations, the concentrations and time variability of α -pinene, which is typically the monoterpene emitted in largest quantity by the

forest, were similar over the plateau and slope forests (Fig. 3A). The P value was 0.61 for the null hypothesis that the 2 sets of α -pinene concentrations were the same over location A and location B (*SI Appendix*, Table S3). The ratio of the isoprene concentration to the α -pinene concentration is plotted in Fig. 3B. An advantage of this concentration ratio, compared to the isoprene concentration alone, is a mitigation of some possible confounding factors related to differences in transport and reactive loss to locations A and B compared to differences in emissions from forest subtypes at locations A and B. Across 09:00 to 13:30, the mean weekly ratios above the slope forest ranged from 11.4 to 23.7. The ratios above the plateau forest ranged from 27.1 to 42.1. These comparative ratios thus also suggest significantly higher emissions of isoprene by the plateau forest compared to those by the slope forest given that the α -pinene concentrations had similar values over the 2 forest subtypes.

Discussion

Isoprene is emitted across the horizontal extent of the forest as myriad point emissions from the leaves of individual plants, and the isoprene concentration at the location of UAV sampling in the atmosphere represents the sum of the contribution of each of these point emissions. After being released from a plant, the emitted isoprene is subject to convection in the vertical, advection in the horizontal, and atmospheric chemical reaction (loss) during transport to the location of sampling. Therefore, forest emissions that are directly underlying the point of UAV sampling, as well as forest emissions that are farther afield and delivered to the point of sampling by regional atmospheric transport, affect the isoprene concentration at the location of UAV sampling. Dispersion and reactive loss of isoprene occur between emission at the source region and arrival at the UAV receptor location. Taking these factors into account is required to relate the observed differences in isoprene concentrations at locations A and B to possible differences in the emissions of the underlying forest subtypes.

Herein, a 2D gradient transport model is used to simulate isoprene concentrations over the atmospheric boundary layer (23, 24). Details of the model are described in *SI Appendix*, section S2. The model simplifies the lower part of the atmosphere as an incompressible fluid at constant pressure and takes into consideration longitudinal and vertical transport as well as possible in situ chemical reactions. To assess the extent to which the local forest subtype influences the concentrations measured at the point of UAV sampling, upwind spatial zones of influence for the point of measurement were determined. The zones of influence are defined as the horizontal upwind distances x_1 , x_2 , x_3 , and x_4 that respectively contribute 0 to 25%, 25 to 50%, 50 to 75%, and 75 to 95% of the total concentration C^+ at the point of UAV sampling. More specifically, a small value of x_1 corresponds to a significant influence by local emissions of the directly underlying and nearby surrounding forest on the atmospheric concentrations sampled by the UAV. Values of x_1 , x_2 , x_3 , and x_4 are obtained from the model (*SI Appendix*, section

S3 and Table S5). For the atmosphere of a tropical forest affected by urban pollution, corresponding to the parameters of the reference case listed in *SI Appendix*, Table S6, the intervals are 0 to 150 m (x_1), 150 to 700 m (x_2), 700 to 2,350 m (x_3), and 8,300 m and beyond (x_4). These values apply to both locations A and B because the meteorological conditions at both sites are similar. Sensitivity analyses were performed to evaluate the effects of the uncertainty in model parameters on the zones of influence, and x_1 varies between 100 and 250 m across the sensitivity analysis compared to 150 m for the reference case (*SI Appendix*, Table S7).

The zones of influence of the reference case are further represented in Fig. 1 in translucent overlay on the forest subtypes surrounding locations A and B in the directional sector of the dominant winds (*SI Appendix*, Fig. S1). The plot shows that 25% of the total isoprene concentration C^+ at location A is modeled as strongly related to the emissions of the nearby plateau forest (i.e., lying within the first dashed line position at x_1) and likewise at location B to the emissions of the nearby slope forest (see also *SI Appendix*, Fig. S2). For the next 25% of C^+ , represented by the second dashed line at x_2 , there is an influence of all 3 forest subtypes, although the specific portions of the forest contributing emissions to locations A and B remain distinct. The next 50% of C^+ beyond the x_2 line can be understood as contributed by a pattern of repeating forest subtypes, representing a nondistinct average across the regional forest. For comparison, a low-flying aircraft or fixed-wing UAV might have an averaging kernel comparable to this local regional average.

The effect of sampling height above the local canopy on the measured concentrations was considered. For the reference case, the ratio $C^+(15\text{ m}):C^+(47\text{ m})$ is modeled as 1.21. UAV sampling was also carried out in late 2017 at height differences of 40 to 50 m over the plateau forest nearby location A, and the average ratio was 1.22 (*SI Appendix*, Table S8). A similar value was observed by sampling at a 44-m height difference along an 80-m tall tower situated in a plateau forest about 100 km away for the daily period of 09:00 to 15:00 (LT) during the wet season (25). The same study showed that the variability in isoprene concentrations at these altitudes over the plateau forest correlated strongly with the variability in emissions from the local forest. The implication of these results is that differences in sampling height over the local canopy height at location B (47 m) compared to location A (15 m) are not sufficient to explain the average ratio of 1.80 in isoprene concentrations, as observed herein. The observed increase of +80% can be partitioned approximately as +20% for differences in height and +60% for differences in emissions.

Inverse modeling was applied to the dataset to determine the emissions difference necessary to sustain a concentration difference of +60% between locations A and B. For the reference case of the model (*SI Appendix*, Tables S5 and S6), a difference between 220 and 330% in emissions between the plateau and slope forest subtypes is needed to sustain the observed concentration difference. The lower estimate of 220% is obtained by

assuming that the emission differences extend to the full range of x_1 and x_2 (700 m) from locations A and B, whereas the upper estimate of 330% is obtained by assuming that the emission differences are fully within the range of x_1 (150 m). The magnitude in differences in emissions for the different forest subtypes can be rationalized by the different species compositions and environmental conditions, keeping in mind the heterogeneous ecosystem of the tropical forest and the estimate that 30% of trees in a tropical forest emit isoprene (26).

Atmospheric Implications.

Although processes at intermediate scales of several hundred meters across an ecosystem are believed to exert significant control over the magnitude and type of VOC emission and deposition, these processes remain incompletely understood qualitatively and less defined quantitatively. Emission models for Amazonia in particular continue to have large uncertainties, including the assignment of base emission capacities, meaning the emission expected for a set of standard environmental conditions. Emission capacities for various landscape types, in Amazonia and elsewhere, are largely estimated by 2 complementary methods (27). 1) In a mechanistic, bottom-up approach, composition data of vegetation species for a landscape, instantaneous canopy conditions at a time of interest, and plant-level functional relationships for those conditions are combined to estimate landscape-scale emissions. 2) In an empirical, one-size-fits-all approach, canopy-level gradient or eddy flux measurements obtained for a location within a landscape type are assumed to hold across the entire landscape.

Method 1 has worked well for temperate and boreal forests because of low species diversity, and under this condition, enclosure measurements of VOC emissions of the known dominant plant types are possible. By comparison, method 1 has large uncertainties for tropical forests because immense biodiversity in species composition challenges an accurate inventory of vegetation species and emission variability among those species presents difficulties for accurate functional relationships. Available literature is small relative to the forest heterogeneity. Ideally, isoprene emission rates characteristic of each of these plant species apparent in Fig. 2 and listed in *SI Appendix*, Table S1, would be known, and accurate bottom-up predictions of isoprene emissions over the different subforests could be possible. In reality, insufficient information is available and difficult to acquire, not just because of the large biodiversity but also because of the dependence of emissions from a single plant on environmental conditions. In this challenging context, UAV-based sample collection provides a capability that effectively represents a local, landscape-average measurement-based integration kernel of emissions at intermediate scales across the myriad leaf-level and plant-level factors to provide datasets and quantify the differences in emissions of the different forest subtypes.

Method 2 has been successful for relatively homogeneous and open ecosystems characteristic of temperate and boreal regions, and vertical profiles from towers and tethered balloons have been successful in determining VOC fluxes and emissions within acceptable uncertainty. For tropical forests, however, method 2, representing a single-point approach, has large uncertainties because of a lack of suitable approaches for quantifying heterogeneity in fluxes over scales of a kilometer or less across the landscape (28). Even locally, tower locations may not be representative because a single tree next to a tower can bias the profile results, especially at lower sampling heights where the small footprint contains only a few trees. In Amazonia, most research towers have been located in locally elevated topographical regions (i.e., plateau forests; *SI Appendix*, Table S4), and previous emission estimates taken as representative of Amazonia can have bias based on the limits of available datasets.

Several of the shortcomings of methods 1 and 2 applied to tropical forests can be ameliorated, at least in part, by the complementary application of the newly emerging technology of UAV-based sampling approaches. The results presented herein demonstrate the possibility of UAV-based sampling to collect information efficiently at the intermediate scales across footprints centered at adjustable longitude–latitude coordinates, as needed for understanding the heterogeneity of tropical forests. Access of this type has potential for improved sampling over undisturbed forests as well as over forests in forbiddingly inhospitable landscapes, such as waterlogged or swampy regions. For example, as a practical matter, the VOC sampler on the UAV flew from location A to location B in 5 min for sampling over 2 different forest subtypes. As a general statement, near-canopy atmospheric measurements described in the literature of tropical forest have been largely confined to a small set of locations where there are towers (e.g., *SI Appendix*, Table S4), implying that spatial heterogeneity has been inadequately captured. UAV systems can be fully operated by powerful onboard computer controllers coordinated with a satellite-based positioning system, all of which are standard on a commercial UAV such as that used in this study. Sampling with a UAV allows takeoff and landing from the Earth's surface without the presence of a tower, thus eliminating an important constraint on the site locations for research. Moreover, a vertically stacked multi-UAV configuration as a type of floating tower is a further possibility. Limitations must also be borne in mind, however. Current commercially available UAVs have short flight times of <1 h due to battery capacity and limited payload capacity (<10 kg), and aerospace regulations can limit flight operations in real-world practice (18).

In summary, the presented results demonstrate intermediate-scale horizontal heterogeneity of VOC concentrations, specifically isoprene concentrations, in the near-canopy atmosphere over central Amazonia. Emission differences implied by the measurements are quantified as 220 to 330% for the different forest subtypes across this biodiverse landscape. For

comparison, the state-of-the-art MEGAN model assumes homogeneity at this scale and provides 0% difference in emissions between the 2 forest subtypes. The explanation is that there has not been sufficient knowledge about horizontal heterogeneity to inform the MEGAN model. These findings call attention once more to readdressing a longstanding scientific unknown related to forest heterogeneity, now in hand with newly emerging UAV-assisted technical possibilities to make progress on this unknown, for understanding and quantifying VOC emissions at intermediate scales to better understand the ecological and Earth system roles of VOCs and to better represent them in climate and air quality model simulations.

Materials and Methods

Sampling Platforms.

The hexacopter UAV (DJI Matrice 600) equipped with the VOC sampler was launched and recovered from a platform (3.5 m × 3.5 m) atop the MUSA tower in the Ducke Reserve. Details of the sampler are described in *SI Appendix*, section S4, and ref. 21. The tower corresponded to location A of the study (3.003° S, 59.940° W; Fig. 1, *Inset*). Ground level was 120 m asl at location A. The tower had a height of 42 m, and local forest canopy height nearby the tower was 25 to 35 m. Location B (2.997° S, 59.936° W) was 711 m distant from the tower. Ground level was 85 m asl. Local canopy height at location B was also 25 to 35 m.

Sampling Strategy.

During a UAV flight, a sampling period for a single cartridge was 2.5 min. More specifically, as an example, 2 flights on 1 d between 09:00 and 10:00 corresponded to 5 min of sampling with 1 cartridge tube. In the same cartridge tube, samples were collected at the same period of the day (e.g., 09:00 to 10:00) for 4 d in a week to ensure sufficient material for chemical analysis, corresponding to 20 min or 3 L of sampling for this cartridge tube (*SI Appendix*, Table S2). This sampling strategy was taken to complement work on semivolatile organic compounds (17.5 min sampling each flight; work not described herein). The strategy of sampling across a broader period also helped to average out otherwise possible confounding effects of sustained downdrafts or updrafts during a single sampling period. Samples were collected simultaneously over location A (with a handheld pump; GilAir PLUS, Gilian) for 15 m above local canopy and over location B (with VOC sampler) for 47 m above local canopy height. The lower ground level (asl) at location B required the sampling at a higher relative height above the canopy so that the UAV remained in the horizontal visual field of the flight operator positioned on the tower platform at location A. The influence of different sampling heights was not significant enough, however, to account for observed concentration differences (see main text).

Chemical Analysis.

Samples were analyzed using thermal desorption gas chromatography coupled with a time-of-flight mass spectrometer (Markes BenchTOF-SeV) and a flame ionization detector (TD-GC-FID/TOFMS). Details of the analysis including TD-GC operation protocols, VOC detection limits, and uncertainties are provided in *SI Appendix*, section S5.

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