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# Plant responses to volcanically-elevated $CO_2$ in two Costa Rican forests

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**Abstract.** We explore the use of active volcanoes to determine the short- and long-term effects of elevated $CO_2$ on tropical trees. Active volcanoes continuously but variably emit $CO_2$ through diffuse emissions on their flanks, exposing the overlying ecosystems to elevated levels of atmospheric $CO_2$. We found tight correlations ($r^2$=0.86 and $r^2$=0.74) between wood stable carbon isotopic composition and co-located volcanogenic $CO_2$ emissions for two species, which documents the long-term photosynthetic incorporation of isotopically heavy volcanogenic carbon into wood biomass. Measurements of leaf fluorescence and chlorophyll concentration suggest that volcanic $CO_2$ also has measurable short-term functional impacts on select species of tropical trees. Our findings indicate significant potential for future studies to utilize ecosystems located on active volcanoes as natural experiments to examine the ecological impacts of elevated atmospheric $CO_2$ in the tropics and elsewhere. Results also point the way toward a possible future utilization of ecosystems exposed to volcanically elevated $CO_2$ to detect changes in deep volcanic degassing by using selected species of trees as sensors.

## 1 Introduction

Tropical forests represent about 40% of terrestrial Net Primary Productivity (NPP) worldwide, store 25% of biomass carbon, and may contain 50% of all species on Earth, but the projected future responses of tropical plants to globally rising levels of $CO_2$ are poorly understood (Leigh et al., 2004; Townsend et al., 2011). The largest source of uncertainty comes from a lack of understanding of long-term $CO_2$ fertilization effects in the tropics (Cox et al., 2013). Reducing this uncertainty would significantly improve Earth system models, advances in which would help better constrain projections in future climate models (Cox et al., 2013; Friedlingstein et al., 2013). Ongoing debate surrounds the question of how much more atmospheric $CO_2$ tropical ecosystems can absorb—the "$CO_2$ fertilization effect" (Gregory et al., 2009; Kauwe et al., 2016; Keeling, 1973; Schimel et al., 2015).

Free Air $CO_2$ Enrichment (FACE) experiments have been conducted to probe this question, but none have been conducted in tropical ecosystems (e.g. Ainsworth and Long, 2005; Norby et al., 2016). Some studies have used $CO_2$-emitting natural springs to study plant responses to elevated $CO_2$, but these have been limited in scope due to the small spatial areas around springs that experience elevated $CO_2$ (Paoletti et al., 2007; Saurer et al., 2003). These studies have suffered from several confounding influences, including other gas species that accompany $CO_2$ emissions at these springs, human disturbances, and difficulty with finding appropriate control locations. Additionally, none have been conducted in the tropics (Pinkard et al., 2010). A series of studies in Yellowstone National Park (USA) used its widespread volcanic hydrothermal $CO_2$ emissions for the same purpose, though it is not in the tropics (Sharma and Williams, 2009; Tercek et al., 2008). Yellowstone was particularly suitable for this type of study, due to its protected status as a National Park, and because the large areas of $CO_2$ emissions made control points more available (Sharma and Williams, 2009; Tercek et al., 2008). These studies reported changes in rubisco and sugar production in leaves similar to results from FACE experiments, suggesting that volcanically-influenced areas like Yellowstone have untapped potential for studying the long-term effects of elevated $CO_2$ on plants.

Tropical ecosystems on the vegetated flanks of active volcanoes offer large and diverse ecosystems that could make this type of study viable. Well over 200 active volcanoes are in the tropics (Global Volcanism Program, 2013) and many of these volcanoes are heavily forested. However, fewer of these tropical volcanic forests have sufficient legal protection to be a source of long-term information, and the effects of diffuse volcanic flank gas emissions on the overlying ecosystems remain largely unknown. Most previous studies focused on extreme conditions, such as tree kill areas associated with extraordinarily high $CO_2$ emissions at Mammoth Mountain, CA (USA) (Biondi and Fessenden, 1999; Farrar et al., 1995; Sorey et al., 1998). However, the non-lethal effects of volcanic $CO_2$—away from the peak emission zones, but still in the theorized fertilization window—have received little attention, and could offer a new approach to studying the effects of elevated $CO_2$ on ecosystems (Cawse-Nicholson et al., 2018). The broad flanks of active volcanoes experience diffuse emissions of excess $CO_2$ because the underlying active magma bodies continuously release gas, dominated by $CO_2$ transported to the surface along fault lines (Chiodini et al., 1998; Dietrich et al., 2016; Farrar et al., 1995). This process has frequently been studied to understand the dynamics of active magma chambers and to assess potential volcanic hazards (Chiodini et al., 1998; Sorey et al., 1998). These emissions are released through faults and fractures on the flanks of the volcano (Burton et al., 2013; Pérez et al., 2011; Williams-Jones et al., 2000)(see Supplementary Figure S1). Volcanic flanks through which these gases emanate are broad, covering typically 50-200 $km^2$, often supporting well-developed, healthy ecosystems. Some of these faults tap into shallow acid hydrothermal aquifers, but by the time these gases reach the surface of most forested volcanoes, soluble and reactive volcanic gas species (e.g., $SO_2$, HF, HCl, $H_2S$) have been scrubbed out in the deep subsurface, leading to a diffusely emanated gas mix of predominantly $CO_2$ with minor amounts of hydrogen, helium, and water vapor reaching the surface (Symonds et al., 2001).

Trees in these locations are continuously exposed to somewhat variably elevated levels of $CO_2$ ($eCO_2$), it was unclear if the trees utilize this excess $CO_2$. Volcanic $CO_2$ has a heavy $\delta^{13}C$ signature typically ranging from -7 to -1 ‰, which is distinct from typical vegetation and noticeably heavier than typical atmospheric values (Mason et al., 2017). If trees incorporate volcanic $CO_2$, then the stable carbon isotopic composition of wood may document the long-term, possibly variable influence of volcanic $CO_2$ during the tree's growth. With this tracer available, volcanic ecosystems could become a valuable natural laboratory to study the long-term effects of elevated $CO_2$ on ecosystems, especially in understudied regions like the tropics. Additionally, short-term effects of $eCO_2$ might be revealed by plant functional measurements at the leaf scale, where the additional $CO_2$ could increase carbon uptake in photosynthesis.

Here we provide preliminary results on the short- and long-term non-lethal impacts of diffuse volcanic $CO_2$ emissions on three species of tropical trees on the flanks of two active volcanoes in Costa Rica. We also explore the viability of studying volcanically-influenced ecosystems to better understand potential future responses to elevated $CO_2$, and suggest adjustments to our approach that will benefit future, similarly-motivated studies.

## 2 Methods

### 2.1 Investigated locations and sampling strategy

Irazú and Turrialba are two active volcanoes located ~25 and 35 km east of San José, Costa Rica. These two volcanoes are divided by a large erosional basin. The two volcanoes cover approximately 315 $km^2$, which is significantly larger than the average forested active volcanic edifice in Costa Rica at 122 $km^2$. The vast majority of the northern flanks of Irazú and Turrialba are covered in legally protected dense old-growth forest, while the southern flanks are dominated by pasture land and agriculture. Turrialba rises 3,300 m above its base and has been active for at least 75,000 years with mostly fumarolic activity since its last major eruption in 1866 (Alvarado et al., 2006). It has experienced renewed activity beginning in 2010, and its current activity is primarily characterized by a near-constant volcanic degassing plume, episodic minor ash emissions, and fumarolic discharges at two of the summit craters, as well as significant diffuse and fumarolic gas emissions across its flanks, focused along fault systems (Martini et al., 2010). Turrialba's $CO_2$ emissions in areas proximal to the crater were calculated at 113 ± 46 tons/d (Epiard et al., 2017). The Falla Ariete, a major regional fault, runs northeast-southwest through the southern part of Turrialba's central edifice and is one of the largest areas of diffuse $CO_2$ emissions on Turrialba (Epiard et al., 2017; Rizzo et al., 2016). Atmospheric $CO_2$ has an average $\delta^{13}C$ value of -9.2 ‰ at Turrialba, and the volcanic $CO_2$ released at the Ariete Fault has significantly heavier $\delta^{13}C$ values clustered around -3.4 ‰ (Malowany et al., 2017).

Irazú has been active for at least 3,000 years, and had minor phreato-magmatic eruptions in 1963 and a single hydrothermal eruption in 1994. Currently, Irazú's activity primarily consists of shallow seismic swarms, fumarolic crater gas emissions, small volcanic landslides, and minor gas emissions on its northern forested flank (Alvarado et al., 2006; Barquero et al., 1995). Diffuse flank emissions represent the vast majority of gas discharge from Irazú, as the main crater releases 3.8 t $d^{-1}$ of $CO_2$ and a small area on the north flank alone releases 15 t $d^{-1}$ (Epiard et al., 2017). Between the two volcanoes, a major erosional depression is partially occupied by extensive dairy farms, and is somewhat less forested.

In this study, we focused on accessible areas between 2,000 and 3,300 m on both volcanoes (Fig. 1). On Irazú, we sampled trees and $CO_2$ fluxes from the summit area to the north, near the approximately north-south striking Rio Sucio fault, crossing into the area dominated by dairy farms on Irazú's lower NE slope. Our sampling locations on Irazú were located along a road from the summit northward down into this low-lying area. On Turrialba, we focused on an area of known strong emissions but intact forests on the SW slope, uphill of the same erosional depression, but cross-cut by the major NE-SW trending active fracture system of the Falla Ariete. We sampled three main areas of the Falla Ariete, each approximately perpendicularly transecting the degassing fault along equal altitude; the upper Ariete fault, the lower Ariete fault, and a small basin directly east of the old Cerro Armado cinder cone on Turrialba's south-western flank. We took samples at irregular intervals depending on the continued availability and specimen maturity of three species present throughout the transect.

All transects are in areas experiencing measurable $CO_2$ enhancements from the Falla Ariete, but not high enough to be in areas generally downwind of the prevailing crater emissions plume (Epiard et al., 2017). We avoided areas that experience ash fall, high volcanic $SO_2$ concentrations, local anthropogenic $CO_2$ from farms, or that were likely to have heavily acidified soil. Excessively high soil $CO_2$ concentrations can acidify soil, leading to negative impacts on ecosystems growing there (McGee and Gerlach, 1998). Because such effects reflect by-products of extreme soil $CO_2$ concentrations rather than direct consequences of elevated $CO_2$ on plants, we avoided areas with $CO_2$ fluxes high enough to possibly cause noticeable $CO_2$-induced soil acidification. Light ash fall on some days likely derived from atmospheric drift, as we were not sampling in areas downwind of the crater. The ash fall did not in any noticeably way affect our samples, as trees showing ash accumulation on their leaves or previous damage were the exception and

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Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


avoided. Altitude, amount of sunlight during measurements, and aspect had no consistent correlations with any of the parameters we measured.

### 2.2 Species studied

Our study focused on three tree species found commonly on Turrialba and Irazú: *Buddleja nitida*, *Alnus acuminata*, and *Oreopanax xalapensis*. *Buddleja. nitida* is a small tree with a typical stem diameter (DBH) ranging from 5 to 40 cm that grows at elevations of 2,000-4,000 m throughout most of Central America (Kappelle et al., 1996; Norman, 2000). The DBH of the individuals we measured ranged from 11.5 to 51.3 cm, with an average of 29.85 cm. It averages 4-15 m in height and grows primarily in early and late secondary forests (Kappelle et al., 1996; Norman, 2000). *Alnus. acuminata* is a nitrogen-fixing pioneer species exotic to the tropics that can survive at elevations from 1,500-3,400 m, although it is most commonly found between 2,000-2,800 m (Weng et al., 2004). The trees we measured had DBH ranging from 14.3 to 112 cm, with an average of 57.14 cm. *Oreopanax. xalapensis* thrives in early and late successional forests, although it can survive in primary forests as well (Kappelle et al., 1996; Quintana-Ascencio et al., 2004). It had the smallest average DBH of the three species, ranging from 6.6 to 40.9 cm, with an average of 22.71 cm.

### 2.3 $CO_2$ concentrations and soil diffuse flux measurements

We used a custom-built soil flux chamber system which contained a LI-COR 840A non-dispersive infrared $CO_2$ sensor (LI-COR Inc., Lincoln NE, USA) to measure soil $CO_2$ flux. A custom-built cylindrical accumulation chamber of defined volume was sealed to the ground and remained connected to the LI-COR sensor. The air within the accumulation chamber was continuously recirculated through the sensor, passing through a particle filter. The sensor was calibrated before deployment and performed within specifications. We recorded cell pressure and temperature, ambient pressure, air temperature, GPS location, time stamps, location description, soil type and cover, wind speed and direction, relative humidity, and slope, aspect, and altitude as ancillary data. In typical operation, each measurement site for flux measurements was validated for leaks (visible in the live data stream display as spikes and breaks in the $CO_2$ concentration slope), and potential external disturbances were avoided (such as vehicle traffic, generators, or breathing animals and humans). Measurements were recorded in triplicate for at least 2 minutes per site. Data reduction was performed using recorded time stamps in the dataset, with conservative time margins to account for sensor response dead time, validated against consistent slope sections of increasing chamber $CO_2$. Fluxes were computed using ancillary pressure and temperature measurements and the geometric chamber constant (chamber volume at inserted depth, tubing volume, and sensor volume). Care was taken to not disturb the soil and overlying litter inside and adjacent to, the chamber.

### 2.4 Leaf function measurements

Chlorophyll fluorescence measurements were conducted on leaves of all three species during the field campaign to obtain information on instantaneous plant stress using an OS30p+ fluorometer (Opti-Sciences Inc., Hudson, NH, USA). Five mature leaves from each individual tree were dark adapted for at least 20 minutes to ensure complete relaxation of the photosystems. After dark adaptation, initial minimal fluorescence was recorded ($F_o$) under conditions where we assume that photosystem II (PSII) was fully reduced. Immediately following the $F_0$ measurement, a 6,000 μmol $m^{-2}$ $s^{-1}$ saturation pulse was delivered from an array of red LEDs at 660 nm to record maximal fluorescence emission ($F_m$), when the reaction centers are assumed to be fully closed. From this, the variable fluorescence was determined as $F_v/F_m = (F_m-F_o)/F_m$. $F_v/F_m$ is a widely used chlorophyll fluorescence variable used to assess the efficiency of PSII and, indirectly, plant stress (Baker and Oxborough, 2004). The five $F_v/F_m$ measurements were averaged to provide a representative value for each individual tree. Some trees had less than five measurements due to the dark adaptation clips slipping off the leaf before measurements could be taken. Ten trees had four measurements, and another six had three measurements

Chlorophyll concentration index (CCI) was measured with a MC-100 Apogee Instruments chlorophyll concentration meter (Apogee Instruments, Inc., Logan, UT, USA). CCI was converted to chlorophyll concentration (μmol $m^{-2}$) with the generic formula derived by Parry et al., 2014. Depending on availability, between three and six leaves were measured for CCI for each tree, and then averaged to provide a single value for each tree. If leaves were not within reach, a branch was pulled down or individual leaves were shot down with a slingshot and collected. Photosynthetically active radiation was measured at each tree with a handheld quantum meter (Apogee Instruments, Logan, UT, USA) (Table S2). Stomatal conductance to water vapor, $g_s$ (mmol $m^{-2}$ $s^{-1}$) was measured between 10:00-14:00 hours using a steady-state porometer (SC-1, Decagon Devices, Inc., Pullman, WA, USA), calibrated before use and read in manual mode. This leaf porometer was rated for humidity<90%, and humidity was sometimes above this limit during our field work. Consequently, we have fewer stomatal conductance measurements than our other data types.

## 2.5 Isotopic analysis

We collected wood cores from 31 individual trees at a 1.5 m height using a 5.15 mm diameter increment borer (JIM GEM, Forestry Suppliers Inc., Jackson, MS, USA). Since no definable tree rings were apparent, we created a fine powder for isotope analysis by drilling holes into dried cores using a dry ceramic drill bit (Dremel) along the outermost 5 cm of wood below the bark. The fine powder (200 mesh, 0.2 – 5 mg) was then mixed and a random sample was used to extract $^{13}C/^{12}C$ ratios (to obtain $\delta^{13}C$ values against the VPDB standard), which we estimated to be representative of roughly the last 2-3 years. Since we only sample the most recent years, no isotopic discrimination against atmospheric $^{13}C$ due to preferential diffusion and carboxylation of $^{12}C$, was conducted. Rather, we assume that $\delta^{13}C$ values are representative of the relative amount of volcanic $CO_2$ vs. atmospheric $CO_2$ sequestered by the tree over the period of growth represented in the sample. $\delta^{13}C$ values were determined by continuous flow dual isotope analysis using a CHNOS Elemental Analyzer and IsoPrime 100 mass spectrometer at the University of California Berkeley Center for Stable Isotope Biogeochemistry. External precision for C isotope determinations is ±0.10 ‰. Ten $\delta^{13}C$ measurements did not have corresponding soil $CO_2$ flux measurements due to the flux measurements being unavailable for the final two days of sampling, and another 5 samples were from trees that showed signs of extreme stress, such as browning leaves or anomalously low fluorescence measurements. Since the purpose of our study was to explore the non-lethal effects of volcanic $CO_2$ on trees, during analysis we excluded all trees that were observed in

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


the field to have significant stress or that were not fully mature. After these exclusions, all remaining tree cores with co-located $CO_2$ flux measurements were from Turrialba.

### 2.6 Sulfur dioxide probability from satellite data

To assess the likelihood of trees having been significantly stressed in the past by volcanic sulfur dioxide ($SO_2$) from the central crater vents, we derived the likelihood of exposure per unit area using satellite data sensitive to $SO_2$ (Fig. 2). The Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER), launched in December 1999 on NASA's Terra satellite, has bands sensitive to $SO_2$ emission in the thermal infrared (TIR), at ~60 m x 60 m spatial resolution. We initially used ASTER Surface Radiance TIR data (AST_09T), using all ASTER observations of the target area over the entirety of the ASTER mission (October 2000 until writing in late 2017). The TIR bands were corrected for downwelling sky irradiance and converted into units of W m$^{-2}$ µm$^{-1}$. For each observation, an absorption product is calculated by subtracting $SO_2$-insensitive from $SO_2$-sensitive bands:

$$S^t = (b_{10} + b_{12}) - 2 \cdot b_{11} \quad (1)$$

Where $S$ is the $SO_2$ index, $t$ is an index representing the time of acquisition, $b_{10}$ is the radiance at band 10 (8.125 - 8.475 µm), $b_{11}$ is the radiance at band 11 (8.475 - 8.825 µm), and $b_{12}$ is the radiance at band 12 (8.925 - 9.275 µm). This is similar to the method of Campion et al., 2010. The granules were then separated into day and night scenes, projected onto a common grid, and then thresholded to $S > 0.1$ W m$^{-2}$ µm$^{-1}$, and converted into a probability. The output is a spatial dataset that describes the probability of an ASTER observation showing an absorption feature above a 0.1 W m$^{-2}$ µm$^{-1}$ threshold across the entirety of the ASTER observations for day or night separately. The number of scenes varies per target, but they tend to be between 200-800 observations in total, over the 17 year time period of satellite observations. However, certain permanent features, such as salt pans, show absorption features in band 11 and therefore have high ratios for the algorithm used. We therefore used a second method that seeks to map transient absorption features. For this method, we subtract the median from each $S^t$, yielding a median deviation stack. By plotting the maximum deviations across all observations, we then get a map of transient absorption features, in our case this is mostly volcanic $SO_2$ plumes, which map out the cumulative position of different plume observations well. To speed up processing, some of the retrieval runs were binned in order to increase the signal-to-noise ratio, since the band difference can be rather noisy.

### 2.7 Modelling the anthropogenic $CO_2$ influence from inventory data

We assessed the likelihood of anthropogenic $CO_2$, enhancements of air from San Jose, Costa Rica's capital and main industrial and population center, influencing our measurements. We used a widely applied Flexible Particle Dispersion Model (Eckhardt et al., 2017; Stohl et al., 1998, 2005; Stohl and Thomson, 1999) in a forward mode (Stohl et al., 2005) to simulate the downwind concentrations of $CO_2$ in the atmosphere (e.g. Belikov et al., 2016), due to inventory-derived fossil fuel (FF) emissions in our study area for the year 2015 (Fig. 2). The National Centers for Environmental Prediction (NCEP) - Climate Forecast System Reanalysis (CFSR) 2.5° horizontal resolution meteorology (Saha et al., 2010b, 2010a), and 1-km Open-Source Date Inventory for Anthropogenic $CO_2$ (ODIAC; Oda and Maksyutov, 2011)

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Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


emissions for 2015 were used to drive the Flexpart model. The $CO_2$ concentrations were generated at a 1 km spatial resolution within three levels of the atmosphere (0-100, 100-300, 300-500 meters) that are possibly relevant to forest canopies in Costa Rica. However, to assess the magnitude of enhancements we only used $CO_2$ concentrations observed within the lowest level of the atmosphere. Validation of the model with direct observations was not required because we were only interested in ensuring that anthropogenic $CO_2$ dispersed upslope from San José was not having a significant effect on our study area. The actual concentration of $CO_2$ and any biogenic influence in the modelled area was irrelevant because the spatial distribution of anthropogenic $CO_2$ was the only factor relevant for this test. 2015 was used as a representative year for simulating the seasonal cycle of $CO_2$ concentrations that would be present in any particular year.

## 3 Results

### 3.1 Volcanic $CO_2$ emissions through the soil

We measured $CO_2$ flux emitted through the soil at 66 points over four days (Fig. 1). The first eight points were on Irazú, and the rest were located near the Ariete Fault on Turrialba. Mean soil $CO_2$ flux values over the entire sampling area varied from 3 to 37 g $m^{-2}$ $day^{-1}$, with an average of 11.6 g $m^{-2}$ $day^{-1}$ and a standard deviation of 6.6 g $m^{-2}$ $day^{-1}$. A 12-bin histogram of mean $CO_2$ flux shows a bimodal right-skewed distribution with a few distinct outliers (Fig. 3). Fluxes were generally larger on Irazú than on Turrialba. This result agrees with previous studies which showed that the north flank of Irazú has areas of extremely high degassing, whereas most of our sampling locations on Turrialba were in areas that had comparatively lower diffuse emissions (Epiard et al., 2017; Stine and Banks, 1991). We used a cumulative probability plot to identify different populations of $CO_2$ fluxes (Fig. 3) (Cardellini et al., 2003; Sinclair, 1974). Our measurements and literature data confirm that ecosystems growing in these locations are consistently exposed to excess volcanic $CO_2$, which may impact chlorophyll fluorescence, chlorophyll concentrations, and stomatal conductance of nearby trees.

We created an inventory-based model of anthropogenic $CO_2$ emissions from the San José urban area, parts of which are less than 15 km from some of our sampling locations (Fig. 2). Our model shows that $CO_2$ emitted from San José is blown west to south-west by prevailing winds. Our study area is directly east of San José, and as such is unaffected by anthropogenic $CO_2$ from San Jose, which is the only major urban area near Turrialba and Irazú. Additionally, we used ASTER data to map probabilities of $SO_2$ across Costa Rica, as a possible confounding factor. The active craters of both Turrialba and Irazú emit measurable amounts of $SO_2$, which is reflected by the high $SO_2$ probabilities derived there (Fig. 2). Our study area is on the flanks of the volcano, where $SO_2$ probability is minimal. Most other volcanoes in Costa Rica emit little to no $SO_2$ on a decadal time scale, shown by the low or non-existent long-term $SO_2$ probabilities over the other volcanoes in Costa Rica (white polygons in Fig. 2).

### 3.2 Tree core isotopes

Bulk wood $\delta^{13}C$ measurements ranged from -24.03 to -28.12 ‰, with most being clustered around -26 ‰ (Fig. 4). A 5-bin histogram of all $\delta^{13}C$ measurements shows a slightly right-skewed unimodal normal distribution, with an average of -26.37 ‰ and a standard deviation of 0.85 ‰. *A. acuminata* and *O. xalapensis* have nearly identical averages (-26.14 and -25.97 ‰, respectively), while *B. nitida* has a noticeably lighter average of -27.02 ‰. As $CO_2$ flux increased, the wood cores contained progressively higher amounts of $^{13}C$ for two of the three species. Tree core $\delta^{13}C$ showed no relationship with stomatal conductance for any species.

### 3.3 Plant function (Fluorescence, Chlorophyll, Stomatal Conductance)

After excluding visibly damaged trees, leaf fluorescence, expressed as Fv/Fm, was very high in most samples. Fv/Fm ranged from 0.75 to 0.89, with most measurements clustering between 0.8 and 0.85 (Fig. 5). The fluorescence data has a left-skewed unimodal distribution. The leaf fluorescence (Fv/Fm) values for *A. acuminata* had a strong positive correlation with soil $CO_2$ flux ($r^2$=0.69, p<.05), while the other two species showed no correlation. No confounding factors measured were correlated with Fv/Fm for any species. In general, *B. nitida* had the highest Fv/Fm values, and *A. acuminata* and *O. xalapensis* had similar values except for a few *O. xalapensis* outliers. Chlorophyll concentration measurements were highly variable, ranging from 260 to 922 μmol $m^{-2}$, with an average of 558 μmol $m^{-2}$ and a standard deviation of 162 μmol $m^{-2}$ (Fig. 6). Chlorophyll concentration had a complicated right-skewed bimodal distribution, likely due to the noticeably different averages for each species. *A. acuminata* and *O. xalapensis* both displayed weak correlations between chlorophyll concentration and soil $CO_2$ flux ($r^2$=0.38 and $r^2$=0.28, respectively), but their trendlines were found to be almost perpendicular (Fig. 6). As $CO_2$ flux increased, *A. acuminata* showed a slight increase in chlorophyll concentration, while *O. xalapensis* had significant decreases in chlorophyll concentration. *B. nitida* individuals growing on steeper slopes had significantly lower chlorophyll concentration measurements ($r^2$=0.42, p<.05) than those on gentler slopes, a trend not expressed by either of the other two species ($r^2$=0.01 for both), demonstrating no significant influence of slope across the majority of samples. Stomatal conductance ranged from 83.5 to 361 mmol $H_20$ $m^{-2}$ $s^{-1}$, with an average of 214 mmol $H_20$ $m^{-2}$ $s^{-1}$ and a standard deviation of 73.5 mmol $H_20$ $m^{-2}$ $s^{-1}$. Distribution was bimodal, with peaks around 150 and 350 mmol $H_20$ $m^{-2}$ $s^{-1}$. *A. acuminata* had a moderate positive correlation ($r^2$=0.51) with soil $CO_2$ flux, but it was not statistically significant due to a lack of data points (Fig. 7) – however this is a result consistent with the observed higher chlorophyll concentration (Fig. 6). The other two species displayed no correlation with soil $CO_2$ flux. *B. nitida* had a moderate negative correlation ($r^2$=0.61) with slope, similar to its correlation between chlorophyll concentration and slope.

## 4 Discussion

### 4.1 Long-term plant uptake of volcanic $CO_2$

Turrialba and Irazú continuously emit $CO_2$ through their vegetated flanks, but prior to this study it was unknown if the trees growing there were utilizing this additional isotopically heavy volcanic $CO_2$. All tree cores with corresponding $CO_2$ flux measurements were from areas proximal to the Ariete Fault on Turrialba, where atmospheric and volcanic $\delta^{13}C$ have significantly different values (-9.2 and -3.4 ‰, respectively) (Malowany et al., 2017). If the trees assimilate volcanic $CO_2$ through their stomata, then we would expect wood $\delta^{13}C$ to trend towards heavier values as diffuse volcanic $CO_2$ flux increases. After excluding damaged samples and stressed trees, $\delta^{13}C$ was strongly correlated with soil $CO_2$ flux for both *B. nitida* and *O. xalapensis* **(**Fig. 4**)**. *A. acuminata* did not have a statistically significant correlation between soil $CO_2$ flux and $\delta^{13}C$, likely because it had the fewest data points and a minimal range of $CO_2$ and $\delta^{13}C$ values. The strong positive correlations between $CO_2$ flux and increasingly heavy $\delta^{13}C$ values suggest that the trees have consistently photosynthesized with isotopically heavy excess volcanic $CO_2$ over the last few years and are therefore growing in $eCO_2$ conditions. Assuming that all variations in $\delta^{13}C$ are caused by the incorporation of heavy volcanic $CO_2$, we can calculate the average concentration of the mean volcanic excess $CO_2$ in the air the plants are exposed to, with a mass balance equation (Eq. 2):

$$C_v = \frac{C_b(\delta_b - \delta_m)}{(\delta_m - \delta_v)} \quad (2)$$

where $C_v$ is the mean volcanic excess component of the $CO_2$ concentration in air, $C_b$ is the atmospheric "background" (i.e., non-volcanic) $CO_2$ concentration, $\delta_b$ is atmospheric $\delta^{13}C$, $\delta_m$ is the difference between background wood $\delta^{13}C$ and another wood $\delta^{13}C$ measurement subtracted from atmospheric $\delta^{13}C$, and $\delta_v$ is $\delta^{13}C$ of the volcanic $CO_2$. Background wood $\delta^{13}C$ is the value of the point for each species with the lowest $CO_2$ flux (Fig. 4), and the other wood $\delta^{13}C$ measurement is any other point from the same species. Values for $\delta_v$ and $\delta_b$ are taken from Malowany et al. 2017, and $C_b$ is assumed to be 400 ppm. For the tree core with the highest measured $CO_2$ flux for *O. xalapensis*, this equation yields a mean excess volcanic $CO_2$ concentration of 155 ppm, bringing the combined mean atmospheric (including volcanic) $CO_2$ concentration these trees are exposed to, to ~555 ppm. For *B. nitida* this equation yields 190 ppm of mean excess volcanic $CO_2$ at the highest flux location, for a combined total mean of ~590 ppm $CO_2$. These calculations show that trees in our study area have been consistently exposed to significantly elevated concentrations of $CO_2$, reflective of predicted atmospheric conditions 60-80 years into the future, assuming a 2 ppm $y^{-1}$ mean atmospheric growth rate (Peters et al., 2007), Additional measurements of tree core $\delta^{13}C$ and associated soil $CO_2$ fluxes would help corroborate our observations, which were based on a limited number of data points. Tree ring $^{14}C$ content in volcanically active areas has been linked to variations in volcanic $CO_2$ emissions, and comparing patterns of $\delta^{13}C$ to $^{14}C$ measurements for the same wood samples could provide additional confirmation of this finding (Evans et al., 2010; Lefevre et al., 2017; Lewicki et al., 2014).

Our data demonstrate that $CO_2$ fluxes through the soil are a representative relative measure for eCO2 exposure of overlying tree canopies. Forest canopy exposure to volcanic $CO_2$ will vary over time, as will volcanic $eCO_2$, once emitted through the soil into the sub-canopy atmosphere, the gas experiences highly variable thermal and wind disturbances which significantly affect dispersion of $CO_2$ on minute to minute, diurnal, and seasonal timescales (Staebler and Fitzjarrald, 2004; Thomas, 2011). These processes cause in-canopy measurements of $CO_2$ concentration to be highly variable, making instantaneous concentration measurements in a single field campaign not representative of long-term relative magnitudes of $CO_2$ exposure. Soil $CO_2$ fluxes are less tied to atmospheric conditions, and are primarily externally modulated by rainfall which increases soil moisture and therefore lowers the soil's gas permeability (Camarda et al., 2006; Viveiros et al., 2009). These fluxes can also be affected by variations in barometric pressure, but both of these factors are easily measurable and therefore can be factored in when conducting field work (Viveiros et al., 2009). Assuming the avoidance of significant rainfall and pressure spikes during sampling (measurements were conducted in the dry season and no heavy rains or significant meteorological variations in pressure occurred during field work), measuring the input of $CO_2$ into the sub-canopy atmosphere as soil $CO_2$ fluxes is therefore expected to better represent long-term input and exposure of tree canopies to $eCO_2$ than direct instantaneous measurements of sub-canopy $CO_2$ concentration. Previous studies at Turrialba have shown that local volcanic $CO_2$ flux is relatively constant on monthly to yearly timescales (de Moor et al., 2016). Therefore, current soil $CO_2$ fluxes should give relatively accurate estimates of $CO_2$ exposure over time. This paper corroborates that expectation by demonstrating strong correlations between volcanically enhanced soil $CO_2$ emissions with stable carbon isotope signals of these emissions documented in the trees' xylem.

A study at the previously mentioned Mammoth Mountain tree kill area examined the connection between $\delta^{13}C$ and volcanic $CO_2$ fluxes, but focused on the difference between trees killed by extreme $CO_2$ conditions and those that were still alive (Biondi and Fessenden, 1999). They concluded that the changes in $\delta^{13}C$ that they observed were due to extreme concentrations of $CO_2$ (soil $CO_2$ concentrations of up to 100%) impairing the functioning of root systems, leading to closure of stomata and water stress (Biondi and Fessenden, 1999). $CO_2$ does not inherently harm trees, but the extreme $CO_2$ concentrations (up to 100% soil $CO_2$) at the Mammoth Mountain area caused major soil acidification, which led to the tree kill (McGee and Gerlach, 1998). We have evidence that those processes are not affecting our $\delta^{13}C$ measurements, and that variations in our $\delta^{13}C$ measurements are more likely to be caused by direct photosynthetic incorporation of heavy volcanic $CO_2$. Our $\delta^{13}C$ measurements have no statistically significant correlation with stomatal conductance, which suggests that our heavier $\delta^{13}C$ measurements are not linked to stomatal closure. Additionally, none of the trees displayed obvious signs of stress, from water or other factors, as indicated by their high fluorescence and chlorophyll concentration values and lack of visible indicators of stress; specifically, our values of Fv/Fm ~0.8 indicate that PSII was operating efficiently in most of the trees we measured (Baker and Oxborough, 2004). The Mammoth Mountain tree kill areas have several orders of magnitude higher $CO_2$ fluxes (well over 10,000 g $m^{-2}$ $day^{-1}$) than the areas we sampled (up to 38 g $m^{-2}$ $day^{-1}$), making it much more likely that stress from soil acidification would be causing stomatal closure and affecting wood $\delta^{13}C$ measurements at Mammoth Mountain (Biondi and Fessenden, 1999; McGee and Gerlach, 1998; Werner et al., 2014). In contrast, most of the diffuse degassing at Turrialba does not lead to soil acidification or pore space saturation, as is evident in our own and others' field data (e.g., Epiard et al 2017). Thus, changes in our $\delta^{13}C$ values are best explained by direct photosynthetic incorporation of isotopically heavy volcanic $CO_2$. To the best of our knowledge, this is the first time that a direct correlation between volcanic soil $CO_2$ flux and wood $\delta^{13}C$ has been documented. Future studies should explore this correlation further, as our findings are based on a limited sample size.

### 4.2 Short-term species response to $eCO_2$

Short-term plant functional responses at the leaf level to elevated $CO_2$ were highly species-dependent. *B. nitida* had no statistically significant functional responses to soil $CO_2$ flux and *O. xalapensis* only had a weak negative correlation between soil $CO_2$ flux and chlorophyll concentration **(**Fig. 6.**)**. *A. acuminata*, a nitrogen fixing species, was the only species with a consistent and positive functional response to elevated $CO_2$, displaying a strong positive correlation with fluorescence and a weak positive correlation with chlorophyll concentration and stomatal conductance (Figs. 5-7). The lack of response in *B. nitida* and *O. xalapensis* could be due to nitrogen limitation, a factor that would not affect *A. acuminata* due to its nitrogen fixing capability. Previous studies have found that nitrogen availability strongly

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


controls plant responses to $eCO_2$ in a variety of ecosystems, including grasslands and temperate forests (Garten et al., 2011; Hebeisen et al., 1997; Lüscher et al., 2000; Norby et al., 2010). Nitrogen limitation has been posited to be an important factor in tropical montane cloud forests, and may be contributing to the lack of responses in *B. nitida* and *O. xalapensis* (Tanner et al., 1998). Due to the exploratory nature of our study, we do not have a large enough dataset to conclude that the nitrogen fixing capability of species like *A. acuminata* is the cause for its positive response to volcanically elevated $CO_2$, as has been speculated before (Schwandner et al., 2004), but it is a possible correlation that deserves further investigation. Future studies should explore this correlation further to determine the extent of nitrogen limitation at Turrialba and Irazú and its impacts on plant responses to $eCO_2$.

### 4.3 Trees as volcanic $CO_2$ sensors

Beyond the potential to advance our understanding of tropical forest ecosystem responses to elevated $CO_2$, our results have importance to the volcanological community. If the link between $\delta^{13}C$ and volcanic $CO_2$ is as strong as our results suggest, it could be used to establish temporal histories of volcanic $CO_2$ emissions at previously unmonitored volcanoes, and fill observational gaps in volcanic activity histories. The data presented in this paper represent approximately the past 2-3 years of growth, but taking $\delta^{13}C$ measurements at regular intervals on the remainder of a tree core should provide a history of temporal variations in volcanic $CO_2$ emissions. This has significant volcanological applications, as it would provide a powerful new tool to study volcanic $CO_2$ emissions in a temporal context. Variations in tree ring $^{14}C$ content have been shown to correlate well with variations in volcanic $CO_2$ flux, but $^{14}C$ is relatively expensive and a limited number of labs are capable of making these measurements (Evans et al., 2010; Lefevre et al., 2017; Lewicki and Hilley, 2014). $\delta^{13}C$ measurements are more accessible, allowing for substantially more data to be acquired compared to $^{14}C$. Comparing wood $\delta^{13}C$ records of past $CO_2$ fluxes to historical records of eruptions could help establish patterns of $CO_2$ fluxes at volcanoes that have minimal $CO_2$ flux datasets available. These patterns of $CO_2$ flux could then be compared to current volcanic $CO_2$ flux data and historical eruption records to fill gaps in the historical and monitoring records – a boon for volcano researchers and observatories using pattern recognition to improve eruption prediction capabilities (Newhall et al., 2017; Pyle, 2017; Sparks et al., 2012). Independent validation, and calibration by wood core dendrochronology via $^{14}C$, tree rings, or chemical event tracers like sulfur spikes, could significantly advance the concept of using wood carbon as archives of past degassing activity. Furthermore, knowledge of short-term real-time response of leaves to variations in volcanic flank $CO_2$, which is more likely to represent deeper processes inside volcanoes than crater-area degassing (Camarda et al., 2012), may permit the use of trees as sensors of transient changes in volcanic degassing indicative of volcanic reactivation and deep magma movement possibly leading up to eruptions (Camarda et al., 2012; Pieri et al., 2016; Schwandner et al., 2017; Shinohara et al., 2008; Werner et al., 2013).

### 4.4 Lessons Learned for Future Studies

This exploratory study reveals significant new potential for future studies to utilize the volcanically enhanced $CO_2$ emissions approach to study tropical ecosystem responses to $eCO_2$. These two Costa Rican volcanoes, as well as several other volcanoes in the country, have large areas of relatively undisturbed old-growth forest on their broad

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


flanks, making them ideal study areas for examining responses of ecosystems to $eCO_2$. However, there are several challenges future studies should take into consideration if attempting to expand upon this preliminary study. Given the enormous tropical species diversity and the need to control for confounding factors, large datasets will be needed to answer these questions conclusively. Unfortunately, field data can be difficult to acquire in these environments as the terrain is rugged and can be challenging to work in. A remote sensing approach using airborne measurements, combined with targeted representative ground campaign field work for validation, could provide sufficiently large data sets to represent species diversity and conditions in conjunction with ground based measurements. Many of the datatypes that would be useful for this type of study can be acquired from airborne platforms, and remote sensing instruments can quickly produce the massive datasets that would be required to provide more comprehensive answers to these questions (Cawse-Nicholson et al., 2018). There are six other forested volcanoes in Costa Rica which are actively degassing $CO_2$ through their flanks (Epiard et al., 2017; Liegler, 2016; Melián et al., 2007; de Moor et al., 2016; Williams-Jones, 1997; Williams-Jones et al., 2000), that would also be viable for this type of study (see polygons in Fig. 2), and datasets from those volcanoes would be helpful as they would provide a wider range of altitudes, precipitation levels, temperatures, and other environmental factors that would help isolate the effects of $eCO_2$.

## 5 Conclusions

We identified multiple areas of dense old-growth tropical forest on two Costa Rican active volcanoes that are consistently and continuously exposed to volcanically-elevated levels of atmospheric $CO_2$, diffusively emitted through soils into overlying forests. These isotopically heavy excess volcanic $CO_2$ emissions are well correlated with increases in heavy carbon signatures in wood cores from two species of tropical trees, suggesting long-term incorporation of enhanced levels of volcanically emitted $CO_2$ into biomass. Confounding factors that are known to influence $\delta^{13}C$ values in wood appear not to have affected our measurements, indicating that the heavier wood isotope values are most likely caused by photosynthetic incorporation of volcanic excess $CO_2$. One of the three species studied (*A. acuminata*) has consistent positive correlations between instantaneous plant function measurements and diffuse $CO_2$ flux measurements, indicating that short-term variations in elevated $CO_2$ emissions may measurably affect trees growing in areas of diffuse volcanic emissions. These observations reveal significant potential for future studies to use these areas of naturally elevated $CO_2$ to study ecosystem responses to elevated $CO_2$, and to use trees as sensors of changing degassing behavior of volcanic flanks, indicative of deep magmatic processes.

*Data availability.* Data can be found in Table S1 and Table S2 in the supplement or can be requested from Florian Schwandner (Florian.Schwandner@jpl.nasa.gov).

*Author contributions.* FMS and JBF designed the study, and RRB, FMS, JBF, and ED conducted the field work and collected all samples and data with some of the equipment borrowed from GN, who helped interpret the results. TSM processed the samples for analysis. JPL conducted the $SO_2$ analysis, wrote the related methods subsection, and helped interpret the results. VY modelled the anthropogenic $CO_2$ emissions, wrote the related methods subsection, and helped

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


Biogeosciences Discussions

interpret the results. CAF created the combined figure showing the $CO_2$ and $SO_2$ results and assisted in writing the manuscript. RRB wrote the publication, with contributions from all co-authors.

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

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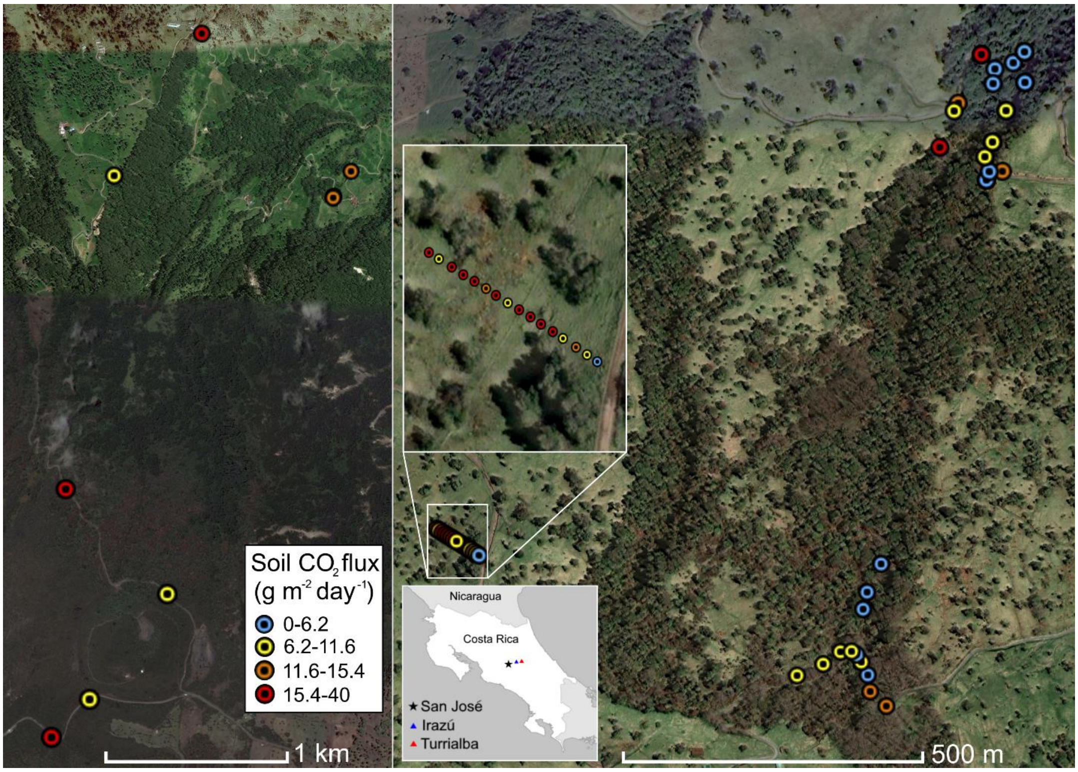


**Fig. 1: Overview of measurement locations in two old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú. Distribution of mean soil $CO_2$ flux across north flank of Irazú (left) and south flank of Turrialba (right). Colors of dots correspond to flux populations (see Fig. 3).**

684

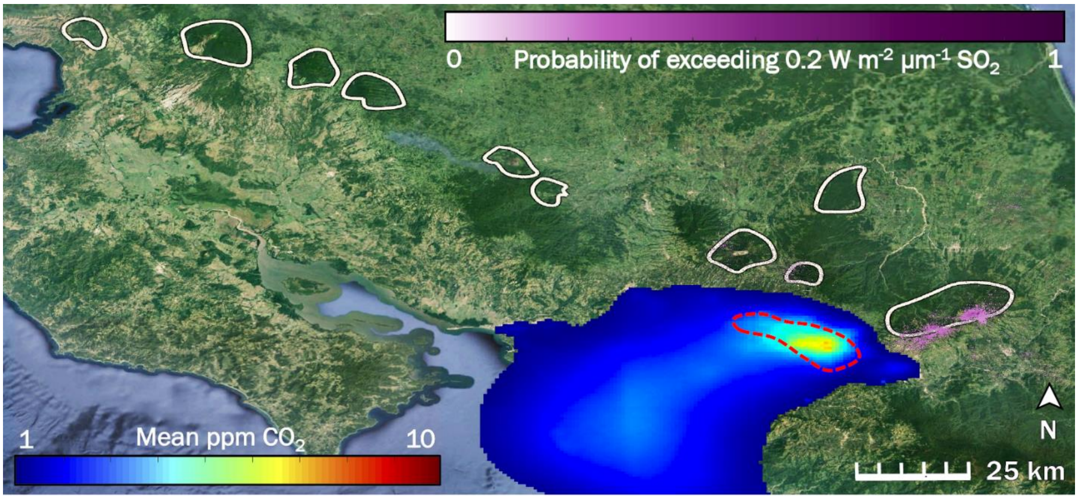


**Fig. 2: The influence of two potentially confounding gases on our study area (right hand white polygon) in Costa Rica is low to non-existent: anthropogenic $CO_2$ from San José (blue to red color scale), and volcanic $SO_2$ (purple color scale). White polygons are drawn around locations of the forested active volcanic edifices in Costa Rica. The dashed red line indicates the rough border of the San José urban area. Prevailing winds throughout the year consistently blow all anthropogenic $CO_2$ away from our study area and from all other white polygons.**

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


Biogeosciences
Discussions

685
686
687

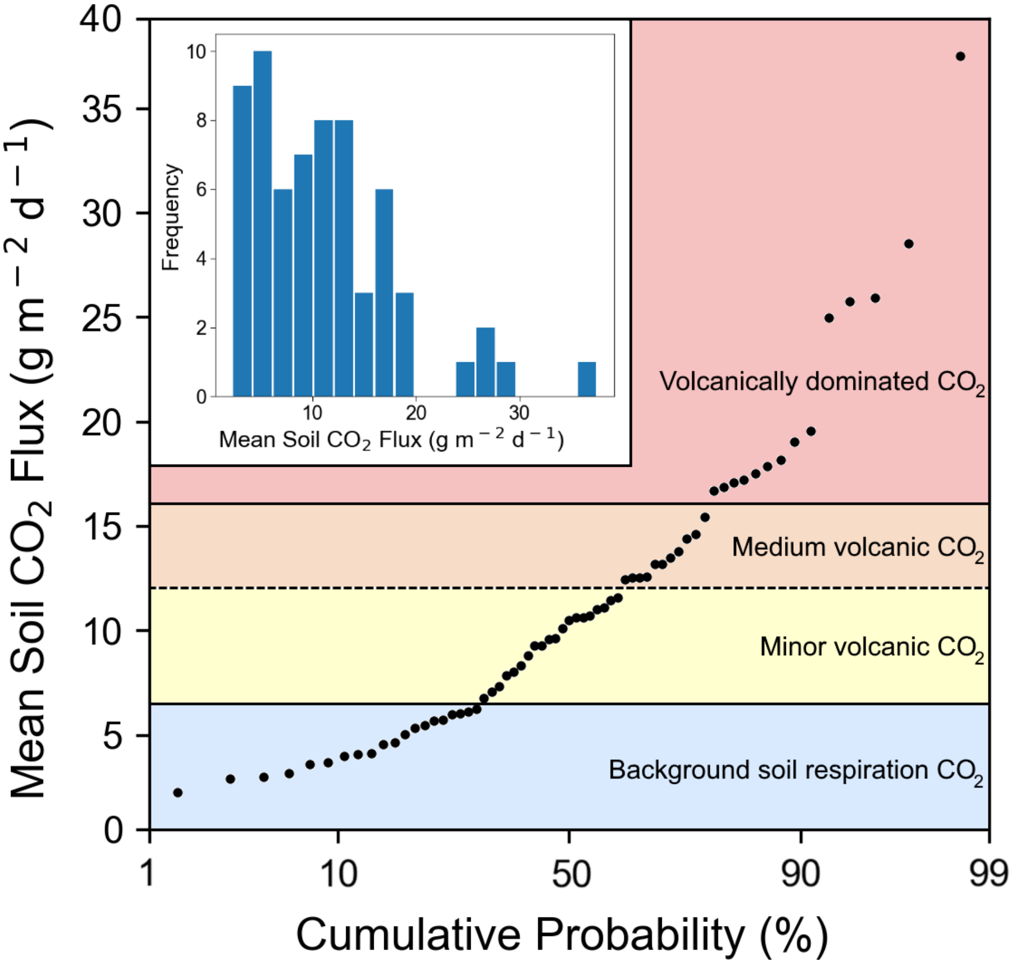


**Fig 3: Soil $CO_2$ flux into the sub-canopy air of forests on the Turrialba-Irazú volcanic complex is pervasively and significantly influenced by a deep volcanic gas source. At least four different overlapping populations of soil $CO_2$ flux were identified, using a cumulative probability plot, where inflection points indicate population boundaries (Sinclair 1974). 69% of sampling locations (45 total) are exposed to varying degrees of volcanically derived elevated $CO_2$. Populations are color-coded based on the same color scale as Fig. 1.**

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


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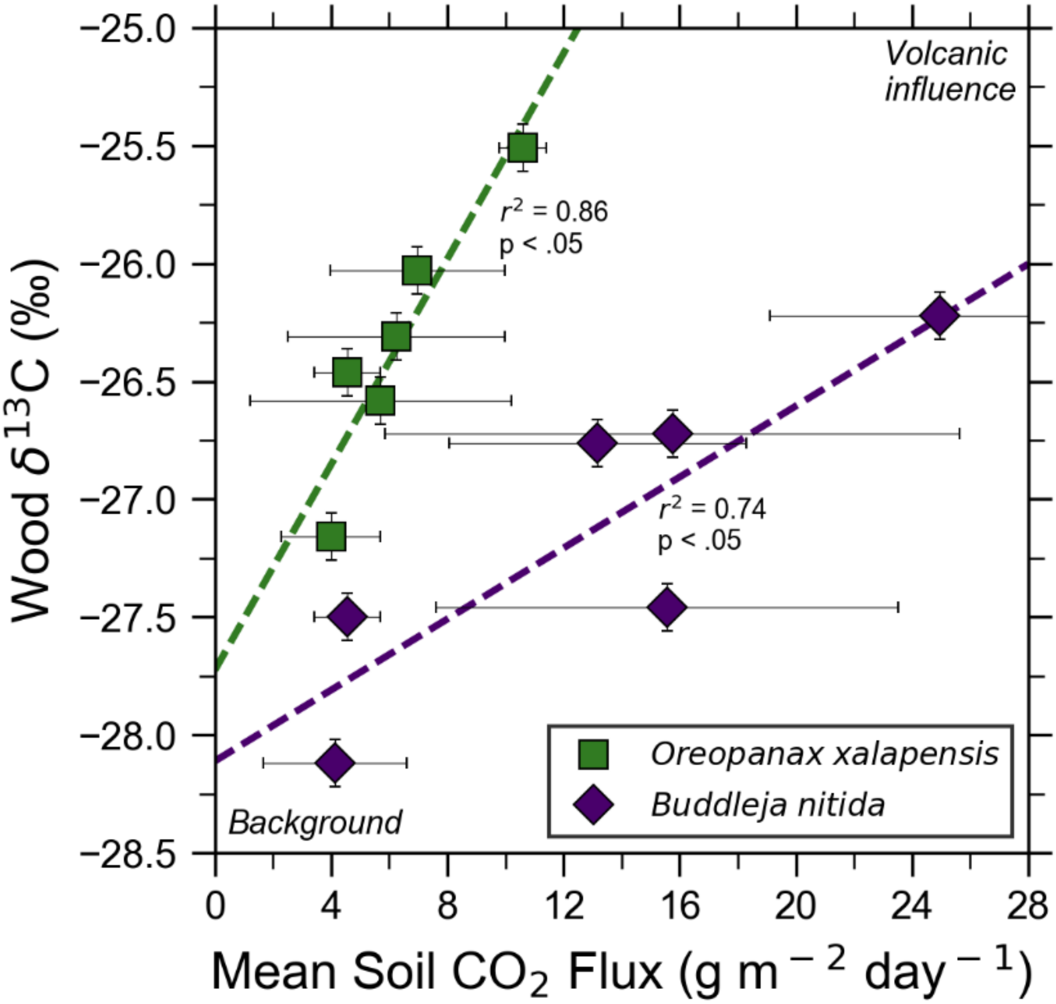


**Fig 4: Bulk wood $\delta^{13}C$ of trees on Costa Rica's Turrialba volcano shows strong correlations with increasing volcanic $CO_2$ flux for two species, *O. xalapensis* and *B. nitida*, indicating long-term photosynthetic incorporation of isotopically heavy volcanic $CO_2$. Stable carbon isotope ratio ($\delta^{13}C$) of wood cores are plotted against soil $CO_2$ flux measured immediately adjacent to the tree that the core sample was taken from. Background and volcanic influence labels apply to both axes – higher $CO_2$ flux and heavier (less negative) $\delta^{13}C$ values are both characteristic of volcanic $CO_2$ emissions.**

Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-100
Manuscript under review for journal Biogeosciences
Discussion started: 5 March 2018


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691

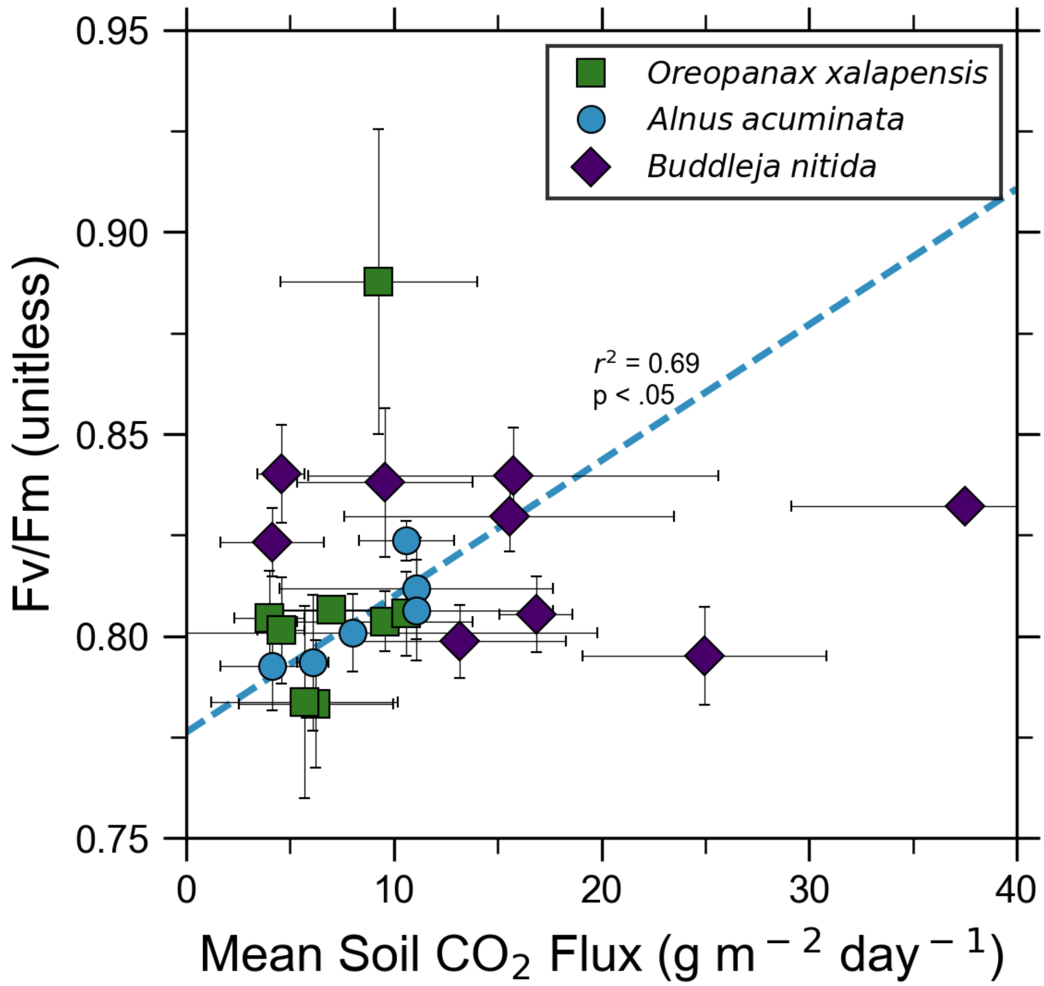
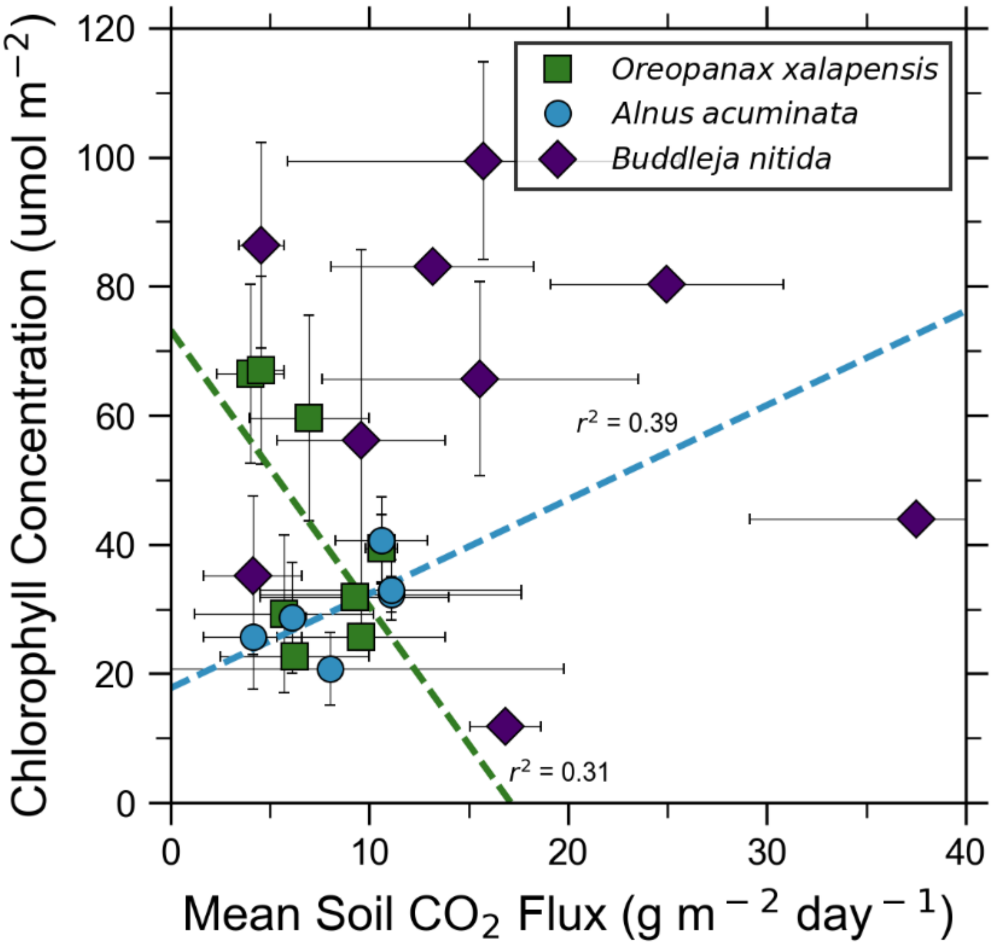



**Fig. 5: Photosynthetic activity of some tree species in old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú, may show short-term response to volcanically elevated $CO_2$. Leaf fluorescence (Fv/Fm) and soil $CO_2$ flux were strongly correlated for *A. acuminata*, but not for other species.**

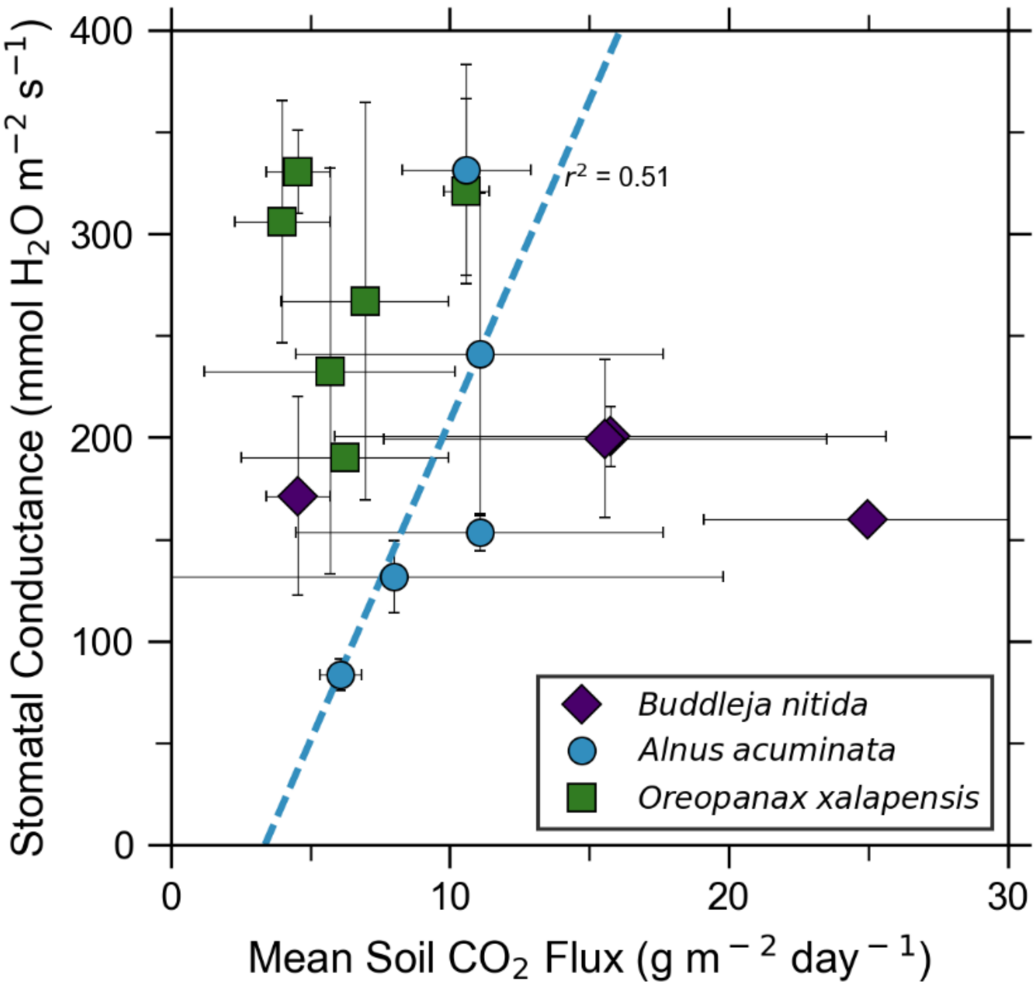



692

**Fig. 6: Some tree species in old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú, may express their short-term response to volcanically elevated $CO_2$ by producing more chlorophyll. A species that showed strong short-term response (*A. Acuminata*, Fig. 5) also shows a positive correlation between chlorophyll concentration and mean soil $CO_2$ flux.**

693

694




695

**Fig. 7: Leaf stomatal conductance of a tree species that strongly responds to volcanically elevated $CO_2$ (Figs. 5, 6) has positive correlations with volcanic $CO_2$ flux, consistent with increased gas-exchange.**

696