Pasadena, CA November 1, 2018

**Re:** bg-2018-100, “Plant responses to volcanically-elevated CO2 in two Costa Rican forests”, Revision 2

Dear Dr Gillikin, Associate Editor,

We here submit our revised manuscript, “**Plant responses to volcanically-elevated CO2 in two Costa Rican forests**”.

We thank you for the editorial handling of our paper, and appreciate the thoughtful and helpful reviews by the two anonymous referees and by yourself. We really appreciate your in-depth consideration of our arguments, and especially your help as an expert as well, which helped in improving this manuscript.

The reviewers highlighted the utility and great potential of using elevated $CO_2$ from volcanoes to understand long-term changes on ecosystems and plant physiology. Following the last communication with you, we made careful revisions, to address all comments and suggestions appropriately. This document is now labeled “revision 2”, and all changes are tracked relative to the original submission, not revision 1, for a comprehensive view on the substantial changes we made to improve the manuscript.

If you have any questions or need further information, please do not hesitate to contact us. Thank you for considering our manuscript for publication in *Biogeosciences*.

On behalf of the co-authors,

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# Detailed Author Replies to:

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

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**REV2 (2018-11-01)**

**Structure of this document:**

Referee and editor comments are answered by the authors in the sequence they appear in the manuscript, structured each as follows: (1) comments from referees, (2) author's response, and (3) author's changes in manuscript. [C1-C5]… page references to the interactive discussion documents refer to the author’s responses documents (posted online at https://www.biogeosciences-discuss.net/bg-2018-100/ ), which quote the concerns and suggestions raised by the reviewers and the editor, as well as the author’s responses. We added further clarification as necessary, since this revision followed suggestions and discussion with the editor after the response period.

**Changes made independently of the reviewer’s & editor’s comments:**

Minor style or spelling adjustments (e.g., consistency of capitalization of “Ariete fault”), and one author affiliation correction, are tracked in the marked-up version submitted together with this revision.

**AUTHOR – General Response to Referee #1 (SC1):**

We thank the reviewer for highlighting the utility and great potential of using elevated $CO_2$ from volcanoes to understand long-term changes on ecosystems. We note that the primary criticism in this study raised by the reviewer is how we analysed the wood core isotopes with respect to the time dimension. We agree that this aspect needed further work. The exact growth chronology was not central to our primary results, so we now reference a range of growth rates from the literature for comparison (Sect. 2.5). We also added substantial discussion of the issue of time by adding a section on “time constraints” (now section 4.3). We address major points in that write-up in Sect. 4.3, and added DBH information in the methods.

Furthermore, we note that we provide growth rate ranges for the same trees and type of environments, giving an upper and lower bound in the expected range, which shows these samples represent similar time frames during the *continuous* exposure to excess volcanic CO2 over the lifetimes of the trees sampled. Due to the *continuous* nature of the volcanic CO2 enhancement, we are not investigating a transient event in time, but spatial variability in excess CO2 availability. We also note that the excess volcanic CO2 through local fault-bound gas seeps provides continuous exposure to all sampled trees over time scales much greater than the lifetimes of individual trees. This is all reflected in the revision text now.

**AUTHOR – General Response to Referee #2 (SC2):**

We thank the reviewer for highlighting the attractiveness of using volcanically elevated CO2 as an extension of FACE experiments, particularly for assessment of long-term changes in tropical ecosystems. We note that the primary criticism in this study raised by the reviewer echoes that of the other reviewer in our analysis of the wood core isotopes with respect to the time dimension. We agree that this aspect needed further clarification as written. The exact growth chronology was not central to our primary results, so we now reference a range of growth rates from the literature for comparison. We also note that the other major comment of the reviewer was the suggestion to use 14C for the analysis. We agree with the reviewer, though the expense was outside the scope of this investigation and the described 14C deficit well-documented in the literature (see Sect. 4.3) makes dating in such environments by 14C not a suitable method. However, we agree that future studies should expand the scope of this study. Due to the spatial and independent nature of the 13C vs CO2 correlation, the time dimension becomes less important though we agree it will have to be addressed better in future studies.

**AUTHOR –Response to Editor**

Please comment on the reviewer's critiques and add discussion to your manuscript regarding the issue of time constraint on your samples pointed out by both reviewers.

How can we be certain that your samples average similar time periods? How can we know if the trees grow faster or slower in these different environments and you are merely time averaging different periods with different atmospheric CO2 d13C values and/or WUE? The ~2 per mil range you see in your samples has been recorded within the stem of a single tree in both tropical and temperate environments, so your results might be explained from time averaging different periods (See Helle & Schleser 2004 Plant Cell and Environment 27 367–380; and Verheyden et al. 2004 Plant Cell and Environment 27 1525–1536). I suggest adding an entire new section to the discussion about the issue of time constraint of your samples - one argument you could use is that one would expect growth rate to correlate with DBH (larger trees typically grow slower) and there is no correlation between d13C and DBH. But this still does not completely rule out variations in growth and thus time. I would also add a note that future studies should do high resolution analyses (see previously noted refs for example).

1. In the ms you note that soil type was recorded, but I don't see this anywhere - could soil type play a role in WUE and influence your data?
2. The data are certainly interesting, but are not perfect. Overall you need to tone down the confidence of your conclusions and open the possibility of the time time averaging issue discussed above (as well as the other issues such as WUE differences or below/above canopy crowns).
3. Without real time constraint on your samples, you cannot be certain about time averaging, and this uncertainty needs to be reflected in the ms.
4. Discussing the limitations of your data will make this a more valuable contribution. I look forward to seeing your revised ms.

**AUTHOR reply:** We thank the editor again for his very thorough and constructive review and suggestions. We believe we addressed all of the editor's comments. We agree with the editor that the data in our study are "*certainly interesting, but are not perfect*" – it is an exploratory study, though at a very intriguing and underexplored interface between geosciences and and biosciences. We emphasize again that due to the completely independent nature of the naturally isotopically heavy volcanic excess CO2 fluxes, the spatial correlation with the co-located d13CO2 data in the xylem of the sampled trees is highly compelling. This study will hopefully point the way to future, more thorough studies that will enable a more precise distinction between the volcanic excess d13CO2 signal and variations in xylem d13C due to confounding factors.

**1.** Regarding the question of soil type: we reviewed our field notes and they are not of sufficient detail and completion to warrant inclusion, so we removed mention of it from the manuscript.

**2.** We blunted our previously too bold and confident conclusions throughout the text and the conclusions, specifically. We discuss WUE and time averaging in the newly added section 4.3 "Time constraints". We additionally address canopy height differences in additional text in Sect. 4.1.

**3.** We added blunting language and a better constraint on uncertainty in the conclusions and several points of the manuscript.

**4.** We believe that the blunted language and the more thorough discussion on time constraints (Sect. 4.3) help put this study in the right context.

**REFEREE #1 (AC1) Comment [C1-C2]:** "*In this paper, the authors investigate the potential use of tree wood carbon stable isotopes as proxies for elevated CO2 exposure in a volcanic environment. The approach has a great potential for understanding the effect of elevated CO2 on plant's physiology. This study, however, suffers from high uncertainty in the methods applied to analyze the 13C from the tree core, There is no clear chronological constrain for tree growth of the time frame (presented here as the 3 growth years) and thereby on the resolution discussed in the analyses. Below are detailed comments. It is never clear how the tree 13C data match the resolution for the soil CO2 flux (as presented in Figure). The methods and results need more details in order to contextualize the implications of the documented elevated CO2 signature*."

**AUTHOR reply:** Establishing quantitative growth rates for the trees studied was outside the scope of this preliminary study but would be very helpful for future studies attempting to use our methods. For comparison, we provide references to a range of analogous growth rates. We will clarify the methods for measurements of CO2 flux and 13C in the revised manuscript. Soil CO2 flux was measured with an accumulation chamber near the base of the tree (generally within 5 meters, terrain permitting) at three different points and then averaged to provide a single CO2 flux value to compare to the 13C measurement of the corresponding tree sample. This technique is intended to provide a simple relative way to compare the CO2 exposure of different trees, as a tree with high CO2 flux near its base should experience consistently higher CO2 concentrations than a tree with lower CO2 flux.

**AUTHOR's changes in revised manuscript:**

For CO2 and 13C experimental methods, we added wording at the beginning of sections 2.3 and in the supplementary material (incl. a new supplementary figure, S2), to clarify our sampling strategy and provide contextual information of these types of emissions.

For analogous growth rates, we added wording and references in section 2.5. We significantly expanded and re-wrote the methods section for context, and added clarifying language throughout the manuscript, including an added section on time constraints, to address the reviewer's comments. However, we also note the clear limitation of using 14C for dating of these cores due to the 14C deficiency in the volcanic excess CO2.

**REFEREE #2 (AC2) Comment [C1-C5]:** "*This paper tries to use volcanically elevated CO2 as a substitute for artificially added CO2 gas in FACE experiments. FACE experiments are expensive, because it uses CO2 from gas cylinders to elevate atmospheric CO2 concentrations in the tree canopy. The paper also explores the possibility of using wood carbon-13 isotope to reconstruct past volcanic activity. These ideas seem attractive but unfortunately this paper suffers from serious flaws in the methods applied to draw their conclusions, as pointed out below. Authors have to deal with issues before publication can be considered.*"

**AUTHOR reply:** We thank the reviewer for noting the scientific contribution of using volcanically elevated CO2 as an analogue to FACE experiments. We respond to the two major comments below."

**REFEREE #2 (AC2) Comment [C1-C5]: Major concern #1:** "*Major concerns: 1) Growth rates of tropical trees can be very different and I do not understand why authors think the wood from the outermost 5cm represents recent growth of 2-3 years. As reviewer #1 suggests, perhaps authors should have tried to analyze 13C of wood in a chronological way. Growth rates of tropical trees, as far as I know, can range from 0.6 mm per year (Kurokawa et al 2003) to 100 mm per year (fast-growing Falcata tree (Paraserianthes falcataria), for example). Which means radial growth of 5cm may represent growth increment from less than 1 year to 83 years. Over the past 83 years, influence of anthropogenic CO2 on wood d13C (Suess effect) can be as large as 4 permil (McCarrol & Loader 2004) and the Suess effect can have variable influence on wood d13C. Kurokawa et al. The age of tropical rain-forest canopy species, Borneo ironwood (Eusideroxylon zwageri), determined by 14C dating. Journal of Tropical Ecology 19(1) 1-7. McCarroll D., Loader NJ. (2004) Stable isotopes in tree rings. Quaternary Science Reviews 23 771-801.*"

**AUTHOR reply:** Establishing quantitative growth rates for the trees studied was outside the scope of this preliminary study but would be very helpful for future studies attempting to use our methods. This assumption is based on the existing literature of analogous growth rates. We will clarify the text that this was not measured by us, and this is explicitly unknown in our study. Generally, the impacts on the trees other than elevated CO2 (e.g., Suess effect, climate, etc.) have a relatively uniform distribution of exposure among the trees, with the primary difference being volcanic CO2 concentration exposure. As such, we are able to assess the effect of CO2 while maintaining relatively consistent control over other factors.

**AUTHOR's changes in revised manuscript:**

For analogous growth rates, we added wording and references in section 2.5. [action repeatedly mentioned below]. We also quantified any potential anthropogenic CO2 variability from the closest major source, the capital region of San Jose, discussed in section 2.7.

**REFEREE #2 (AC2) Comment [C1-C5]: Major concern #2:** "*2) Carbon isotope ratio of -26 peril is within the normal natural range and I still suspect that if there was significant contribution of volcanic CO2 to the wood. Even when large amount of 13CO2 (or 14CO2) is added to the crown, often it is blown away by wind and you do not see any trace of such carbon in the wood (for example, please read: Leavitt, S.W. and Long, A., 1989. Accelerator-measured 14C activity in tree rings from the vicinity of the first atomic bomb test. Radiocarbon 31:762-765.) If other environmental parameters such as radiation happen to have the same increasing patterns with Soil CO2 flux, then you may observe a pseudo-correlation between volcanic CO2 and wood d13C. To prove d13C increase is really caused by the volcanic CO2, authors should analyze 14C and 13C/14C ratio should be plotted against mean soil CO2 flux to prove the incorporation of volcanic CO2 into the plants. Volcanic CO2 is old and therefore 14C (half life of ca. 5300 years) concentration should be almost zero, I assume. Higher incorporation of volcanic CO2 means higher 13C concentration and lower 14C concentration, i.e. higher 13C/14C ratio. It is expensive to analyze 14C of wood (costs about 900 USD per sample in my country) compared to 13C (10 USD per sample). But there are many companies that offer such services. If you measure 14C concentrations of 12 data points in Fig.4, then it would be about 10800 USD. Is this possible?*"

**AUTHOR reply:** We agree with the reviewer that 14C is a valuable tracer for confident traceability of elevated volcanic CO2 exposure for the trees. Other studies have utilized this approach (e.g. Lewicki et al 2014, cited in manuscript). Unfortunately, as the reviewer notes, 14C analysis is significantly more expensive to analyze than 13C. This study did not have the budget that the reviewer suggests (e.g., $10,800USD) for this additional analysis. Future studies should expand the scope of this study to incorporate more measurements.

**AUTHOR's changes in revised manuscript:**

We added clarifying wording in the discussion (also answers referee #2's "Line 388" and "Line 426" comments). We note again the clear limitation of using 14C for dating of these cores due to the 14C deficiency in the volcanic excess $CO_2$ and the independence of the excess volcanic $CO_2$ signal, spatially correlated with co-located tree core samples. We believe that 14C analyses would have little bearing on the paper beyond pattern confirmation, which we discuss in Sect. 4.1.

**REFEREE #2 (AC2) Comment [C4-C5]:** " *Line 44. "*including other gas species that accompany CO2 emissions at these springs*" There are some studies that show effects of acidic deposition (SO2 and other pollutants) on leaf d13C.* *Santruckova et al. 2007 Carbon Isotopes in Tree Rings of Norway Spruce Exposed to Atmospheric Pollution. Environ. Sci. Technol., 2007, 41 (16), pp 5778–5782. Are effects of SO2 gas on leaves really absent? Acidic pollutants such as SO2 are known to affect stomata, hence, d13C of trees. Authors should analyze SO2 concentration in the air at the crowns/the leaf surfaces, then compare these concentrations with those of other literature so that they can be sure that effect of SO2 gas on d13C is absent.*"

**AUTHOR reply:** "This concern is certainly warranted, as many volcanic systems around the world do exhibit other emissions. Throughout Costa Rica's volcanoes, however, almost none of them emit SO2 to any significant degree. Further, we note that in general SO2 is emitted only out of the craters; whereas, CO2 is emitted both from the craters and from the flank areas (Symonds et al 2001). It is the forested flank areas exposed to elevated CO2 that are the focus of interest to our study. As such, SO2 is very minimal in our study. Nonetheless, Turrialba is one of the only Costa Rican volcanoes with SO2 emissions (see Pieri et al 2013; Diaz et al 2015; Xi et al 2016), which is why we made sure to assess the distribution and impact on the surrounding forests. Fortunately, the prevailing winds tend to blow the crater emissions away from the forested areas.

Pieri, D., Diaz, J.A., Bland, G., Fladeland, M., Madrigal, Y., Corrales, E., Alegria, O., Alan, A., Realmuto, V., Miles, T. and Abtahi, A., 2013. In situ observations and sampling of volcanic emissions with NASA and UCR unmanned aircraft, including a case study at Turrialba Volcano, Costa Rica. Geological Society, London, Special Publications, 380(1), pp.321-352. Diaz, J.A., Pieri, D., Wright, K., Sorensen, P., Kline-Shoder, R., Arkin, C.R., Fladeland, M., Bland, G., Buongiorno, M.F., Ramirez, C. and Corrales, E., 2015. Unmanned aerial mass spectrometer systems for in-situ volcanic plume analysis. Journal of the American Society for Mass Spectrometry, 26(2), pp.292-304. Xi, X., Johnson, M.S., Jeong, S., Fladeland, M., Pieri, D., Diaz, J.A. and Bland, G.L., 2016.Constraining the sulfur dioxide degassing flux from Turrialba volcano, Costa Rica using unmanned aerial system measurements. Journal of Volcanology and Geothermal Research, 325, pp.110-118. Symonds, R.B., Gerlach, T.M. and Reed, M.H., 2001. Magmatic gas scrubbing: implications for volcano monitoring. Journal of Volcanology and Geothermal Research, 108(1-4), pp.303-341.

**AUTHOR's changes in revised manuscript:**

This had already been addressed at the end of the next paragraph (lines 68-72) in the original submission. We did not consider or here quote high temperature volcanic vents which cause acidic environments, but cold volcanic flank gas emissions, where no acid gases reach the surface. We also detailed our extreme caution by considering any possible distal SO2 influence in section 2.6, discussed in the last paragraph of section 3.1 (orig. version lines 257-261). To clarify this even more, we added wording and references to the second paragraph of Section 3.1, including 5 new references. We added clarifying sentences at the beginning of Sect. 2.6, and in the second paragraph of discussion Sect. 3.1. Also, the SO2 distribution in the air around Turrialba volcano is well measured and monitored by

OVSICORI (Costa Rica's volcano monitoring agency), though not at the canopy level – hence our description. We added text in Sect. 1, Sect. 2.6 (incl. a SO2 /CO2 ratios in air at Turrialba reference), Sect. 3.1 to clarify the SO2 Situation.

**REFEREE #2 (AC2) Comment [C4-C5]:** "*Lines 133-134 "*It averages 4-15 m in height*" Was there any difference in tree heights in the three species studied? It is important because it affects how strongly the tree crowns are affected by volcanic CO2, which comes up from the ground. I suspect it is related to the different slopes of the two species in Fig.4.*"
**AUTHOR reply:** We agree that measurements of tree height are important to understanding CO2 exposure. We do not have precise canopy height measurements, though we do have DBH measurements, which are related to canopy height. Detailed canopy height measurements were outside the scope of our study, but future studies should measure canopy height.
**AUTHOR's changes in revised manuscript:**
We added and clarified DBH information in Sect. 2.2, and Sect. 4.3.

**REFEREE #1 (AC1) Comment [C2]:** "*Line 50: you introduce rubisco without defining what it is.*"
**AUTHOR reply:** We will define rubisco in this sentence in the revised manuscript.
**AUTHOR's changes in revised manuscript:**
Added phrase for clarification

**REFEREE #1 (AC1) Comment [C2]:** "*It is" instead of "it was" unclear*"
**AUTHOR reply:** This wording will be edited in the revised manuscript.
**AUTHOR's changes in revised manuscript:**
Corrected

**REFEREE #1 (AC1) Comment [C2]:** "*In the Investigated locations and sampling strategy section: there is no reference to figure 1 where sampling transects are described.*"
**AUTHOR reply:** A reference to Figure 1 will be added.
**AUTHOR's changes in revised manuscript:**
Added reference to Fig 1 in the text

**REFEREE #1 (AC1) Comment [C3]:** "*section 2.2 title: "Species studied" replace by "studied tree species*"
**AUTHOR reply:** This change will be made in the revised manuscript.
**AUTHOR's changes in revised manuscript:**
Title changed accordingly

**REFEREE #1 (AC1) Comment [C3]:** "*The authors describe that the sampling for isotopes was conducted using a drill and drilling holes in the outermost 5 cm. Was this at any specific resolution? or just aimed at generating wood powder for analyses?*"
**AUTHOR reply:** This was only intended to generate wood powder for 13C analyses. We will clarify this in the revised manuscript.
**AUTHOR's changes in revised manuscript:**
Added phrase for clarification

**REFEREE #1 (AC1) Comment [C3]:** "*The authors estimated that the outermost 5 cm correspond to the last 2-3 years? What is this assumption based on?*"
**AUTHOR reply:** This assumption is based on the existing literature of analogous growth rates. We will clarify the text that this was not measured by us, and this is explicitly unknown in our study.
**AUTHOR's changes in revised manuscript:**
Added literature growth rates for comparison (incl. a new reference), and wording to put it into context. See also discussion on DBH and growth rates in Sect 2.2 and 4.3.

**REFEREE #2 (AC2) Comment [C5]:** "*Line 186 "*which we estimated to be representative of roughly the last 2-3 years*" You may be able to prove this, for example, by analyzing oxygen isotope cycles at high resolution or finding 14C bomb spike peak around 1964.*"

**AUTHOR reply:** "*14C and high-resolution oxygen isotopes would be useful tools to determine precise growth rates, but are unfortunately out of the budget and scope of this study. We thank the reviewer for this design suggestion for future studies.*"

**AUTHOR's changes in revised manuscript:**

Added sentence to Sect. 4.4 (moved from conclusions). Following on from our note above and in the text regarding the challenges in using 14C dating in environments strongly affected by volcanic $CO_2$ , which is isotopically "dead" – the resulting 14C deficit makes dating usually not possible: We note that oxygen isotopes in volcanic CO2 are heavily shifted to heavy values as well, obscuring the natural bomb spike signal in a similar way as the 14C deficit in volcanic $CO_2$ – the volcanic gas oxygen isotope signal shifts far from the meteoric water line (see for example, Taran, Y. and Zelenski, M., 2015. Systematics of water isotopic composition and chlorine content in arc-volcanic gases. Geological Society, London, Special Publications, 410(1), pp.237-262. Giggenbach, W.F., 1992. Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. Earth and planetary science letters, 113(4), pp.495-510. Fiebig, J., Chiodini, G., Caliro, S., Rizzo, A., Spangenberg, J. and Hunziker, J.C., 2004. Chemical and isotopic equilibrium between CO2 and CH4 in fumarolic gas discharges: Generation of CH4 in arc magmatic-hydrothermal systems 1. Geochimica et Cosmochimica Acta, 68(10), pp.2321-2334. Cartwright, I., Weaver, T., Tweed, S., Ahearne, D., Cooper, M., Czapnik, K. and Tranter, J., 2002. Stable isotope geochemistry of cold CO2-bearing mineral spring waters, Daylesford, Victoria, Australia: sources of gas and water and links with waning volcanism. Chemical Geology, 185(1-2), pp.71-91.)

**REFEREE #2 (AC2) Comment [C5-C6]:** "*Line 199-222 Why you did not measure SO2 (and CO2) concentrations at the canopy? The model estimates may not reflect the concentrations of these gases surrounding the leaves*."

**AUTHOR reply:** We discuss this from lines 323-341. Longer-term studies could benefit from installing gas sensors in the canopy at various heights, but since we were measuring each site only once, each concentration measurement is more likely to reflect instantaneous meteorological conditions than long-term CO2 exposure. Thus, for our preliminary study measuring the input of CO2 to the system (volcanic soil fluxes) made more sense.

**AUTHOR's changes in revised manuscript:**

We added clarifying sentences at the beginning of Sect. 2.6, and in the second paragraph of discussion Sect. 3.1. The SO2 distribution in the air around Turrialba volcano is well measured and monitored by OVSICORI (Costa Rica's volcano monitoring agency), though not at the canopy level – hence our description. We added text in Sect. 1, Sect. 2.6 (incl. a $SO_2$ /$CO_2$ ratios in air at Turrialba reference), Sect. 3.1 to clarify the $SO_2$ Situation.

**REFEREE #1 (AC1) Comment [C3-C4]:** "*Lines 232-233: Are there any information about the canopy height, it seems that the 0-100 m would be the most appropriate level. Does the model capture finer vertical differences in the CO2 concentration within the canopy for e.g. between 10m and 40m*?"

**AUTHOR reply:** "The modelled atmosphere up to 500 m agl may see a CO2 concentration influence from, or have an influence on, the air in the tree canopy. The broad scale of the modelled domain was designed to assess if an external influence of CO2 from San José is a significant measurable component of the air above the measurement sites, but not to model the under-canopy or within-canopy air flows. The model results shown in Fig. 2 represent only the 0-100 m agl air. We will clarify this in the wording in the revised manuscript. We do not have precise canopy height measurements, but all trees measured ranged from ~5-30 m and we estimate canopy heights at about 20-30 m on average at our measured sites. We do have DBH measurements, which are related to canopy height, but future studies should measure canopy height. We did not measure or model vertical differences in CO2 concentrations; but, we agree that this would be important for future studies. As such, we acknowledge that limitation to our study, and frame our results as suggestive rather than definitive, pointing to this type of design for future studies."

**AUTHOR's changes in revised manuscript:**

We added clarifying words and phrasing to explain the modeled atmospheric levels.

**REFEREE #1 (AC1) Comment [C4]:** "*Lines 250-252. The measurements in this study reveal that CO2 levels are high based on CO2 fluxes data. The ecosystem growing in this environment are certainly exposed to those high CO2 concentration levels, however, the results described in this section do not show the link to stomatal conductance and chlorophyll concentrations*."

**AUTHOR reply:** We thank the reviewer for noting the elevated CO2 concentrations that ecosystems are exposed to in this environment. For clarity, we will move the mention of the specific measurements (i.e. stomatal conductance and chlorophyll concentrations) to the appropriate section (3.3).

**AUTHOR's changes in revised manuscript:**

Moved sentence to correct context.

**REFEREE #1 (AC1) Comment [C4]:** "*The CO2 concentration level are measured at soil level, do you expect the concentration to remain similar at higher canopy level, say ~15-20 m*?"

**AUTHOR reply:** We note that we present soil CO2 fluxes, not concentrations. As mentioned above, vertical changes in volcanic CO2 concentration were outside the scope of our study but would definitely be important for future studies. We added substantial text to the introduction, methods, discussion, and supplement, to clarify this question thoroughly.
**AUTHOR's changes in revised manuscript:**
We added clarifying wording in multiple locations in Sect. 2.1 and 2.3, and in the supplement including an additional supplemental figure (S2). The relationships presented in our analysis were on a per species basis to avoid complications resulting from different growth rates *across* species. This is important because d13C values provide an integral value of assimilated carbon by the entire tree (not just individual leaves), and since the depth of tree core sample was identical for each species (the outermost part of the trunk) we can safely assume that the volcanic CO2 exposure has been consistent over the time period under investigation.

**REFEREE #1 (AC1) Comment [C4]:** "*Lines 265-266: the 13C values for A. acuminata and O. xalapensis are identical (statistically not different). Was the difference between the two species and B. nitidia tested statistically*?"
**AUTHOR reply:** No, because the current study did not focus on quantifying interspecific differences. Such testing would be important for future studies.
**AUTHOR's changes in revised manuscript:**
No changes since none were requested.

**REFEREE #2 (AC2) Comment [C6]:** "*Line 263 Average d13C values of -26 per mil are observed in trees unaffected by volcanic CO2.* "
**AUTHOR reply:** This statement is somewhat ambiguous, but we assume that the reviewer is referring to our reported average 13C value of -26 per mil. This average is independent of reported volcanic CO2 fluxes, and does not indicate that trees with values near -26 per mil are unaffected by volcanic CO2.
**AUTHOR's changes in revised manuscript:**
We clarified this with an addition in the first sentence of 3.2.

**REFEREE #1 (AC1) Comment [C4-C5]: Line 266** "*The following sentences are confusing.* As CO2 flux increased, the wood cores contained progressively higher amounts of 13C for two of the three species. Tree core 13C showed no relationship with stomatal conductance for any species. *As CO2 fluxes increased over time or spatially? how was that tested in the case of time? There is no mention of stomatal conductance data or else and here a brief description of the relationship between 13C and stomatal conductance?* "
**AUTHOR reply:** "We will rework this section to improve flow and add clarity. All changes in CO2 flux are spatial, and the temporal variability of the higher, geologically dominated CO2 fluxes (>12 g m-2 d-1, see Fig. 3) is known to be a very dampened, long-term signal related principally to very slow (decadal to centennial) changes in deep geological CO2 supply, and changes in top soil permeability (we conducted all measurements in the dry season). With regard to stomatal conductance, our data were preliminary and instantaneous, and were not meant to be compared with values of 13C. Again, such a comparison would be informative in future work."
**AUTHOR's changes in revised manuscript:**
We reworked this section to improve flow and add clarity. Also added 2 references to explain better our line of argumentation, and the character of the natural system being observed.

**REFEREE #1 (AC1) Comment [C5]:** "*In the discussion, the authors argue that the existing significant correlation between the 13C in the trees and soil does not imply that trees were incorporating the heavy volcanic CO2. The values of tree's 13C should reflect the incorporation of eCO2*"
**AUTHOR reply:** "We apologize for confusion in our wording. The reviewer is correct in that the values of the tree 13C reflects the incorporation of eCO2. We will edit this statement in the paper for added clarity."
**AUTHOR's changes in revised manuscript:**
We did not find such a statement reflected in our text. However, we tried to add clarity throughout Sect. 3.2, 4.1, the new section 4.3, 4.4, and the conclusions. This also answers one of the later requests by the referee, to merge original version sections 4.3 and 4.4 (now combined as Section 4.4).

**REFEREE #2 (AC2) Comment [C6-C7]:** "*Fig 4, Why are the slopes of the two regression lines are different? Is it related to the difference in tree height between Oreopanax xalapensis and Buddeleja nitida*?"
**AUTHOR reply:** This is a great question. It is more likely due to species or trait differences in physiology than due to height or exposure, but could be both. This difference highlights the challenge with inferring ecosystem-level responses across measurements of only a few species. To do so would necessitate a much larger sampling across

samples and species - very clearly needed. In the discussion, we will add a section that mentions the value of a more thorough study, whereby more species are sampled, potentially by aircraft or satellite.
**AUTHOR's changes in revised manuscript:**
We added sentences in Sect. 4.1 to reflect our reply, in addition to existing text in sections 2.2, 2.5.

**REFEREE #1 (AC1) Comment [C5]:** "*Line 312, Why is it assumed to be 400 ppm? if it is the atmospheric value is 400 ppm for the particular period: several years from tree rings then it should be referenced to from atmospheric measurements (Mauna Loa for example).*"
**AUTHOR reply:** 400 ppm was chosen as a mean value, and a few ppm in either direction makes little difference to the final result (the Mauna Loa values vary by a mean of 2 ppm year-to-year, which is much less than the seasonal variability in CO2 in air at 12-15 ppm range). We did not intend for these calculations to represent perfectly accurate measurements of volcanic CO2 exposure, but merely to give an idea of the magnitude of CO2 enhancement. We will edit this section to better reflect this intent.
**AUTHOR's changes in revised manuscript:**
We removed the mention of 400ppm, but refer to it via Malowany et al 2017 instead. Note that the localized ambient mean concentration may deviate from the broader scale mean background. The mean local free tropospheric CO2 concentration is not know too well but satellite measurements in our group (e.g., Schwandner et al, 2017, Science, Fig. 1) show that 400 ppm in the northern hemispheric spring is actually quite representative. We also discovered a mistake in the formula used and corrected the formula and results in the text.

**REFEREE #2 (AC2) Comment [C6]:** "*Lines 319 "*Tree ring 14C content in volcanically active areas has been linked to variations in volcanic CO2 emissions, and comparing patterns of d13C to 14C measurements for the same wood samples provide additional confirmation of this finding" *I can not understand why you did not measure 14C, especially after reading this sentence in your paper*."
**AUTHOR reply:** "See response to major concern 2. We will edit this sentence to avoid confusion with an expectation of 14C measurements in our study."
**AUTHOR's changes in revised manuscript:**
We edited this sentence to clarify what we studied and what we didn't study. See above notes regarding the utility of 14C measurements in environments heavily affected by the volcanic excess $CO_2$ 14C deficiency effect.

**REFEREE #2 (AC2) Comment [C6]:** "*Line 352* "Additionally, none of the trees displayed obvious signs of stress" *This part seems to contradict with the following part: Line 195* "during analysis we excluded all trees that were observed in the field to have significant stress. . ." *By the way, how many trees were excluded*?"
**AUTHOR reply:** We will edit these lines for clarity in the revised manuscript. Of 51 total trees sampled, 17 were excluded.
**AUTHOR's changes in revised manuscript:**
Added statement on number of samples and a clarifying sentence. We also (see above notes) added significant clarifying text regarding SO2.

**REFEREE #1 (AC1) Comment [C6]:** "*the sections 4.3 and 4.4 are very speculative as the results presented and discussed in the paper are exploratory and bear some weaknesses in the sample processing, particularly the tree cores age and investigated period. These two sections can be shortened and merged*."
**AUTHOR reply:** We agree with the reviewer and will shorten and merge these two sections. We put these as separate sections because 4.3 is intended as a theoretical framework for the implications of trees recording volcanic CO2 emissions, whereas 4.4 is more directly intended to aid potential future studies that intend to study the same areas and questions that we explored.
**AUTHOR's changes in revised manuscript:**
Combined, reworded and straightened out these two into one section, as requested.

**REFEREE #2 (AC2) Comment [C7]:** "*Line388* "but 14C is relatively expensive and a limited number of labs are capable of making these measurements" *Now there are lab services that offer 14C analysis and I don't know if* "limited number of labs are capable of making these measurements" *is true now*."
**AUTHOR reply:** We apologize for the confusion, we meant that they are limited in comparison to 13C, which is comparatively more straightforward and inexpensive to analyze. We will edit this line for clarity in the revised manuscript.
**AUTHOR's changes in revised manuscript:**

This sentence was a casualty of the reorganization of Sections 4.3 & 4.4, and is not in the text anymore.

**REFEREE #1 (AC1) Comment [C6]:** "*Line 422. The statement of identifying areas of dense old-growth forest is not based on any chronological framework. They are potentially old but the methods used in this study did not provide any dating of the trees.*"
**AUTHOR reply:** "We agree that this statement was more for discussion, as opposed to a detailed dendrochronology. We will remove this statement to avoid confusion.
**AUTHOR's changes in revised manuscript:**
Removed "old growth".

**REFEREE #2 (AC2) Comment [C7]:** "*Line 426 "*Confounding factors that are known to influence d13C 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 CO2*" I disagree with this statement and strongly feel that authors should measure 14C of the wood powder at least for the wood samples plotted in Fig.4*."
**AUTHOR reply:** We agree with the reviewer in that 14C would certainly help support our results, although it is not possible for us to include in this paper due to our limited budget. We will edit this sentence to incorporate the sentiments from the reviewer.
**AUTHOR's changes in revised manuscript:**
Edited this sentence for clarity, and to reflect the reviewer's sentiment on confounding variables, which was thoroughly addressed in above changes already ($SO_2$). Also addressed thoroughly in the discussion on the 14C deficit in volcanic $CO_2$ Influenced environments.

**References added in Revision:** **(listed alphabetically here)**

Aiuppa, A., Caleca, A., Federico, C., Gurrieri, S. and Valenza, M.: Diffuse degassing of carbon dioxide at Somma–Vesuvius volcanic complex (Southern Italy) and its relation with regional tectonics, J. Volcanol. Geotherm. Res., 133(1), 55–79, doi:10.1016/S0377-0273(03)00391-3, 2004. **Citation added to section 3.2**

D'Arcy, F.: Novel Methods of volcanic gas measurement using drones and tree ring geochemistry at Turrialba volcano, Costa Rica. MSc thesis, McGill university, Montreal, Canada, 63pp, 2018. URL: http://digitool.Library.McGill.CA:80/R/-?func=dbin-jump-full&object_id=154622&silo_library=GEN01 **Citation added to section 3.1**

Delmelle, P. and Stix, J.: Volcanic Gases, edited by H. Sigurdsson, B. Houghton, H. Rymer, J. Stix, and S. McNutt, Encylopedia Volcanoes, 1417, 1999. **Citation added to section 2.1**

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Ortega-Pieck, A., López-Barrera, F., Ramírez-Marcial, N. and García-Franco, J. G.: Early seedling establishment of two tropical montane cloud forest tree species: The role of native and exotic grasses, For. Ecol. Manag., 261(7), 1336–1343, doi:10.1016/j.foreco.2011.01.013, 2011. **Citation added to sections 2.5 & 4.3**

Peiffer, L., Wanner, C. and Lewicki, J. L.: Unraveling the dynamics of magmatic CO2 degassing at Mammoth Mountain, California, Earth Planet. Sci. Lett., 484, 318–328, doi:10.1016/j.epsl.2017.12.038, 2018. **Citation added to section 3.2**

Verheyden, A., Helle, G., Schleser, G. H., Dehairs, F., Beeckman, H. and Koedam, N.: Annual cyclicity in high-resolution stable carbon and oxygen isotope ratios in the wood of the mangrove tree Rhizophora mucronata, Plant Cell Environ., 27(12), 1525–1536, doi:10.1111/j.1365-3040.2004.01258.x, 2004. **Citation added to section 4.3**

Vodnik, D., Thomalla, A., Ferlan, M., Levanič, T., Eler, K., Ogrinc, N., Wittmann, C. and Pfanz, H.: Atmospheric and geogenic CO2 within the crown and root of spruce (Picea abies L. Karst.) growing in a mofette area, Atmos. Environ., 182, 286–295, doi:10.1016/j.atmosenv.2018.03.043, 2018. **Citation added to section 1**

**References removed:**

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**Changes to supplementary material:**

Changes made to the supplementary material are uploaded in a combined pdf file (together with the marked-up revision and the point-by-point response to reviewers), and are also described here:

- Added a second text paragraph (rationale above, p.2 of this document, in response to reviewer #2 comments)
- Added second supplementary figure (Fig. S2) to support the added text.
- NO changes to the existing figure or text from the originally submitted version of the supplementary material.

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

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**Abstract.** ~~Here we~~We explore the use of active volcanoes~~ as a study area~~ 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 ~~serves to document~~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 ~~some~~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 response~~s~~ of tropical plants to globally rising levels of $CO_2$ ~~are~~ is 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 ~~in turn~~ 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). ~~Other~~ 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~~points~~. 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 ~~more~~ suitable for this type of study, ~~as it is protected from human influence~~ 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~~rubisco, an enzyme central to $CO_2$ fixation, 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 ~~Many tropical volcanoes are heavily vegetated, but~~ 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 cold volcanic CO$_2$ emissions—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; Vodnik 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). ~~A significant portion of t~~These emissions are released through faults and fractures on the flanks of the volcano~~, which often support well-developed, healthy ecosystems~~ (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$_2$S) 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$_2$), ~~but given that trees discriminate against isotopically heavy CO$_2$ (Cernusak et al., 2013; Keeling et al., 2017), it remains~~though it is unclear if the trees utilize this excess CO$_2$. Volcanic CO$_2$ has a heavy δ$^{13}$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$_2$ ~~would power~~could increase carbon uptake in photosynthesis.

Here we provide ~~exploratory~~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$_2$~~ fertilization effects~~, and ~~present notable~~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 (Fig. 1). These two volcanoes are divided by a large erosional basin. ~~This~~ The two volcanoes ~~combined forested volcanic edifice~~cover~~s~~ approximately 315 km$^2$, which is ~~somewhat~~ significantly larger than the average forested active volcanic edifice in Costa Rica ~~of~~ at 122 km$^2$. The vast majority of the northern flanks of Irazú and Turrialba are covered in legally protected dense old-growth ~~primary~~ forest, while the southern flanks are dominated by pasture land and agriculture. Turrialba rises ~~almost~~ 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~~it last erupted~~ 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 ~~volcanic~~ 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 ~~flank~~ $CO_2$ emissions in areas proximal to the crater were calculated ~~computed~~ at 113 ± 46 tons/d (Epiard et al., 2017). The Falla Ariete (Ariete fault), 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~~, 1977,~~ 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 ~~infrequent minor phreatic explosions~~ minor gas emissions on its northern forested flank (Alvarado et al., 2006; Barquero et al., 1995). Diffuse cold flank emissions of volcanic $CO_2$ represent the vast majority of gas discharge from Irazú, as the main crater releases 3.8 t~~/d~~ d$^{-1}$ of $CO_2$ and a small area on the north flank alone releases 15 t~~/d~~ 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 than their flanks.

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~~roughly~~ north-south ~~trending~~ striking Rio Sucio fault, crossing into the area dominated by dairy farms on Irazú's lower ~~NE~~ northeastern slope. Of significant importance for this type of study is that all active volcanoes on Earth continuously emit $CO_2$ diffusely through fractures and diffuse degassing structures on their flanks, at distances hundreds to thousands of meters away from the crater (Dietrich et al., 2016; Epiard et al., 2017), and this elevated $CO_2$ degassing persists continuously and consistently over decades to centuries (Burton et al., 2013; Delmelle and Stix, 1999; Nicholson, 2017). There is no inherent seasonal or meteorological variability of the source gas pressure, and no dependence on shallow soil or vegetation chemistry or biology (though increased soil moisture in the rainy season, wind, and atmospheric pressure can modulate gas permeability of the shallow soil) (Camarda et al., 2006). The soil overlying deep reaching fracture systems acts as a diffuser through which the volcanic gas percolates and enters the sub-canopy air. For our study sites, portions of the volcanoes with active "cold" $CO_2$ degassing have already been assessed and mapped previously (Epiard et al., 2017; Malowany et al., 2017).

Our sampling locations on Irazú were located along a road from the summit northward down into~~ a large intravolcanic erosional basin~~ this low- lying area. On Turrialba, we focused on an area of known strong emissions but intact forests on the SW slope, uphill of ~~said~~ the same ~~intravolcanic~~ erosional depression, but cross-cut by the major NE-SW trending active fracture system of the Falla Ariete. We sampled three main areas ~~on Turrialba, all on or near~~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 a total of 51 tree samples (17 were excluded after stress screening) at ~~sporadically~~ 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 in altitude to be in areas generally downwind of the prevailing crater emissions plume (Epiard et al., 2017). We avoided ~~Trees and~~ areas that experience ash fall, high volcanic SO$_2$ concentrations, local anthropogenic CO$_2$~~, or~~ from farms, or that were likely to have heavily acidified soil~~ were avoided during our sampling trip. High~~. 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. ~~There was light~~Light ash fall on some days~~, but the only~~ 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 ~~we examined that had~~showing ash accumulation on their leaves ~~were already heavily damaged and too close to the central cone of the volcano, and thus were excluded from analysis.~~or previous damage were the exception and avoided. Altitude, ~~light~~amount of sunlight during measurements, and aspect had no consistent correlations with any of the parameters we measured.

## **2.2 ~~Species studied~~Studied tree species**

Our study focused on three tree species found commonly on Turrialba and Irazú: *Buddleja nitida*, *Alnus acuminata*, and *Oreopanax xalapensis*. *B. 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). *A. 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. *O. 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

Soil $CO_2$ flux was measured with an accumulation chamber near the base of the tree (generally within 5 meters, terrain permitting) at three different points and then averaged to provide a single $CO_2$ flux value to compare to the $^{13}C$ measurement of the corresponding tree sample. This technique is intended to provide a simple relative way to compare the $CO_2$ exposure of different trees, as a tree with high $CO_2$ flux near its base should experience consistently higher $CO_2$ concentrations than a tree with lower $CO_2$ flux. We also measured concentrations at ground level and 1.5 – 2.0 m above ground level, though these were expectedly highly variable in time and location. We analyzed $CO_2$ fluxes, not concentrations, because the diffuse emissions of excess volcanic $CO_2$ through the soil, fed from a deep magma source and location-dependent on constant deep geological permeability, are highly invariant in time compared to under-canopy air concentrations. In contrast, instantaneous concentration measurements in the sub-canopy air are modulated by many factors including meteorology, respiration of vegetation and animals, uptake by plants for photosynthesis, and diurnal dynamic and slope effects. An approach of instantaneous highly variable concentration measurements is thus not representative of long-term exposure. The approach of measuring the largely invariant soil-to-atmosphere volcanic $CO_2$ fluxes is much more representative of long-term exposure, varying mostly spatially and the site-to-site differences are therefore more representative of the lifetime of exposure of the trees.

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 ~~with~~to the ground and remained connected to the LI-COR sensor. ~~Incoming gas~~The air within the accumulation chamber was ~~actively pumped~~continuously recirculated through the sensor, passing through a ~~set of filters~~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 $CO_2$~~, and fluxes~~. 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) ~~is~~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 ~~an average~~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 (~~umol~~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. ~~As such~~Consequently, we have fewer stomatal conductance measurements than our other ~~datatypes~~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, which was chosen to represent the most recent carbon signal for $^{13}C$ analyses. 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 ~~assume~~ to be ~~are~~ representative ~~of~~ at least ~~roughly~~ the last 2-3 years~~.~~, based on analogous literature growth rate values: *O. xalapensis* and *A. acuminata* range from 0.25 - 2.5 cm/y and 0.6 - 0.9 cm/y, respectively (Kappelle et al., 1996; Ortega-Pieck et al, 2011). These rates result in a 5 cm range of at least 2 and 5.5 years, though the high rates were determined for very young trees under very different conditions and it is explicitly unknown in our study. 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 the field to ~~have significant~~show visible signs of 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~~ past~~ likelihood of trees having been significantly stressed in the past by volcanic sulfur dioxide ($SO_2$) from the central crater vents, we took two approaches. First, we were guided by in-situ measurements taken in the same areas by Jenkins et al. (2012), who assessed the physiological interactions of $SO_2$ and $CO_2$ on vegetation on the uppers lopes of Turrialba and demonstrated a rapid exponential decay of $SO_2$ away from the central vent. Second, for long-term exposure 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 (~~give wavelength~~8.125 - 8.475 µm), $b_{11}$ is the radiance at band 11 (~~give wavelength~~8.475 - 8.825 µm), and $b_{12}$ is the radiance at band 12 (~~give wavelength~~8.925 - 9.275 µm). This is similar to the method of ~~Campion et al., 2010~~ Campion et al., 2010. The granules ~~are~~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. ~~Some~~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~~, which speeds up processing~~.

### 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 (~~for further details on forward mode see;~~ Stohl et al., 2005), Flexpart, 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~~o~~° horizontal resolution meteorology (Saha et al., 2010b, 2010a), and 1-km Open-Source Date Inventory for Anthropogenic $CO_2$ (ODIAC; Oda and Maksyutov, 2011) emissions for 2015 were used to drive the Flexpart model. The $CO_2$ concentrations were generated at a 1 km spatial resolution within three vertical 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 modelled level of the atmosphere, from 0-100 meters. 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, we were not aiming to capture intra-canopy variability, typically at tens to hundreds of ppm variable, which is not relevant to the better mixed, distal single-digit or less ppm signal from San Jose. 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 ~~our study~~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 ~~52~~66 points over four days (Fig. 1). The first eight points were on Irazú, and the rest were located near the Ariete ~~fault~~ 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 previously ~~published results~~ 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 ~~as described in Sinclair 1974~~ (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 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 ~~all~~ $CO_2$ 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 ~~completely~~ unaffected by anthropogenic $CO_2$ from San Jose, which is the only major urban area near Turrialba and Irazú. Since the trees sampled are spatially close to each other, they are exposed to the same regional background $CO_2$ variability. 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 ~~significant~~measurable amounts of $SO_2$, which is reflected by the high $SO_2$ probabilities ~~sensed~~derived there (Fig. ~~2).~~2). Tropospheric $SO_2$ quickly converts to sulfate, a well-studied process intensified by the presence of volcanic mineral ash, plume turbulence, and a humid tropical environment (Oppenheimer et al., 1989; Eatough et al., 1994); furthermore, the bulk of the $SO_2$ emissions is carried aloft. Consequently, any remaining $SO_2$ causing acid damage effects on trees at Turrialba is limited to a narrow band of a few 100 m around the mostly quietly steaming central vent, which has been thoroughly ecologically evaluated for acid damage (Jenkins et al., 2012). D'Arcy (2018) has assessed this narrow, heavily $SO_2$-affected area immediately surrounding the central crater vent of Turrialba, which we avoided, and our sampling sites are mostly within their control zone not considered majorly affected by $SO_2$, but where diffuse $CO_2$ degassing dominates the excess gas phase (Epiard et al, 2017). Our study area is on the flanks of the volcano, where ASTER-derived $SO_2$ probability is minimal~~.~~, and $SO_2$ influence not detectable on the ground (Jenkins et al., 2012; Campion et al., 2012). 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 ~~in the rest of the~~over the other volcanoes in Costa Rica (white polygons in Fig. 2~~.~~).

### 3.2 Tree core isotopes

Bulk wood $\delta^{13}C$ measurements of all samples in this study, independent of exposure, ranged from -24.03 to -28.12 ‰, with most being ~~clumped~~ 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 ‰. ~~Each species has slightly different averages;~~ *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 ‰. Diffuse excess $CO_2$ emissions throughout the investigation areas reflect a deep volcanic source which typically varies little in time (Epiard et al., 2017), but such diffuse emissions spatially follow geological subsurface structures (Giammanco et al., 1997). Their temporal variability therefore reflects long-term low-amplitude modulation of the volcanic heavy-$\delta^{13}CO_2$ signal, and their spatial distribution is mostly constant over tree lifetimes (Aiuppa et al., 2004; Peiffer et al., 2018; Werner et al., 2014), providing a constant long-term spatial gradient of $CO_2$ exposure to the forest canopy. Our data show that in areas where ~~As~~$CO_2$ flux ~~increases~~is higher, the wood cores contained progressively higher amounts of $^{13}C$ for two of the three species. Interestingly, our t~~T~~ree core $\delta^{13}C$ showed no relationship with instantaneous stomatal conductance for any species, indicating that no stress threshold was exceeded during measurement across the sample set.

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

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. After excluding visibly damaged trees, leaf fluorescence, expressed as Fv/Fm, was very high in most samples. Fv/Fm ranged from 0.~~684~~75 to 0.~~888~~89, with most measurements clustering between 0.8 and

~~0~~f0.85 (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 ~~had~~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 ~~index (CCI)~~ measurements were highly variable, ranging from ~~11.86~~260 to ~~nearly 100~~922 µmol m$^{-2}$, with an average of ~~43.46~~558 µmol m$^{-2}$ and a standard deviation of ~~21.5~~162 µmol m$^{-2}$ (Fig. 6). ~~CCI~~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 ~~CCI~~chlorophyll concentration and soil $CO_2$ flux ($r^2$=0.~~39~~38 and $r^2$=0.~~35~~28, respectively), but their trendlines were found to be almost perpendicular (Fig. 6). As $CO_2$ flux ~~increases~~increased, *A. acuminata* ~~sees~~showed a slight increase in ~~CCI values~~chlorophyll concentration, while *O. xalapensis* ~~has~~had significant decreases in ~~CCI. *B.*~~chlorophyll concentration. *B. nitida* individuals growing on steeper slopes had significantly lower ~~CCI~~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~~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 ~~CCI~~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~~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 difference in regression slope between *B. nitida* and *O. xalapensis* (Fig. 4) may be due to physiological differences across traits or species, and/or due to differences in exposure owing to canopy height differences. Resolving this question would require a much larger multi-species sample size which could only be sufficiently obtained using remote sensing methods. The strong positive correlations between $CO_2$ flux and increasingly heavy $\delta^{13}C$ values suggest that the trees have consistently ~~photosynthesize~~photosynthesized with isotopically heavy excess volcanic $CO_2$ over ~~long time-scales~~the last few years, and are therefore growing in $eCO_2$ conditions. Assuming that ~~all~~most of the variations in $\delta^{13}C$ are caused by ~~uptake~~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):

$$C_v = \cancel{\frac{C_b(\delta_b - \delta_m)}{(\delta_m - \delta_v)}}\frac{(\delta_b - \delta_t)}{(\delta_a - \delta_v)} C_a \qquad (2)$$

where $C_v$ is the mean volcanic excess component of the $CO_2$ concentration in air, ~~$C_b$~~$C_a$ is the atmospheric "background" (i.e., non-volcanic) $CO_2$ concentration, ~~$\delta_b$~~$\delta_a$ is atmospheric $\delta^{13}C$, ~~δm is the difference between background wood $\delta^{13}C$ and another wood $\delta^{13}C$ measurement subtracted from atmospheric δ13C, and~~$\delta_b$ is the most negative $\delta^{13}C$ measurement for the species being studied, $\delta_t$ is the $\delta^{13}C$ value for the tree that volcanic $CO_2$ exposure is being calculated, 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 $\delta_b$~~, $\delta_a$, and $C_a$ 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 115 ppm, bringing the combined mean atmospheric ~~and~~(including volcanic) $CO_2$ concentration tree exposure to potentially around ~520~~550~~ ppm. For *B. nitida* this equation yields ~~124~~133 ppm of mean excess volcanic $CO_2$ at the highest flux location, for a combined total mean of potentially ~538~~524~~ ppm $CO_2$. ~~These calculations show that trees in our study area are consistently exposed to significantly elevated concentrations of $CO_2$.~~ These numbers may be on the high side as the calculation assumes that carbon isotope discrimination remains constant for all trees within a given species, but they serve as estimate of the approximate magnitude of the average amount of $CO_2$ that these trees are exposed to. A tree ring study at Mammoth Mountain found an average yearly volcanic excess $CO_2$ exposure of 20-70 ppm over a 15-year period (Lewicki et al., 2014). Turrialba is significantly more active than Mammoth Mountain, so trees growing in high emission areas of Turrialba may be exposed to similar or higher amounts of $CO_2$ than the tree in the Mammoth Mountain study. Additional measurements of tree core $\delta^{13}C$ and associated soil $CO_2$ fluxes would help corroborate ~~this link, as it is~~our observations, which were based on a limited number of data points. Though tree ring $^{14}C$ content in volcanically active areas has been linked to variations in volcanic $CO_2$ emissions, ~~so~~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)~~.~~, this additional dimension was outside the scope of this exploratory study. However, beyond such pattern confirmation, using $^{14}C$ dating of trees exposed to naturally isotopically distinct excess $CO_2$ is, in fact, unfortunately not a reliable method for these environments due to the well-known $\delta^{14}C$ deficiency in trees exposed to excess volcanic $CO_2$ which is isotopically "dead" with respect to $^{14}C$, creating spurious patterns that preclude dating by $^{14}C$ (e.g., Lefevre et al., 2017; Lewicki et al., 2014).

Our data demonstrate that $CO_2$ fluxes through the soil may be 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, ~~so~~making instantaneous concentration measurements in a single field campaign ~~will~~ not ~~accurately~~ representative of long-term relative magnitudes of $CO_2$ exposure. Soil $CO_2$ fluxes are ~~significantly~~ 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 ~~They~~ can also be affected by variations in barometric pressure, but both of these factors are easily measurable and therefore ~~avoidable~~ 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~~, so current soil $CO_2$ fluxes should give relatively accurate estimates of $CO_2$ exposure over time~~ (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 spatial correlations between volcanically enhanced soil $CO_2$ emissions with co-located 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 $CO_2$) ~~in this~~at the Mammoth Mountain area caused major soil acidification, which led to the tree kill (McGee and Gerlach, 1998). ~~However, we~~We have evidence that those acidification 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 isotopically 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~~None of the trees included in the analysis (displayed obvious signs of stress, from water or other factors, as indicated by their high fluorescence and ~~CCI~~ 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 ~~of necessity~~ 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 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 conclu~~sively~~de~~ say~~ 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 ~~noteworthy~~ 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 CO2 sensors~~

~~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. The data presented in this paper represents roughly the past 2-3 years of growth, so taking $\delta^{13}C$ measurements at regular intervals on the rest 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 has 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 significantly 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). Calibration and wood core dendrochronology via $^{14}C$, tree rings, or chemical event tracers like sulfur spikes, would be needed for this process, which holds significant potential.~~

### 4.3 Time constraints

To support these results, we further assessed the possibility of effects of time constraints on growth rates and isotopic signals, despite the compelling spatial variability of the independent variable (naturally isotopically labelled excess volcanic $CO_2$ ~~sensors~~) in our study (Helle and Schleser, 2004; Verheyden et al., 2004). As tropical trees typically lack tree rings, it is difficult to directly constrain the precise time period that the data represent. However, since we sampled from the outside in, all of the samples appear to at least have the most recent growth period in common. To assess how far back in time our samples could likely represent, we compared our sampled core depths to reported growth rates for the same species in similar environments. Reported growth rates for two of our species, *O. xalapensis* and *A. acuminata*, range from 0.25 - 2.5 cm y-1 and 0.6 - 0.9 cm y-1, respectively (Kappelle et al., 1996; Ortega-Pieck et al., 2011). Given that our samples are bulk measurements of the outer 5 cm of wood, each sample would represent between 2 and 5.5 years, although the conditions that these growth rates were measured in were different than in our study. Clear time constraints would be necessary for higher resolution analysis, but this need is somewhat mitigated by the continuous, long-term, and over multiple decades mostly invariant nature of diffuse volcanic $CO_2$ emissions, which is completely independent of any non-volcanic environmental influences on growth rates. By providing an upper and lower bound in the expected growth span represented in our samples, we believe that these samples represent similar time frames during the continuous exposure to excess volcanic $CO_2$ over the lifetimes of the trees sampled. Due to the continuous nature of the volcanic $CO_2$ enhancement, we are not investigating and analyzing transient events, but our results instead represent spatial variability in excess $CO_2$ availability, averaged over similar time periods.

Although we do not believe our samples represent a long enough time period for long term variations in $\delta^{13}C$ (Seuss effect) to be relevant, if it does affect our samples it would be beneficial for detection of volcanic $CO_2$ as the Seuss effect is gradually increasing the gap between atmospheric and volcanic $\delta^{13}C$. Since our $\delta^{13}C$ values likely represent several years of growth, small scale temporal variations in excess volcanic $CO_2$ release are unlikely to significantly impact the results. Larger trees tend to grow slower than smaller trees, so the outer 5 cm of wood should represent a longer time period on larger trees. Thus, if temporal variations had a significant effect on our $\delta^{13}C$ measurements, we would expect this to be represented by some correlation between DBH and $\delta^{13}C$, which is not present for any species studied. Three of the five *B. nitida* individuals measured were very large (150-190 cm DBH), whereas the other two are much smaller (11.5 and 15.3 cm DBH). Although the age and growth rates of these two groups of trees likely vary significantly, we found no correlation between DBH and $\delta^{13}C$; though we did find a strong correlation between the completely independent diffuse excess (volcanic) $CO_2$ flux and wood $\delta^{13}C$. Furthermore, the relationships presented are on a per species basis to avoid complications resulting from different growth rates across species. This is important because $\delta^{13}C$ values provide an integral value of assimilated carbon by the entire tree (not just individual leaves). The depth of tree core sample was identical for each species (the outermost part of the trunk) and we can safely assume that the volcanic $CO_2$ exposure has been consistent over the time period under investigation.

Because individual time variability of growth rates can possibly affect these signals as well, future studies that attempt to study tree ring isotopes in this context at higher resolutions will likely require stricter and more detailed time constraints and cell-level stress analysis, to average out the effects of long term variations in δ$^{13}$C (Seuss effect), seasonal cycles, potential short-term transient stress-induced growth rate variations, effects of water use efficiency (WUE), and potential short-term variations in CO$_2$ flux, all of which may result in time-averaged isotopic shifts over different growth periods (Helle and Schleser, 2004; Verheyden et al., 2004). We include these notes as guidance in Section 4.4: Lessons Learned for Future Studies. Despite the additional difficulty of conducting higher time resolution analysis, this type of study holds great potential for attempting to reconstruct volcanic CO$_2$ histories and to study its potential fertilization effect, due to the completely independent nature of the volcanic excess CO$_2$ supply to the sub-canopy air.

### 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~~ — one of the largest uncertainties in climate projections. Costa ~~Rican~~Rica's volcanoes~~, as well as several other volcanoes in the country, have~~ are host to large areas of relatively undisturbed ~~primary forest growing on their flanks~~rainforest, 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 ~~to ensure that we are studying~~conclusively. One open question for example is how WUE in upper and lower canopy leaves of same and different individuals within a species may affect isotopic sequestration of CO$_2$. Since the excess volcanic CO$_2$ is naturally isotopically labelled, this could be assessed by a much more detailed by-individual tree leaf, branch, and xylem core study coupled with long-term measurements of evapotranspiration, heat stress, and stomatal conductance, the latter of which in our study showed no significant correlation with the δ$^{13}$C signal ~~rather than noise. Unfortunately,~~in the wood cores across spatial gradients. Field data can be difficult to acquire in these ~~environments as the terrain is~~ rugged and ~~often has very steep slopes that can be~~ challenging ~~to work around.~~environments. A remote sensing ~~campaign~~approach using airborne measurements~~ from drones and/or airplanes would circumvent this problem, and we would strongly recommend pursuing this approach in conjunction with~~, validated by targeted representative ground ~~based measurements.~~campaigns, could provide sufficiently large data sets to represent species diversity and conditions appropriately. Many of the datatypes that would be useful for this type of study can be acquired from airborne ~~instruments~~platforms, and ~~airborne~~remote sensing instruments can quickly produce the massive datasets ~~that would be~~ required to provide more comprehensive answers to these questions~~. There are six other forested active volcanoes in Costa Rica 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$_2$~~.

Our results also offer significant new tools for the volcanology, where reconstructing past volcano behavior through eruption histories is hampered by severe preservation gaps in the stratigraphic record. A strong link between δ$^{13}$C and volcanic CO$_2$ could be a game-changer by establishing long-term histories of volcanic CO$_2$ emission variations . These proxy signals could be traced back in time using living and preserved dead trees, in order to fill gaps in the historical and monitoring records – a boon for volcano researchers and observatories to improve eruption prediction capabilities (Newhall et al., 2017; Pyle, 2017; Sparks et al., 2012). However, this would require orders of magnitudes more analyses than currently done in volcanology. While variations in tree ring $^{14}$C content have been shown to correlate well with variations in volcanic $CO_2$ flux (Evans et al., 2010; Lefevre et al., 2017; Lewicki and Hilley, 2014), $^{13}$C is inexpensive to measure at more laboratories, allowing for substantially more data to be acquired. Independent validation, and calibration by wood core dendrochronology via $^{14}$C, tree rings, or chemical event tracers like sulfur isotopes, could significantly advance the concept of using wood carbon as archives of past degassing activity. Furthermore, knowledge of the short-term real-time response of leaves to diffusely emitted $eCO_2$, 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).

## 5 Conclusions

~~We identified multiple~~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 cold-emitted through soils into overlying forests. These isotopically heavy ~~diffuse~~ volcanic $CO_2$ emissions, which are mostly invariant, not accompanied by acidic gases, and independent of processes affecting growth rates, are well correlated with increases in heavy carbon signatures in wood cores from two species of tropical trees~~. Confounding~~, possibly suggesting long-term incorporation of enhanced levels of volcanically emitted $CO_2$ into biomass. Each tree studied was co-located with a soil $CO_2$ flux measurement and their soil $CO_2$ flux signals vary spatially around a continuous long-term local natural excess volcanic $CO_2$ source, which creates a local $CO_2$ gradient within which all the sampled trees are found. The excess volcanic $CO_2$ through local fault-bound gas seeps provides continuous exposure to all sampled trees over time scales much greater than the lifetimes of individual trees. Based on our limited exploratory measurements, confounding factors that are known to influence $\delta^{13}$C values in wood appear not to have significantly affected our measurements, indicating that the heavier wood ~~isotope~~$\delta^{13}$C values ~~are most likely~~could be 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 ~~the~~ short-term variations in elevated $CO_2$ emissions may measurably affect trees growing in areas of diffuse volcanic gas 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, which is 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 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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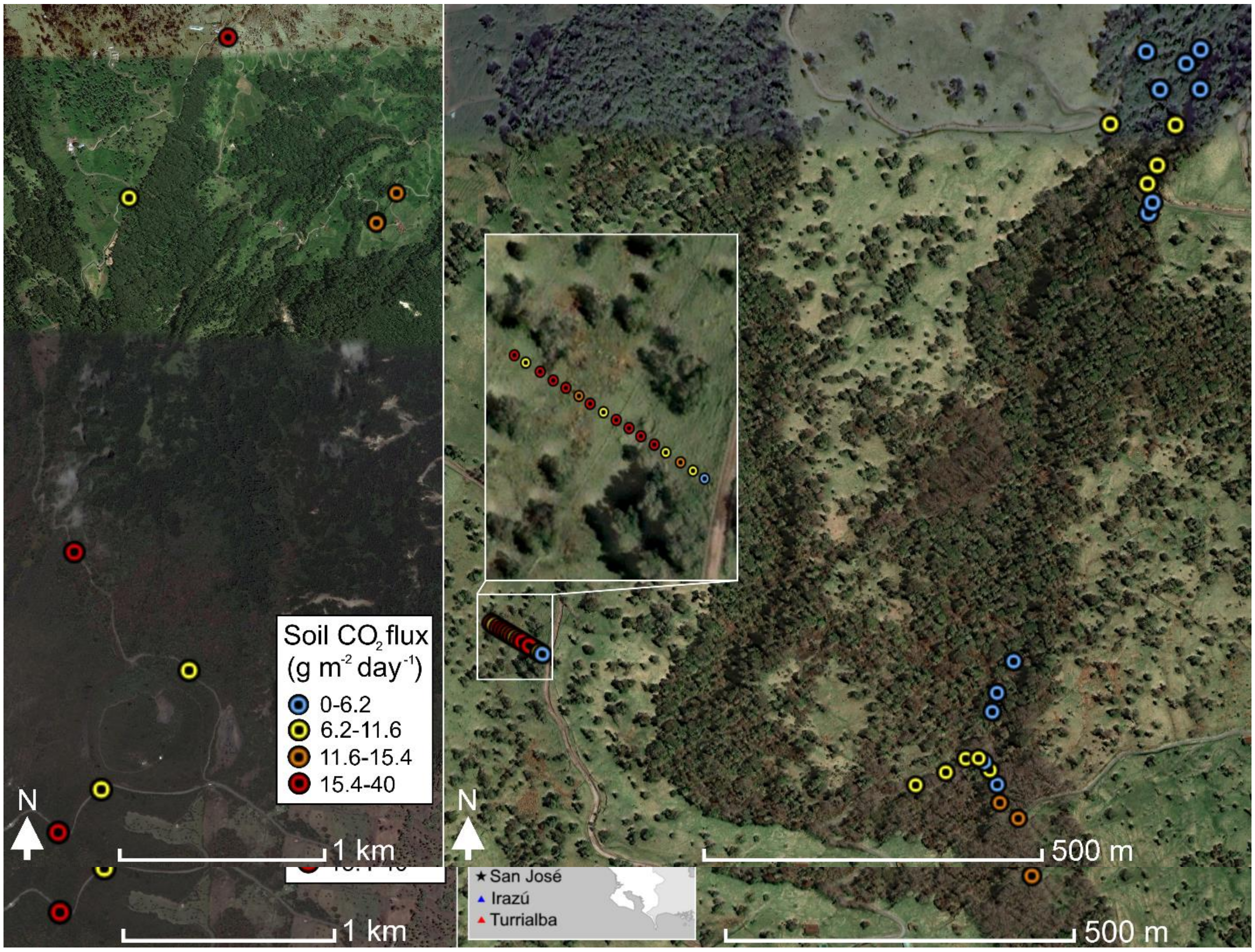


~~**Fig. 1: Distribution of mean soil CO$_2$ flux across north flank of Irazú (left) and south flank of Turrialba (right). Color of dots corresponds to flux population (see Fig. 3).**~~ **Fig. 1: Overview of measurement locations in two old-growth forests on the upper flanks of two active volcanoes in 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).**

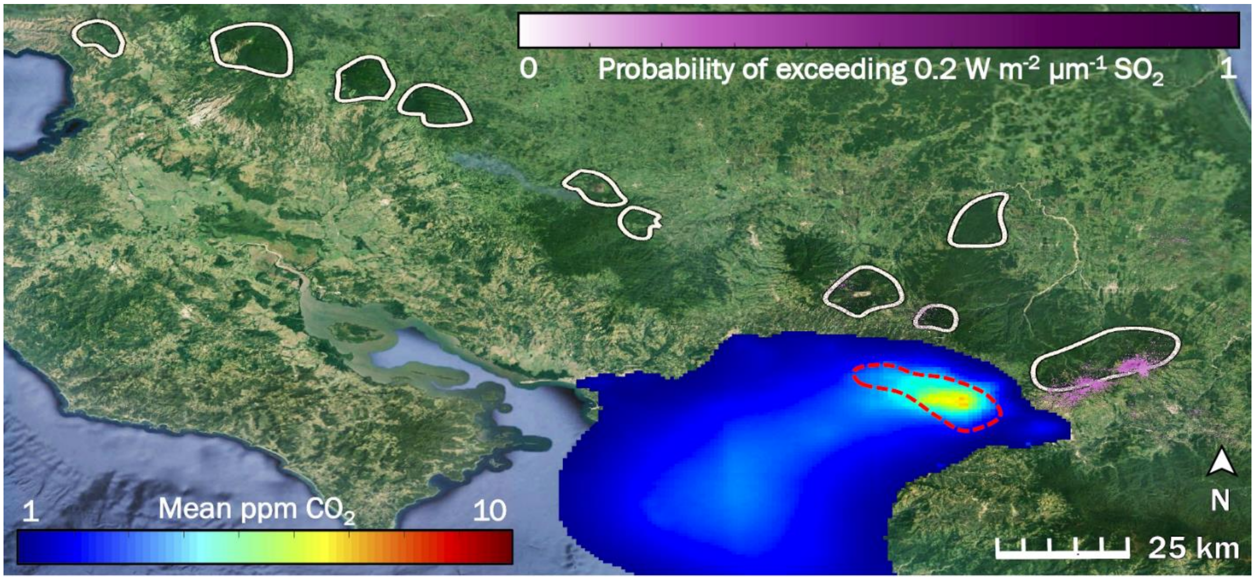
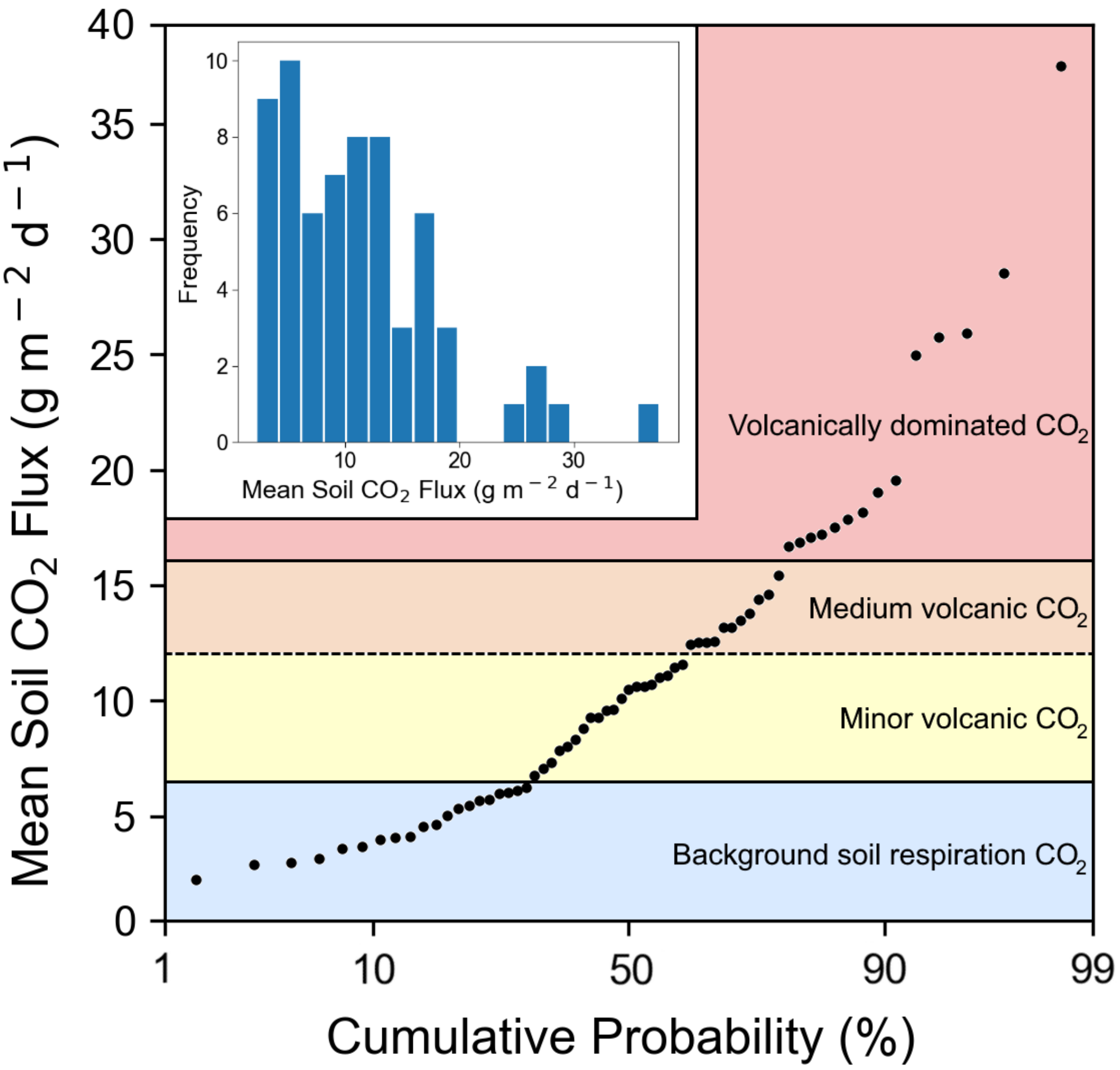


**Fig. 2: ~~Influence~~The influence of two potentially confounding gases on our study area (right hand white polygon) in Costa Rica is low to non-existent: anthropogenic $CO_2$ from San José (blue to red color scale), and ~~volcanically-sourced~~volcanic $SO_2$ ~~is low to non-existent in our study area (bottom-right white polygon~~(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~~, as well as the rest of the forested volcanic edifices in Costa Rica~~ and from all other white polygons.**



~~Fig 3: Four different populations of soil $CO_2$ flux identified by using a cumulative probability plot, as described in Sinclair 1974. Data is split into different populations based on natural breaks within the data. Populations are color-coded based on the same color scale as Fig. 1.~~ 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 CO2 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.

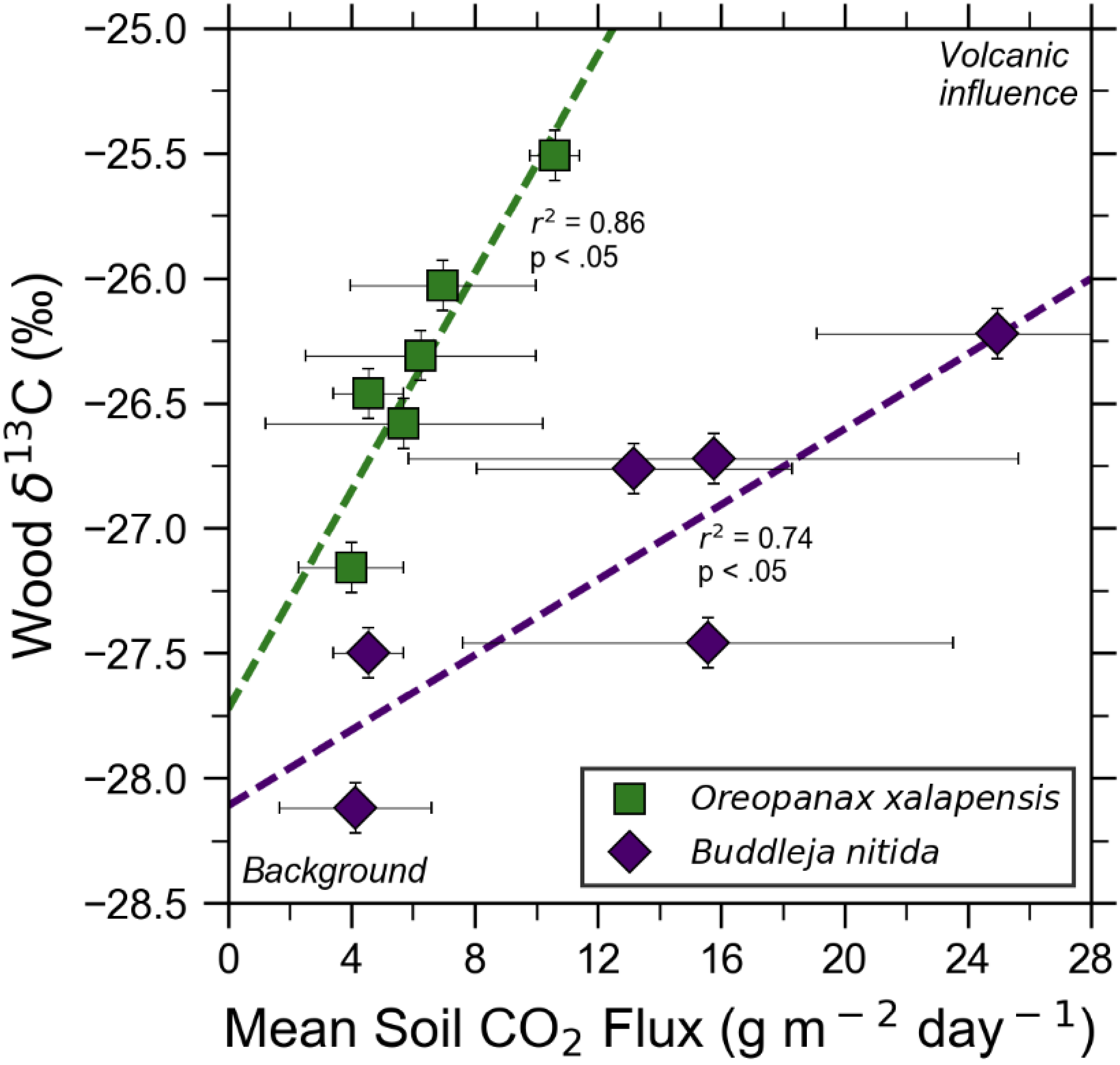


**Fig 4: Bulk wood $\delta^{13}C$ of trees on Costa Rica's Turrialba volcano shows strong correlations with increasing $CO_2$ flux for two species, ~~both~~ *O. xalapensis* and *B. nitida*, indicating long-term photosynthetic incorporation of isotopically heavy volcanic $CO_2$. Stable carbon isotope ratio ($\delta^{13}C$) of wood cores are plotted against soil $CO_2$ flux measured immediately adjacent ~~next~~ to the tree that the core sample was taken from. ~~*A. acuminata* is not plotted due to lack of data.~~ Background and volcanic influence labels apply to both axes – higher $CO_2$ flux and heavier (less negative) $\delta^{13}C$ values are both characteristic ~~associated with~~ of volcanic $CO_2$ emissions.**

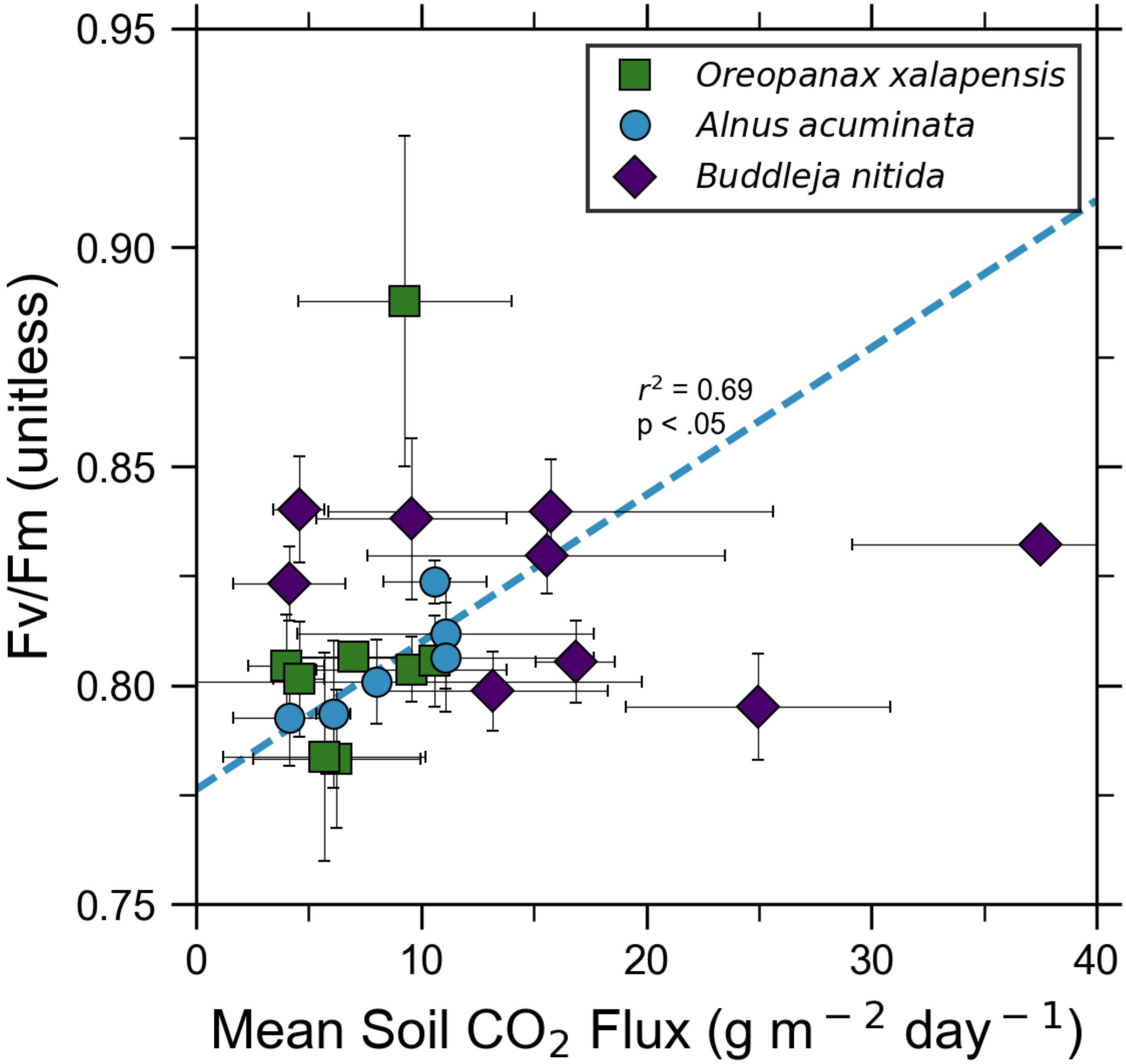
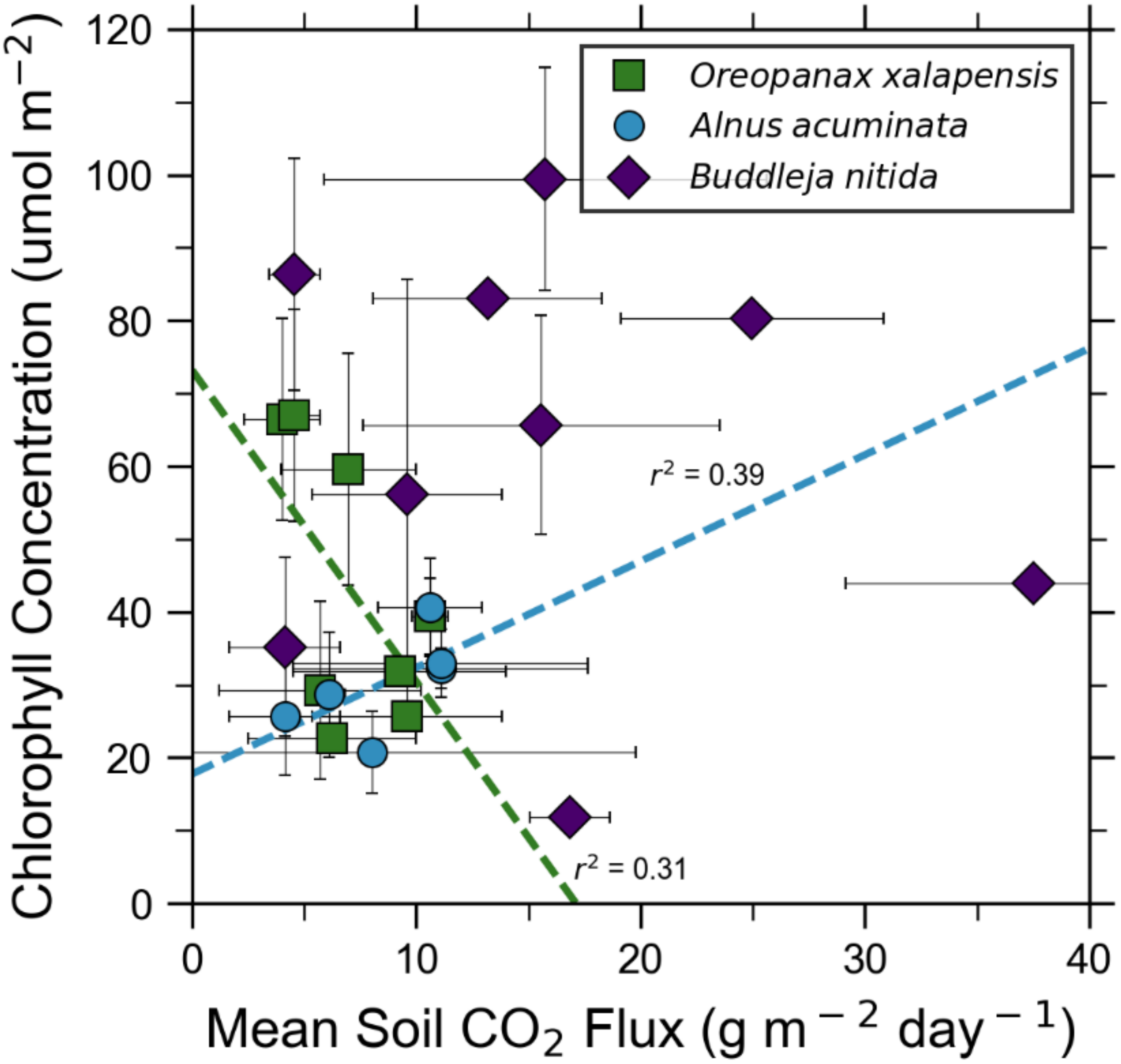


**Fig. 5: Photosynthetic activity of some tree species in old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú, may show short-term response to volcanically elevated $CO_2$. Leaf fluorescence (Fv/Fm) and soil $CO_2$ flux were strongly correlated for *A. acuminata*,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



~~**Fig. 6: Chlorophyll concentration index (CCI) shows opposing trends for different species when plotted against soil $CO_2$ flux. The linear fit for *B. nitida* was omitted for lack of significance.**~~ **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.**

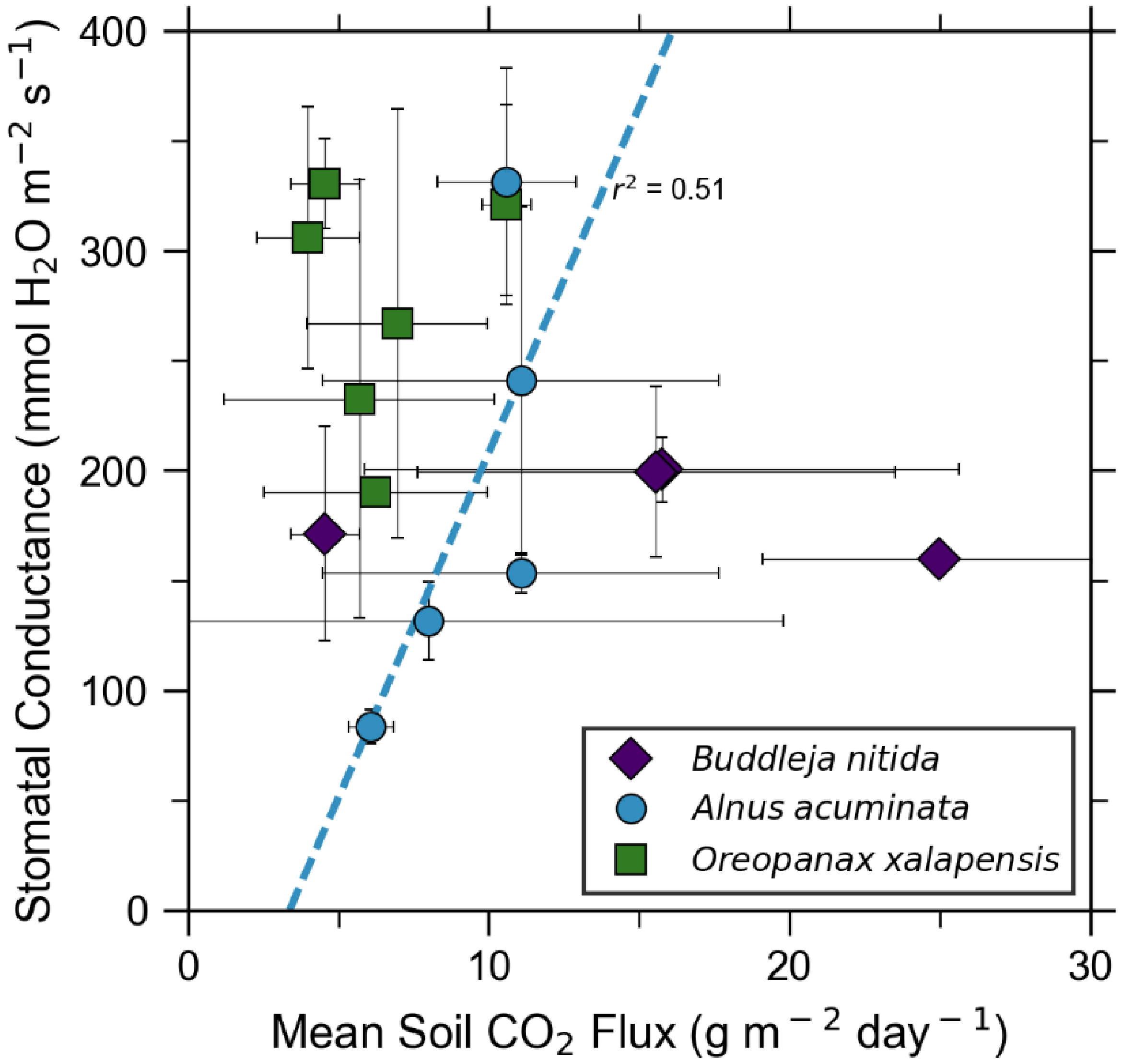


**Fig. 7: Leaf stomatal conductance** of a tree species that strongly responds to volcanically elevated ~~has two weak positive correlations with~~ **$CO_2$** ~~flux~~(Figs. 5, 6) has positive correlations with volcanic CO2 flux, consistent with increased gas-exchange.~~, although both are hindered by lack of data. Neither line had p < .05. The linear fit for *O. xalapensis* was omitted for lack of significance.~~

## ~~6~~ Supplementary Info

~~We created a figure to show how $CO_2$ emissions vary spatially along radial transects across volcanoes from around the world. To do this, we took published data from a variety of volcanoes, either in the form of individual point measurements or spatially simulated flux maps. Because magnitude of $CO_2$ emissions varies significantly between volcanoes, we took the $\log_{10}$ of the flux or concentration values and then transformed these values into a relative scale from 0 to 1, where 1 was the maximum flux or concentration at a specific volcano. For some groups of transects that had similar magnitudes of $CO_2$ emissions they were all put on the same relative scale. All $CO_2$ data was then linearly detrended. The distance along the radial transect was also put into a relative scale from 0 to 1, where 0 was the beginning of the transect and 1 was the end of the transect. The volcanoes and publications we took data from are as follows: Arenal (Williams-Jones, 1997), Teide (Hernández et al., 1998), Furnas (Viveiros et al., 2010), Vesuvius (Frondini et al., 2004), Vulcano (Schwandner et al., 2004), Cerro Negro (Salazar et al., 2001), Etna (Allard et al., 1991), Irazú (our collected data), and Mammoth Mountain (Werner et al., 2014).~~

We analyzed how $CO_2$ emissions vary spatially along radial transects across a sample of volcanoes from around the world. We used published data from a variety of volcanoes, either in the form of individual point measurements or spatially simulated flux maps. Because magnitude of $CO_2$ emissions varies significantly between volcanoes, we took the $\log_{10}$ of the flux or concentration values and then transformed these values into a relative scale from 0 to 1, where 1 was the maximum flux or concentration at a specific volcano. For some groups of transects that had similar magnitudes of $CO_2$ emissions they were all put on the same relative scale. All $CO_2$ data was then linearly detrended. The distance along the radial transect was also put into a relative scale from 0 to 1, where 0 was the beginning of the transect and 1 was the end of the transect. The volcanoes and publications we took data from are as follows: Arenal (Williams-Jones, 1997), Teide (Hernández et al., 1998), Furnas (Viveiros et al., 2010), Vesuvius (Frondini et al., 2004), Vulcano (Schwandner et al., 2004), Cerro Negro (Salazar et al., 2001), Etna (Allard et al., 1991), Irazú (our collected data), and Mammoth Mountain (Werner et al., 2014). The data plotted in the supplemental Figure 1 show that all volcanoes studied show significant variations in volcanic $CO_2$ flux across their flanks, likely due to varying permeability (substrate) and fracture-controlled advective transport of $CO_2$ feeding these emissions from depth. These variations allow to study volcanically enhanced levels of $CO_2$ emissions as proxies for future atmospheric conditions via two modes: a local, substrate- and altitude-independent mode on the order of 50-200 meters, and a broad-scale enhancement mode, covering much of the volcanic flanks (distances on the order of 5-20 km) at lower levels of enhancements.

To validate the understanding that $CO_2$ in sub-canopy air is highly variable and not well mixed, while $eCO_2$ flux through the soil to the atmosphere is highly stable, we assessed the differences in variability between instantaneous concentrations in sub-canopy air and that inside the measurement chamber. The $CO_2$ concentration in air were collected at approx. 0.2 m and 2.0 m above ground level, before and after flux measurements were performed. Supplemental figure 2 shows a sample of near-simultaneous $CO_2$ concentrations recorded on March 24, 2017 at ground level (0.2 m agl) and at 2 m above ground, at a site near the Arieta Fault, in unmanaged forest ~1.3 km southwest of Turrialba's central crater, a site of known high eCO$_2$ flux (Epiard et al., 2017). CO$_2$ concentrations inside the measurement chamber during soil-to-atmosphere eCO$_2$ flux measurements show continuous and highly stable addition of eCO$_2$ to the chamber air from below. The measurements in the sub-canopy air consistently showed very high variability. For instantaneous survey measurements of eCO$_2$ over a range of sites, long-term averaging and flux modeling to assess in-canopy exposure enhancements is not feasible. In contrast, emission of eCO$_2$ through the soil can be quickly and stably assessed in surveys using in-situ chamber flux measurements. The excess component (relative to the regional background) that is closer to the ground likely represents a stronger volcanic eCO$_2$ portion from the direct area of emission measured on the ground, than the excess component shown in the 2 m above ground data, which show stronger temporary deviations. Because absolute mean eCO$_2$ exposures at canopy level are hard to assess, we utilize the highly stable emission rates of volcanic eCO$_2$ through the soil as a relative proxy for long-time eCO$_2$ exposure differences between sites.

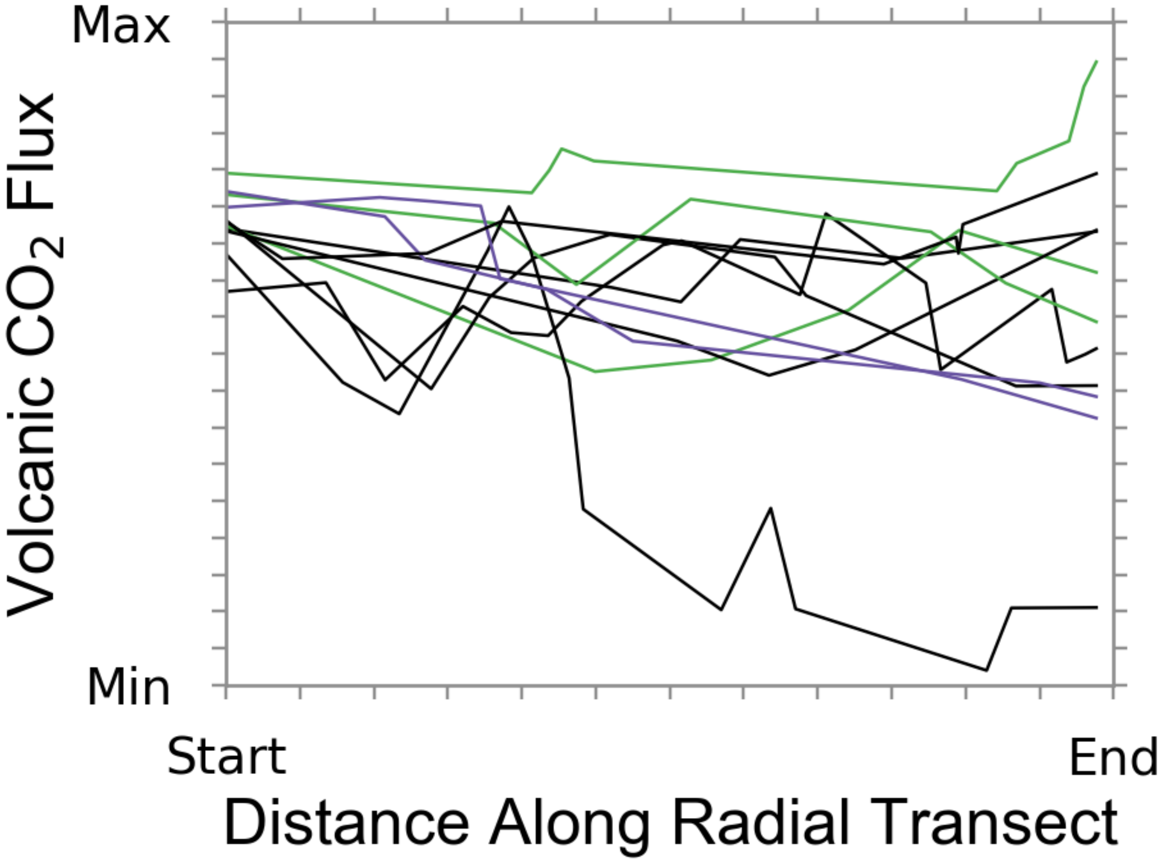


**Fig. S1: CO$_2$ flux varies significantly along radial transects from 11 volcanoes around the world.**

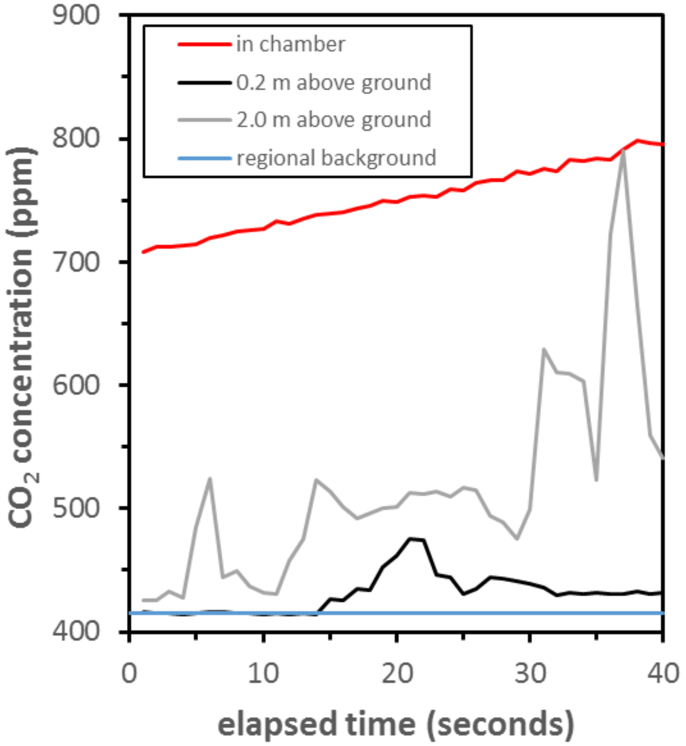


**Fig. S2: $CO_2$ concentrations and fluxes in sub-canopy air are highly variable, while soil-to-atmosphere $eCO_2$ fluxes are stable representations of long-term $eCO_2$ addition (March 24, 2017, in a forest near the Ariete fault on Turrialba volcano).**

| Species | Latitude | Longitude | Max $CO_2$ flux (g $m^{-2}$ $day^{-1}$) | Mean $CO_2$ flux (g $m^{-2}$ $day^{-1}$) | $CO_2$ flux 1σ | $\delta^{13}C$ (‰) | CCI | CCI 1σ | Chlorophyll concentration (umol m^-2) | Chlorophyll concentration 1σ | Fv/Fm | Fv/Fm 1σ | $g_s$ | $g_s$ 1σ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A. acuminata | 10° 0'14.42"N | 83°46'7.31"W | 7.1 | 6.1 | 0.7 | -26.1 | 28.7 | 8.6 | 452.4 | 135.5 | 0.793 | 0.017 | 83.5 | 7.8 |
| A. acuminata | 10° 0'17.87"N | 83°46'9.20"W | 18.5 | 11.1 | 6.6 | -26.58 | 32.3 | 2.7 | 485.6 | 41.1 | 0.812 | 0.013 | 153.5 | 9.2 |
| A. acuminata | 10° 0'18.52"N | 83°46'7.11"W | 6.5 | 4.1 | 2.5 | -24.48 | 25.7 | 8.0 | 423.5 | 132.7 | 0.793 | 0.011 | | |
| A. acuminata | 10° 0'17.69"N | 83°46'8.72"W | 18.5 | 11.1 | 6.6 | -26.22 | 33.0 | 4.7 | 491.8 | 70.0 | 0.806 | 0.013 | 241.0 | 79.2 |
| A. acuminata | 9°59'52.79"N | 83°46'13.90"W | 8.8 | 8.0 | 0.8 | -25.76 | 20.8 | 5.6 | 371.9 | 100.7 | 0.801 | 0.010 | 131.5 | 17.7 |
| A. acuminata | 9°59'52.45"N | 83°46'14.53"W | 13.0 | 10.6 | 2.3 | -26.24 | 40.7 | 6.7 | 556.1 | 91.5 | 0.824 | 0.005 | 331.5 | 51.6 |
| B. nitida | 9°58'60.00"N | 83°50'9.15"W | 15.7 | 9.6 | 4.2 | | 56.1 | 29.6 | 669.4 | 352.8 | 0.838 | 0.018 | | |
| B. nitida | 9°59'16.85"N | 83°50'26.77"W | 18.1 | 16.8 | 1.8 | | 11.9 | 0.1 | 259.6 | 2.5 | 0.805 | 0.009 | | |
| B. nitida | 10° 0'41.38"N | 83°50'4.43"W | 43.4 | 37.5 | 8.4 | | 44.0 | 1.9 | 582.0 | 24.8 | 0.832 | 0.004 | | |
| B. nitida | 10° 0'14.38"N | 83°46'6.65"W | 18.7 | 13.2 | 5.1 | -26.76 | 83.1 | 1.4 | 834.6 | 14.5 | 0.799 | 0.009 | | |
| B. nitida | 10° 0'18.54"N | 83°46'7.15"W | 6.5 | 4.1 | 2.5 | -28.12 | 35.2 | 12.3 | 510.9 | 178.5 | 0.823 | 0.009 | | |
| B. nitida | 10° 0'15.89"N | 83°46'10.65"W | 31.5 | 25.0 | 5.9 | -26.22 | 80.3 | 1.9 | 819.0 | 19.4 | 0.795 | 0.012 | 160.0 | 0.0 |
| B. nitida | 9°59'56.46"N | 83°46'31.92"W | 5.7 | 4.6 | 1.1 | -27.5 | 86.4 | 15.9 | 852.7 | 156.6 | 0.840 | 0.012 | 171.3 | 48.9 |
| B. nitida | 9°59'57.83"N | 83°46'33.99"W | 19.7 | 15.7 | 9.9 | -26.72 | 99.5 | 15.3 | 921.9 | 141.5 | 0.840 | 0.012 | 200.5 | 14.8 |
| B. nitida | 9°59'55.11"N | 83°46'36.36"W | 21.5 | 15.6 | 7.9 | -27.46 | 65.7 | 15.1 | 731.8 | 167.8 | 0.830 | 0.009 | 199.5 | 38.9 |
| O. xalapensis | 9°58'60.00"N | 83°50'9.15"W | 15.7 | 9.6 | 4.2 | | 25.7 | 2.1 | 424.0 | 34.2 | 0.804 | 0.007 | | |
| O. xalapensis | 10° 0'11.84"N | 83°49'39.52"W | 9.3 | 9.3 | 4.7 | | 31.9 | 0.9 | 482.0 | 14.1 | 0.888 | 0.038 | | |
| O. xalapensis | 10° 0'20.32"N | 83°46'7.94"W | 8.8 | 6.2 | 3.7 | -26.31 | 22.7 | 2.0 | 393.2 | 35.3 | 0.783 | 0.016 | 190.0 | 0.0 |
| O. xalapensis | 9°59'56.41"N | 83°46'12.18"W | 12.2 | 5.7 | 4.5 | -26.58 | 29.3 | 12.2 | 458.5 | 191.2 | 0.784 | 0.024 | 232.5 | 99.7 |
| O. xalapensis | 9°59'51.80"N | 83°46'14.70"W | 24.2 | 10.6 | 11.8 | -25.51 | 39.4 | 5.2 | 546.1 | 72.2 | 0.806 | 0.010 | 321.0 | 45.3 |
| O. xalapensis | 9°59'52.21"N | 83°46'12.76"W | 10.0 | 7.0 | 3.0 | -26.03 | 59.6 | 15.9 | 692.3 | 185.1 | 0.807 | 0.001 | 267.0 | 97.6 |
| O. xalapensis | 9°59'50.79"N | 83°46'12.73"W | 5.5 | 4.0 | 1.7 | -27.16 | 66.5 | 13.9 | 736.8 | 153.5 | 0.804 | 0.012 | 306.0 | 59.4 |
| O. xalapensis | 9°59'56.47"N | 83°46'31.92"W | 5.7 | 4.6 | 1.1 | -26.46 | 67.0 | 14.5 | 740.1 | 160.4 | 0.801 | 0.013 | 330.5 | 20.5 |

Table S1: Data used to generate all plots.

| Species | Latitude | Longitude | Altitude (m) | Pressure (mbars) | Humidity (%) | PAR (μmol m$^{-2}$ s$^{-1}$) | Air T (°C) | Leaf T (°C) | Wind (m/s) | Aspect (degrees) | Slope (degrees) | DBH (cm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A. acuminata | 10° 0'14.42"N | 83°46'7.31"W | 2638 | 734.4 | 64 | 198 | 15.8 | 16 | 0 | 270 | 5 | 24.9 |
| A. acuminata | 10° 0'17.87"N | 83°46'9.20"W | 2640 |  | 70.55 | 150 | 12.5 | 13 |  |  | 0 | 14.3 |
| A. acuminata | 10° 0'18.52"N | 83°46'7.11"W | 2636 | 734.6 | 77.1 | 110 | 13.7 | 14.1 | 0 | 215 | 60 | 23 |
| A. acuminata | 10° 0'17.69"N | 83°46'8.72"W | 2633 | 734.8 | 84.5 | 173 | 15.5 | 15.4 | 0 | 290 | 5 | 45.3 |
| A. acuminata | 9°59'52.79"N | 83°46'13.90"W | 2432 |  | 64.9 | 200 | 15 | 15.4 |  | 135 | 25 | 58 |
| A. acuminata | 9°59'52.45"N | 83°46'14.53"W | 2434 |  | 65.2 | 325 | 15.4 | 15.5 |  | 110 | 20 | 90.3 |
| B. nitida | 9°58'60.00"N | 83°50'9.15"W | 3016 | 700 | 86.5 | 363 | 10.8 | 11.3 | 0 | 140 | 45 | 22.7 |
| B. nitida | 9°59'16.85"N | 83°50'26.77"W | 2968 |  |  | 94 | 12 | 11.2 |  | 20 | 50 | 50.2 |
| B. nitida | 10° 0'41.38"N | 83°50'4.43"W | 2322 | 763.7 | 84.4 | 86 | 12.9 | 13.4 | 0.5 | 120 | 55 | 43.5 |
| B. nitida | 10° 0'14.38"N | 83°46'6.65"W | 2619 | 735.9 | 67.6 | 800 | 12.6 | 13.4 | 1.7 | 190 | 35 | 15.3 |
| B. nitida | 10° 0'18.54"N | 83°46'7.15"W | 2615 | 736.4 | 89.5 | 172 | 13.4 | 12.9 | 0.4 | 215 | 60 | 11.5 |
| B. nitida | 10° 0'15.89"N | 83°46'10.65"W | 2625 |  | 85.7 | 334 | 13.6 | 13.8 | 1 | 200 | 15 | 26 |
| B. nitida | 9°59'56.46"N | 83°46'31.92"W | 2515 | 745.8 | 49.3 | 128 | 13.7 | 14 | 0 | 250 | 25 | 190 |
| B. nitida | 9°59'57.83"N | 83°46'33.99"W | 2511 | 746.2 | 67.7 | 157 | 13.9 | 13.9 | 0.2 | 180 | 5 | 180 |
| B. nitida | 9°59'55.11"N | 83°46'36.36"W | 2514 | 745.9 | 78.2 | 98 | 12.8 | 12.9 | 0 | 125 | 10 | 150 |
| O. xalapensis | 9°58'60.00"N | 83°50'9.15"W | 3016 | 700 | 86.5 | 43 | 10.4 | 10 | 0 | 45 | 58 | 15 |
| O. xalapensis | 10° 0'11.84"N | 83°49'39.52"W | 2101 | 785.4 | 100 | 37 | 15.4 | 15.2 | 0 | 80 | 30 | 11 |
| O. xalapensis | 10° 0'20.32"N | 83°46'7.94"W | 2619 | 736.1 | 77.9 | 170 | 13.5 |  | 0 | 150 | 55 | 15.4 |
| O. xalapensis | 9°59'56.41"N | 83°46'12.18"W | 2437 | 753 | 64.7 | 29 | 12 | 11.8 | 0 | 190 | 15 | 20.2 |
| O. xalapensis | 9°59'51.80"N | 83°46'14.70"W | 2438 |  | 65.5 | 325 | 14.7 | 14.7 |  | 190 | 55 | 20.3 |
| O. xalapensis | 9°59'52.21"N | 83°46'12.76"W | 2439 |  | 65.7 | 388 | 15.5 | 14.9 |  | 310 | 40 | 25 |
| O. xalapensis | 9°59'50.79"N | 83°46'12.73"W | 2438 | 752.9 | 65.8 | 338 | 17.7 | 17.7 | 0 | 285 | 60 | 22.5 |
| O. xalapensis | 9°59'56.47"N | 83°46'31.92"W | 2515 | 745.8 | 49.3 | 553 | 13.9 | 17.4 | 0 | 250 | 25 | 27.2 |

Table S2: Supplementary info for data presented in Table S1.

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