Pasadena, CA July 19, 2018

Re: bg-2018-100, “Plant responses to volcanically-elevated CO2 in two Costa Rican forests”, Revision 1

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, which we answered in detail on May 29th, 2018 online in the Interactive Discussion. Both reviewers highlighted the utility and great potential of using elevated CO_2 from volcanoes to understand long-term changes on ecosystems and plant physiology. We made careful revisions accordingly, to address all comments appropriately.

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 CO2 in two Costa Rican forests

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REV1 (2018-07-19)

Structure of this document:

Referee 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. Line and page numbers are indicated.

[C1-C5]… page references to the interactive discussion documents refer to the author's responses documents, which fully quote all concerns and suggestions raised by the reviewers, as well as the author's responses.

Changes made independently of the reviewer's comments:

Very few 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 CO2 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.

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. Future studies should expand the scope of this study.

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:
REV 1 p. 4 L105; p.5 LL142-147; p.6 L189; p.8 LL257-264; Supplement:
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.
REV 1 p.6 LL191-195:
For analogous growth rates, we added wording and references in section 2.5.

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:
REV 1 p.6 LL191-195:
For analogous growth rates, we added wording and references in section 2.5. [action repeatedly mentioned below]

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:

REV 1 p.13-14 LL446-450:

We added clarifying wording in the discussion (also answers referee #2's "Line 388" and "Line 426" comments).

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:

REV 1 p.2 L43; p.9 LL278-287:

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.

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:
REV 1 p.5 L134:
No action taken as none was requested.

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:
REV 1 p.2 L50:
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:
REV 1 p.3 L74:
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:
REV 1 p.3 L88:
Added reference to Fig 1

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:
REV 1 p.5 L129:
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:
REV 1 p.6 L189:
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:
REV 1 p.6 LL191-195:
Added literature growth rates for comparison (incl. a new reference), and wording to put it into context.

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:

REV 1 p.6 L192:

Added sentence to conclusions.

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:

REV 1 p.7 LL210-213; p9 LL278-287:

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.

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:

REV 1 p.8 LL244, 246, 248-250:

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:

REV 1 p.9 LL271; p.10 LL304-306:

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 will add lines to the discussion to clarify this.

AUTHOR’s changes in revised manuscript:

REV 1 p.8 LL257-264; Supplement text:

Added clarifying wording.

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:
REV 1 p.9 L294:
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:
REV 1 p.9 L291:
We clarified this with an addition in the first sentence of 3.2.

REFEREE #1 (AC1) Comment [C4-C5]: "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:
REV 1 p.9-10 LL295-306:
We reworked this section to improve flow and add clarity. Also added 2 references (1 new) 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 the discussion and the latter sections (section 4.3), which answers one of the later requests by the referee, to merge original version sections 4.3 and 4.4 (now combined as Section 4.3).

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:
REV 1 p.11 LL338-341:
Added sentences to reflect our reply.

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:
<u>REV 1 p.11 LL352-353:</u>
Added clarifying wording. Note that the localized ambient mean concentration may deviate from the broader scale mean background.

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:
<u>REV 1 p11 LL361-364:</u>
We edited this sentence to clarify what we studied and what we didn't study.

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:
<u>REV 1 P4 L116, p12 L394:</u>
Added statement on number of samples (Rev 1 L 116) and clarifying sentence (Rev p12 L394 = orig. L352).

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:
<u>REV 1 p.13-14 LL422-455:</u>
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:
<u>REV 1 p.14 LL447-449:</u>
We clarified this sentence.

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:

REV 1 p.14 L457:
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:
REV 1 p.14 L462:
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).

References added in Revision 1: **(listed alphabetically here)**

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**

Eatough, D.J., Caka, F.M. and Farber, R.J.: The conversion of SO2 to sulfate in the atmosphere, Israel J. Chem., 34(3-4), 301-314, 1994. **Citation added to section 3.1**

Giammanco, S., Gurrieri, S. and Valenza, M.: Soil CO2 degassing along tectonic structures of Mount Etna (Sicily): the Pernicana fault, Appl. Geochem., 12(4), 429-436, 1997. **Citation added to section 3.2**

Jenkins, M.W., Krofcheck, D.J., Teasdale, R., Houpis, J. and Pushnik, J.: Exploring the edge of a natural disaster, Open J. Ecol., 2(04), 222-232, 2012. **Citation added to section 3.1**

Oppenheimer, C., Francis, P. and Stix, J.: Depletion rates of sulfur dioxide in tropospheric volcanic plumes, Geophys. Res. Lett., 25(14), 2671-2674, 1998. **Citation added to section 3.1**

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. Manage., 261(7), 1336-1343, 2011. **Citation added to section 2.5**

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

1 Introduction

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

Free Air CO_2 Enrichment (FACE) experiments have been conducted to probe this question, but none have been conducted in tropical ecosystems (e.g. Ainsworth and Long, 2005; Norby et al., 2016). Some studies have used CO_2-emitting natural springs to study plant responses to elevated CO_2, but these have been limited in scope due to the small spatial areas around springs that experience elevated CO_2 (Paoletti et al., 2007; Saurer et al., 2003). These studies have suffered from several confounding influences, including other gas species that accompany CO_2 emissions at these springs, human disturbances, and difficulty with finding appropriate control locations. Additionally, none have been conducted in the tropics (Pinkard et al., 2010). A series of studies in Yellowstone National Park (USA) used its widespread volcanic hydrothermal CO_2 emissions for the same purpose, though it is not in the tropics (Sharma and Williams, 2009; Tercek et al., 2008). Yellowstone was particularly suitable for this type of study, due to its protected status as a National Park, and because the large areas of CO_2 emissions made control points more available (Sharma and Williams, 2009; Tercek et al., 2008). These studies reported changes in rubisco, 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 the effects of diffuse volcanic flank gas emissions on the overlying ecosystems remain largely unknown. Most previous studies focused on extreme conditions, such as tree kill areas associated with extraordinarily high CO_2 emissions at Mammoth Mountain, CA (USA) (Biondi and Fessenden, 1999; Farrar et al., 1995; Sorey et al., 1998). However, the non-lethal effects of volcanic CO_2—away from the peak emission zones, but still in the theorized fertilization window—have received little attention, and could offer a new approach to studying the effects of elevated CO_2 on ecosystems (Cawse-Nicholson et al., 2018). The broad flanks of active volcanoes experience diffuse emissions of excess CO_2 because the underlying active magma bodies continuously release gas, dominated by CO_2 transported to the surface along fault lines (Chiodini et al., 1998; Dietrich et al., 2016; Farrar et al., 1995). This process has frequently been studied to understand the dynamics of active magma chambers and to assess potential volcanic hazards (Chiodini et al., 1998; Sorey et al., 1998). These emissions are released through faults and fractures on the flanks of the volcano (Burton et al., 2013; Pérez et al., 2011; Williams-Jones et al., 2000)(see Supplementary Figure S1). Volcanic flanks through which these gases emanate are broad, covering typically 50-200 km^2, often supporting well-developed, healthy ecosystems. Some of these faults tap into shallow acid hydrothermal aquifers, but by the time these gases reach the surface of most forested volcanoes, soluble and reactive volcanic gas species (e.g., SO_2, HF, HCl, H_2S) have been scrubbed out in the deep subsurface, leading to a diffusely emanated gas mix of predominantly CO_2 with minor amounts of hydrogen, helium, and water vapor reaching the surface (Symonds et al., 2001).

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

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

2 Methods

2.1 Investigated locations and sampling strategy

Irazú and Turrialba are two active volcanoes located ~25 and 35 km east of San José, Costa Rica (Fig. 1). These two volcanoes are divided by a large erosional basin. The two volcanoes cover approximately 315 km^2, which is significantly larger than the average forested active volcanic edifice in Costa Rica at 122 km^2. The vast majority of the northern flanks of Irazú and Turrialba are covered in legally protected dense old-growth forest, while the southern flanks are dominated by pasture land and agriculture. Turrialba rises 3,300 m above its base and has been active for at least 75,000 years with mostly fumarolic activity since its last major eruption in 1866 (Alvarado et al., 2006). It has experienced renewed activity beginning in 2010, and its current activity is primarily characterized by a near-constant volcanic degassing plume, episodic minor ash emissions, and fumarolic discharges at two of the summit craters, as well as significant diffuse and fumarolic gas emissions across its flanks, focused along fault systems (Martini et al., 2010). Turrialba's CO_2 emissions in areas proximal to the crater were calculated at 113 ± 46 tons/d (Epiard et al., 2017). The Falla Ariete (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~~ fault has significantly heavier $\delta^{13}C$ values clustered around -3.4 ‰ (Malowany et al., 2017).

Irazú has been active for at least 3,000 years, and had minor phreato-magmatic eruptions in 1963 and a single hydrothermal eruption in 1994. Currently, Irazú's activity primarily consists of shallow seismic swarms, fumarolic crater gas emissions, small volcanic landslides, and minor gas emissions on its northern forested flank (Alvarado et al., 2006; Barquero et al., 1995). Diffuse 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^{-1} of CO_2 and a small area on the north flank alone releases 15 t d^{-1} (Epiard et al., 2017). Between the two volcanoes, a major erosional depression is partially occupied by extensive dairy farms, and is somewhat less forested 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 north-south striking Rio Sucio fault, crossing into the area dominated by dairy farms on Irazú's lower NE slope. Our sampling locations on Irazú were located along a road from the summit northward down into this low-lying area. On Turrialba, we focused on an area of known strong emissions but intact forests on the SW slope, uphill of the same erosional depression, but cross-cut by the major NE-SW trending active fracture system of the Falla Ariete. We sampled three main areas of the Falla Ariete, each approximately perpendicularly transecting the degassing fault along equal altitude; the upper Ariete fault, the lower Ariete fault, and a small basin directly east of the old Cerro Armado cinder cone on Turrialba's south-western flank. We took a total of 51 tree samples (17 were excluded after stress screening) at irregular intervals depending on the continued availability and specimen maturity of three species present throughout the transect.

All transects are in areas experiencing measurable CO_2 enhancements from the Falla Ariete, but not high enough to be in areas generally downwind of the prevailing crater emissions plume (Epiard et al., 2017). We avoided areas that experience ash fall, high volcanic SO_2 concentrations, local anthropogenic CO_2 from farms, or that were likely to have heavily acidified soil. Excessively high soil CO_2 concentrations can acidify soil, leading to negative impacts on ecosystems growing there (McGee and Gerlach, 1998). Because such effects reflect by-products of extreme soil CO_2 concentrations rather than direct consequences of elevated CO_2 on plants, we avoided areas with CO_2 fluxes high enough to possibly cause noticeable CO_2-induced soil acidification. Light ash fall on some days likely derived from atmospheric drift, as we were not sampling in areas downwind of the crater. The ash fall did not in any noticeably way affect our samples, as trees showing ash accumulation on their leaves or previous damage were the exception and avoided. Altitude, amount of sunlight during measurements, and aspect had no consistent correlations with any of the parameters we measured.

2.2 S~~pecies s~~tudied tree species

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

2.3 CO_2 concentrations and soil diffuse flux measurements

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

2.4 Leaf function measurements

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

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

2.5 Isotopic analysis

We collected wood cores from 31 individual trees at a 1.5 m height using a 5.15 mm diameter increment borer (JIM GEM, Forestry Suppliers Inc., Jackson, MS, USA). Since no definable tree rings were apparent, we created a fine powder for isotope analysis by drilling holes into dried cores using a dry ceramic drill bit (Dremel) along the outermost 5 cm of wood below the bark, 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 to be representative of ~~roughly~~ at least the last 2-3 years, based on analogous literature growth rate values:~~.~~ *Oreopanax xalapensis* and *Alnus 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~~ show visible signs of ~~significant~~ stress, or that were not fully mature. After these exclusions, all remaining tree cores with co-located CO_2 flux measurements were from Turrialba.

2.6 Sulfur dioxide probability from satellite data

To assess the likelihood of trees having been significantly stressed in the past by volcanic sulfur dioxide (SO_2) from the central crater vents, we 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:

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

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

To speed up processing, some of the retrieval runs were binned in order to increase the signal-to-noise ratio, since the band difference can be rather noisy.

2.7 Modelling the anthropogenic CO_2 influence from inventory data

We assessed the likelihood of anthropogenic CO_2, enhancements of air from San Jose, Costa Rica's capital and main industrial and population center, influencing our measurements. We used a widely applied Flexible Particle Dispersion Model (Eckhardt et al., 2017; Stohl et al., 1998, 2005; Stohl and Thomson, 1999) in a forward mode (Stohl et al., 2005), 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° 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 this test. 2015 was used as a representative year for simulating the seasonal cycle of CO_2 concentrations that would be present in any particular year.

3 Results

3.1 Volcanic CO_2 emissions through the soil

We measured CO_2 flux emitted through the soil at 66 points over four days (Fig. 1). The first eight points were on Irazú, and the rest were located near the Ariete ~~Fault~~ fault on Turrialba. We analyzed CO_2 fluxes, not concentrations, because the diffuse CO_2 emissions through the soil, fed from a deep magma source and dependent on deep permeability, are highly invariant in time compared to under-canopy air concentrations. In contrast, instantaneous concentration measurements are modulated by many factors including meteorology, respiration of vegetation and animals, uptake by plants for photosynthesis, and diurnal dynamic and slope effects. The highly variable concentration measurements are thus not representative of long-term exposure. 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. Mean soil CO_2 flux values over the entire sampling area varied from 3 to 37 g m^{-2} day^{-1}, with an average of 11.6 g m^{-2} day^{-1} and a standard deviation of 6.6 g m^{-2} day^{-1}. A 12-bin histogram of mean CO_2 flux shows a bimodal right-skewed distribution with a few distinct outliers

(Fig. 3). Fluxes were generally larger on Irazú than on Turrialba. This result agrees with previous studies which showed that the north flank of Irazú has areas of extremely high degassing, whereas most of our sampling locations on Turrialba were in areas that had comparatively lower diffuse emissions (Epiard et al., 2017; Stine and Banks, 1991). We used a cumulative probability plot to identify different populations of CO_2 fluxes (Fig. 3) (Cardellini et al., 2003; Sinclair, 1974). ~~Our measurements and literature data confirm that ecosystems growing in these locations are consistently exposed to excess volcanic CO_2, which may impact chlorophyll fluorescence, chlorophyll concentrations, and stomatal conductance of nearby trees.~~

We created an inventory-based model of anthropogenic CO_2 emissions from the San José urban area, parts of which are less than 15 km from some of our sampling locations (Fig. 2). Our model shows that CO_2 emitted from San José is blown west to south-west by prevailing winds. Our study area is directly east of San José, and as such is unaffected by anthropogenic CO_2 from San Jose, which is the only major urban area near Turrialba and Irazú. Additionally, we used ASTER data to map probabilities of SO_2 across Costa Rica, as a possible confounding factor. The active craters of both Turrialba and Irazú emit measurable amounts of SO_2, which is reflected by the high SO_2 probabilities derived there (Fig. 2). 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 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 clustered around -26 ‰ (Fig. 4). A 5-bin histogram of all $\delta^{13}C$ measurements shows a slightly right-skewed unimodal normal distribution, with an average of -26.37 ‰ and a standard deviation of 0.85 ‰. *A. acuminata* and *O. xalapensis* have nearly identical averages (-26.14 and -25.97 ‰, respectively), while *B. nitida* has a noticeably lighter average of -27.02 ‰. 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, 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 ~~increased~~is higher, the wood cores contained progressively higher amounts of

^{13}C for two of the three species. Interestingly, our t~~T~~ree core δ^{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 0.75 to 0.89, with most measurements clustering between 0.8 and 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 showed no correlation. No confounding factors measured were correlated with Fv/Fm for any species. In general, *B. nitida* had the highest Fv/Fm values, and *A. acuminata* and *O. xalapensis* had similar values except for a few *O. xalapensis* outliers. Chlorophyll concentration measurements were highly variable, ranging from 260 to 922 µmol m^{-2}, with an average of 558 µmol m^{-2} and a standard deviation of 162 µmol m^{-2} (Fig. 6). Chlorophyll concentration had a complicated right-skewed bimodal distribution, likely due to the noticeably different averages for each species. *A. acuminata* and *O. xalapensis* both displayed weak correlations between chlorophyll concentration and soil CO_2 flux ($r^2=0.38$ and $r^2=0.28$, respectively), but their trendlines were found to be almost perpendicular (Fig. 6). As CO_2 flux increased, *A. acuminata* showed a slight increase in chlorophyll concentration, while *O. xalapensis* had significant decreases in chlorophyll concentration. *B. nitida* individuals growing on steeper slopes had significantly lower chlorophyll concentration measurements ($r^2=0.42$, $p<.05$) than those on gentler slopes, a trend not expressed by either of the other two species ($r^2=0.01$ for both), demonstrating no significant influence of slope across the majority of samples. Stomatal conductance ranged from 83.5 to 361 mmol H_20 m^{-2} s^{-1}, with an average of 214 mmol H_20 m^{-2} s^{-1} and a standard deviation of 73.5 mmol H_20 m^{-2} s^{-1}. Distribution was bimodal, with peaks around 150 and 350 mmol H_20 m^{-2} s^{-1}. *A. acuminata* had a moderate positive correlation ($r^2=0.51$) with soil CO_2 flux, but it was not statistically significant due to a lack of data points (Fig. 7) – however this is a result consistent with the observed higher chlorophyll concentration (Fig. 6). The other two species displayed no correlation with soil CO_2 flux. *B. nitida* had a moderate negative correlation ($r^2=0.61$) with slope, similar to its correlation between chlorophyll concentration and slope.

4 Discussion

4.1 Long-term plant uptake of volcanic CO_2

Turrialba and Irazú continuously emit CO_2 through their vegetated flanks, but prior to this study it was unknown if the trees growing there were utilizing this additional isotopically heavy volcanic CO_2. All tree cores with corresponding CO_2 flux measurements were from areas proximal to the Ariete ~~Fault~~ fault on Turrialba, where atmospheric and volcanic δ^{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 photosynthesized with isotopically heavy excess volcanic CO_2 over the last few years, and are therefore growing in eCO_2 conditions. Assuming that all variations in $\delta^{13}C$ are caused by the incorporation of heavy volcanic CO_2, we can calculate the average concentration of the mean volcanic excess CO_2 in the air the plants are exposed to, with a mass balance equation (Eq. 2):

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

where C_v is the mean volcanic excess component of the CO_2 concentration in air, C_b is the atmospheric "background" (i.e., non-volcanic) CO_2 concentration, δ_b is atmospheric $\delta^{13}C$, δ_m is the difference between background wood $\delta^{13}C$ and another wood $\delta^{13}C$ measurement subtracted from atmospheric $\delta^{13}C$, and δ_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 δ_v and δ_b are taken from Malowany et al. 2017, and C_b is assumed to be 400 ppm, a robust invariant since the year-to-year mean northern hemispheric change by ~2 ppm is by far exceeded by local, seasonal, and excess component variability. For the tree core with the highest measured CO_2 flux for *O. xalapensis*, this equation yields a mean excess volcanic CO_2 concentration of 155 ppm, bringing the combined mean atmospheric (including volcanic) CO_2 concentration these trees are exposed to, to ~555 ppm. For *B. nitida* this equation yields 190 ppm of mean excess volcanic CO_2 at the highest flux location, for a combined total mean of ~590 ppm CO_2. These calculations show that trees in our study area have been consistently exposed to significantly elevated concentrations of CO_2, reflective of predicted atmospheric conditions 60-80 years into the future, assuming a 2 ppm y^{-1} mean atmospheric growth rate (Peters et al., 2007), ~~A~~additional measurements of tree core $\delta^{13}C$ and associated soil CO_2 fluxes would help corroborate our observations, which were based on a limited number of data points. Though tree ring ^{14}C content in volcanically active areas has been linked to variations in volcanic CO_2 emissions, and comparing patterns of $\delta^{13}C$ to ^{14}C measurements for the same wood samples could provide additional confirmation of this finding (Evans et al., 2010; Lefevre et al., 2017; Lewicki et al., 2014), this additional dimension was outside the scope of this exploratory study, which focuses on trees' use of excess ^{13}C.

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

A study at the previously mentioned Mammoth Mountain tree kill area examined the connection between $\delta^{13}C$ and volcanic CO_2 fluxes, but focused on the difference between trees killed by extreme CO_2 conditions and those that were still alive (Biondi and Fessenden, 1999). They concluded that the changes in $\delta^{13}C$ that they observed were due to extreme concentrations of CO_2 (soil CO_2 concentrations of up to 100%) impairing the functioning of root systems, leading to closure of stomata and water stress (Biondi and Fessenden, 1999). CO_2 does not inherently harm trees, but the extreme CO_2 concentrations (up to 100% soil CO_2) at the Mammoth Mountain area caused major soil acidification, which led to the tree kill (McGee and Gerlach, 1998). We have evidence that those 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, n~~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 chlorophyll concentration values and lack of visible indicators of stress; specifically, our values of Fv/Fm ~0.8 indicate that PSII was operating efficiently in most of the trees we measured (Baker and Oxborough, 2004). The Mammoth Mountain tree kill areas have several orders of magnitude higher CO_2 fluxes (well over 10,000 g m^{-2} day^{-1}) than the areas we sampled (up to 38 g m^{-2} day^{-1}), making it much more likely that stress from soil acidification would be causing stomatal closure and affecting wood $\delta^{13}C$ measurements at Mammoth Mountain (Biondi and Fessenden, 1999; McGee and Gerlach, 1998; Werner et al., 2014). In contrast, most of the diffuse degassing at Turrialba does not lead to soil acidification or pore space saturation, as is evident in our own and others' field data (e.g., Epiard et al 2017). Thus, changes in our $\delta^{13}C$ values are best explained by direct photosynthetic incorporation of isotopically heavy volcanic CO_2. To the best of our knowledge, this is the first time that a direct correlation between volcanic soil CO_2 flux and wood $\delta^{13}C$ has been documented. Future studies should explore this correlation further, as our findings are based on a limited sample size.

4.2 Short-term species response to eCO$_2$

Short-term plant functional responses at the leaf level to elevated CO$_2$ were highly species-dependent. *B. nitida* had no statistically significant functional responses to soil CO$_2$ flux and *O. xalapensis* only had a weak negative correlation between soil CO$_2$ flux and chlorophyll concentration **(**Fig. 6.**)**. *A. acuminata*, a nitrogen fixing species, was the only species with a consistent and positive functional response to elevated CO$_2$, displaying a strong positive correlation with fluorescence and a weak positive correlation with chlorophyll concentration and stomatal conductance (Figs. 5-7). The lack of response in *B. nitida* and *O. xalapensis* could be due to nitrogen limitation, a factor that would not affect *A. acuminata* due to its nitrogen fixing capability. Previous studies have found that nitrogen availability strongly controls plant responses to eCO$_2$ in a variety of ecosystems, including grasslands and temperate forests (Garten et al., 2011; Hebeisen et al., 1997; Lüscher et al., 2000; Norby et al., 2010). Nitrogen limitation has been posited to be an important factor in tropical montane cloud forests, and may be contributing to the lack of responses in *B. nitida* and *O. xalapensis* (Tanner et al., 1998). Due to the exploratory nature of our study, we do not have a large enough dataset to conclude that the nitrogen fixing capability of species like *A. acuminata* is the cause for its positive response to volcanically elevated CO$_2$, as has been speculated before (Schwandner et al., 2004), but it is a possible correlation that deserves further investigation. Future studies should explore this correlation further to determine the extent of nitrogen limitation at Turrialba and Irazú and its impacts on plant responses to eCO$_2$.

4.3 Lessons Learned for Future Studies ~~Trees as volcanic CO$_2$ sensors~~

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$_2$—one of the largest uncertainties in climate projections.~~,~~ Costa Rica's volcanoes are host to large areas of relatively undisturbed 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 conclusively. Field data can be difficult to acquire in these rugged and challenging environments. A remote sensing approach using airborne measurements, validated by targeted representative ground 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 platforms, and remote sensing instruments can quickly produce the massive datasets required to provide more comprehensive answers to these questions (Cawse-Nicholson et al., 2018). There are eight forested volcanoes in Costa Rica which are actively degassing CO$_2$ through their flanks (Epiard et al., 2017; Liegler, 2016; Melián et al., 2007; de Moor et al., 2016; Williams-Jones, 1997; Williams-Jones et al., 2000), viable for this type of study (see polygons in Fig. 2). Datasets from those volcanoes would provide a wider range of altitudes, precipitation levels, temperatures, and other environmental factors that would help isolate the effects of eCO$_2$.

~~Beyond the potential to advance our understanding of tropical forest ecosystem responses to elevated CO$_2$, ~~O~~o~~ur results also ~~have~~ offer significant new tools for~~importance to~~ the volcanolog~~ical community~~y, where reconstructing past volcano behavior through eruption histories is hampered by severe preservation gaps in the stratigraphic record. ~~If the~~ A strong link between $\delta^{13}C$ and volcanic CO_2 ~~is as strong as our results suggest, it~~ could be ~~used to~~a game-changer by establishing long-term ~~temporal~~ histories of volcanic CO_2 emission variations ~~at previously unmonitored volcanoes.~~ ~~, and fill observational gaps in volcanic activity histories.~~ 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 v~~The data presented in this paper represent approximately the past 2-3 years of growth, but taking $\delta^{13}C$ measurements at regular intervals on the remainder of a tree core should provide a history of temporal variations in volcanic CO_2 emissions. This has significant volcanological applications, as it would provide a powerful new tool to study volcanic CO_2 emissions in a temporal context. V~~ariations 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), ~~but ^{14}C~~ ^{13}C is ~~relatively~~ inexpensive ~~expensive~~ to measure at more~~and a limited number of~~ laboratories,~~s are capable of making these measurements (Evans et al., 2010; Lefevre et al., 2017; Lewicki and Hilley, 2014)~~allowing~~. $\delta^{13}C$ measurements are more accessible, allowing~~ for substantially more data to be acquired~~compared to ^{14}C~~. ~~Comparing wood $\delta^{13}C$ records of past CO_2 fluxes to historical records of eruptions could help establish patterns of CO_2 fluxes at volcanoes that have minimal CO_2 flux datasets available. These patterns of CO_2 flux could then be compared to current volcanic CO_2 flux data and historical eruption records to fill gaps in the historical and monitoring records – a boon for volcano researchers and observatories using pattern recognition to improve eruption prediction capabilities (Newhall et al., 2017; Pyle, 2017; Sparks et al., 2012).~~ Independent validation, and calibration by wood core dendrochronology via ^{14}C, tree rings, or chemical event tracers like sulfur isotopes~~spikes~~, 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~~to variations in volcanic flank CO_2~~, which is more likely to represent deeper processes inside volcanoes than crater-area degassing (Camarda et al., 2012), may permit the use of trees as sensors of transient changes in volcanic degassing indicative of volcanic reactivation and deep magma movement possibly leading up to eruptions (Camarda et al., 2012; Pieri et al., 2016; Schwandner et al., 2017; Shinohara et al., 2008; Werner et al., 2013).

~~4.4 Lessons Learned for Future Studies~~

~~This exploratory study reveals significant new potential for future studies to utilize the volcanically enhanced CO_2 emissions approach to study tropical ecosystem responses to eCO_2. These two Costa Rican volcanoes, as well as several other volcanoes in the country, have large areas of relatively undisturbed old-growth forest on their broad flanks, making them ideal study areas for examining responses of ecosystems to eCO_2. However, there are several challenges future studies should take into consideration if attempting to expand upon this preliminary study. Given the enormous tropical species diversity and the need to control for confounding factors, large datasets will be needed to answer these questions conclusively. Unfortunately, field data can be difficult to acquire in these environments as the terrain is rugged and can be challenging to work in. A remote sensing approach using airborne measurements, combined with targeted representative ground campaign field work for validation, could provide sufficiently large~~

~~data sets to represent species diversity and conditions in conjunction with ground based measurements. Many of the datatypes that would be useful for this type of study can be acquired from airborne platforms, and remote sensing instruments can quickly produce the massive datasets that would be required to provide more comprehensive answers to these questions (Cawse-Nicholson et al., 2018). There are six other forested volcanoes in Costa Rica which are actively degassing CO_2 through their flanks (Epiard et al., 2017; Liegler, 2016; Melián et al., 2007; de Moor et al., 2016; Williams-Jones, 1997; Williams-Jones et al., 2000), that would also be viable for this type of study (see polygons in Fig. 2), and datasets from those volcanoes would be helpful as they would provide a wider range of altitudes, precipitation levels, temperatures, and other environmental factors that would help isolate the effects of eCO_2.~~

5 Conclusions

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

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

Author contributions. FMS and JBF designed the study, and RRB, FMS, JBF, and ED conducted the field work and collected all samples and data with some of the equipment borrowed from GN, who helped interpret the results. TSM processed the samples for analysis. JPL conducted the SO_2 analysis, wrote the related methods subsection, and helped interpret the results. VY modelled the anthropogenic CO_2 emissions, wrote the related methods subsection, and helped interpret the results. CAF created the combined figure showing the CO_2 and SO_2 results and assisted in writing the manuscript. RRB wrote the publication, with contributions from all co-authors.

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

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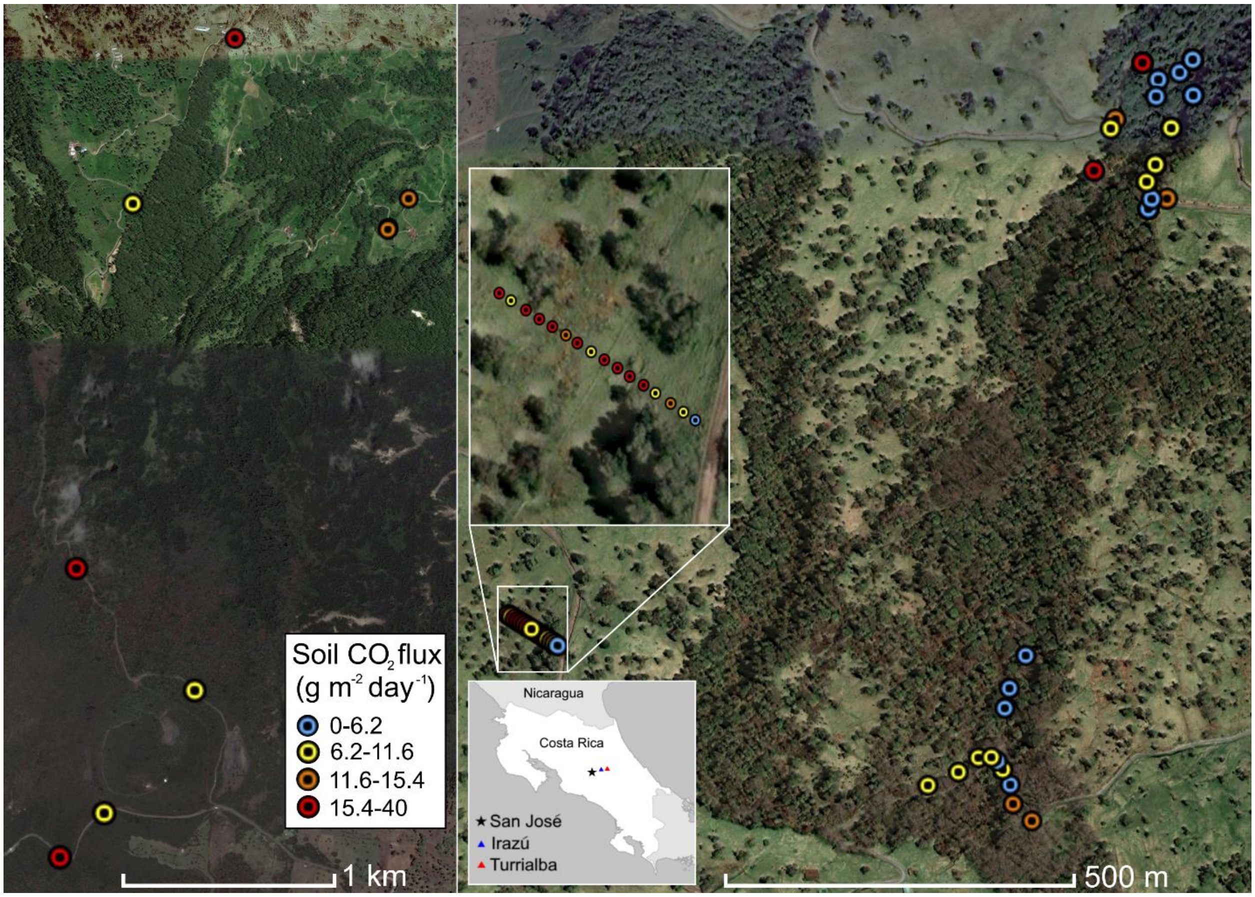

Fig. 1: Overview of measurement locations in two old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú. Distribution of mean soil CO_2 flux across north flank of Irazú (left) and south flank of Turrialba (right). Colors of dots correspond to flux populations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

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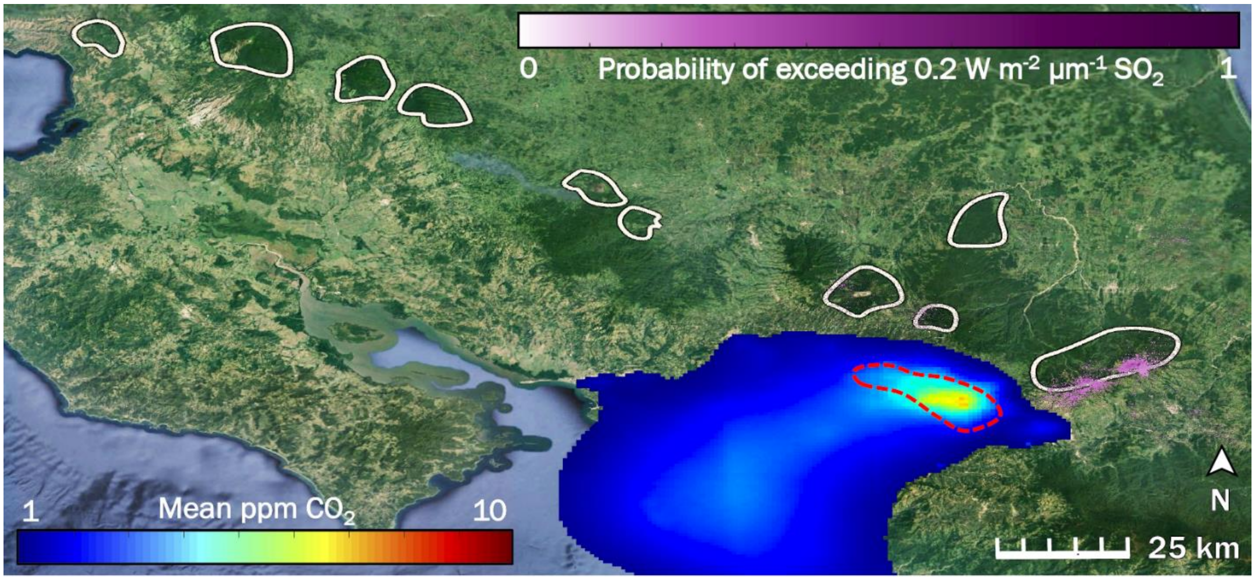

Fig. 2: The influence of two potentially confounding gases on our study area (right hand white polygon) in Costa Rica is low to non-existent: anthropogenic CO_2 from San José (blue to red color scale), and volcanic SO_2 (purple color scale). White polygons are drawn around locations of the forested active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

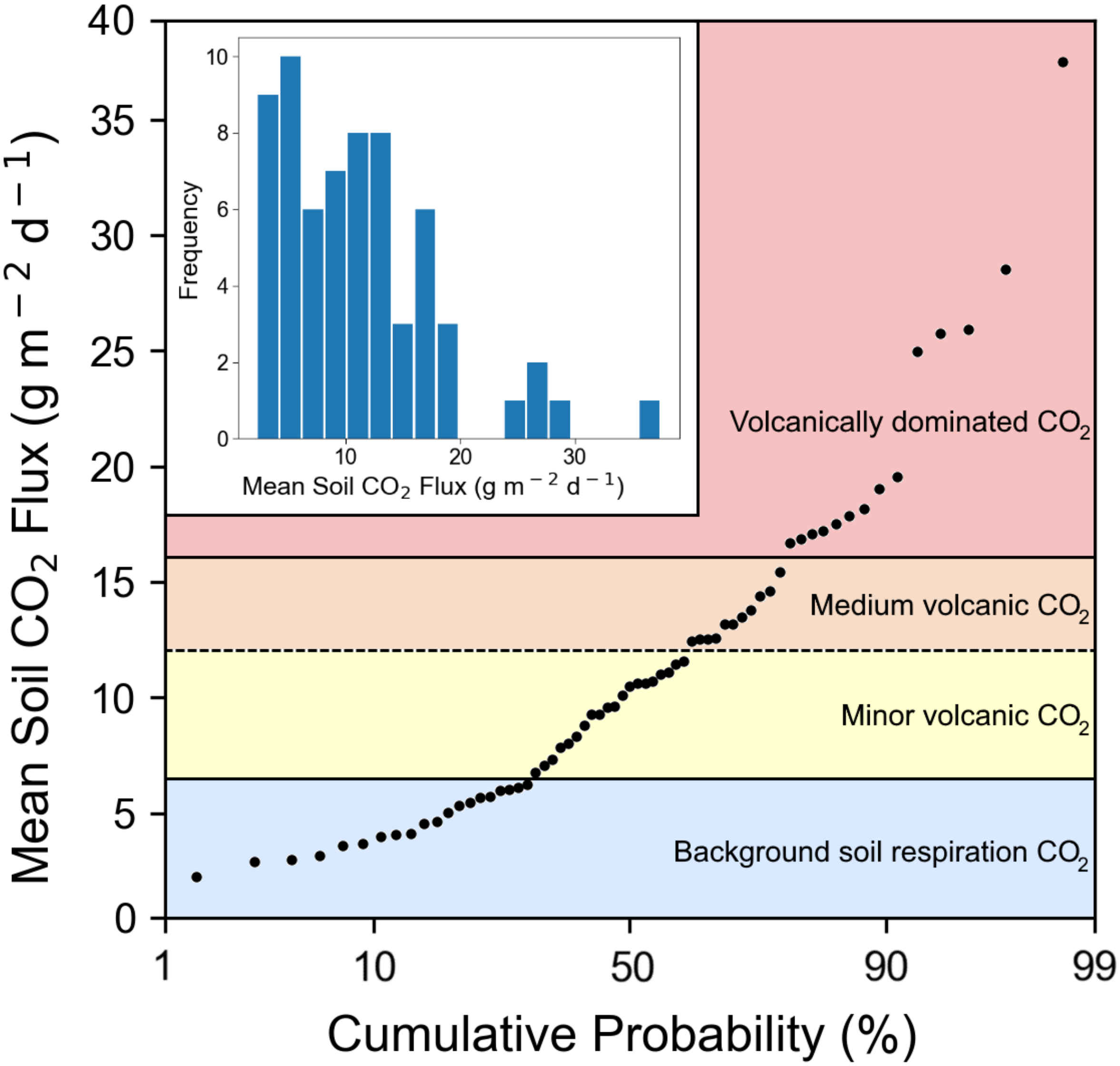

Fig 3: Soil CO_2 flux into the sub-canopy air of forests on the Turrialba-Irazú volcanic complex is pervasively and significantly influenced by a deep volcanic gas source. At least four different overlapping populations of soil CO_2 flux were identified, using a cumulative probability plot, where inflection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

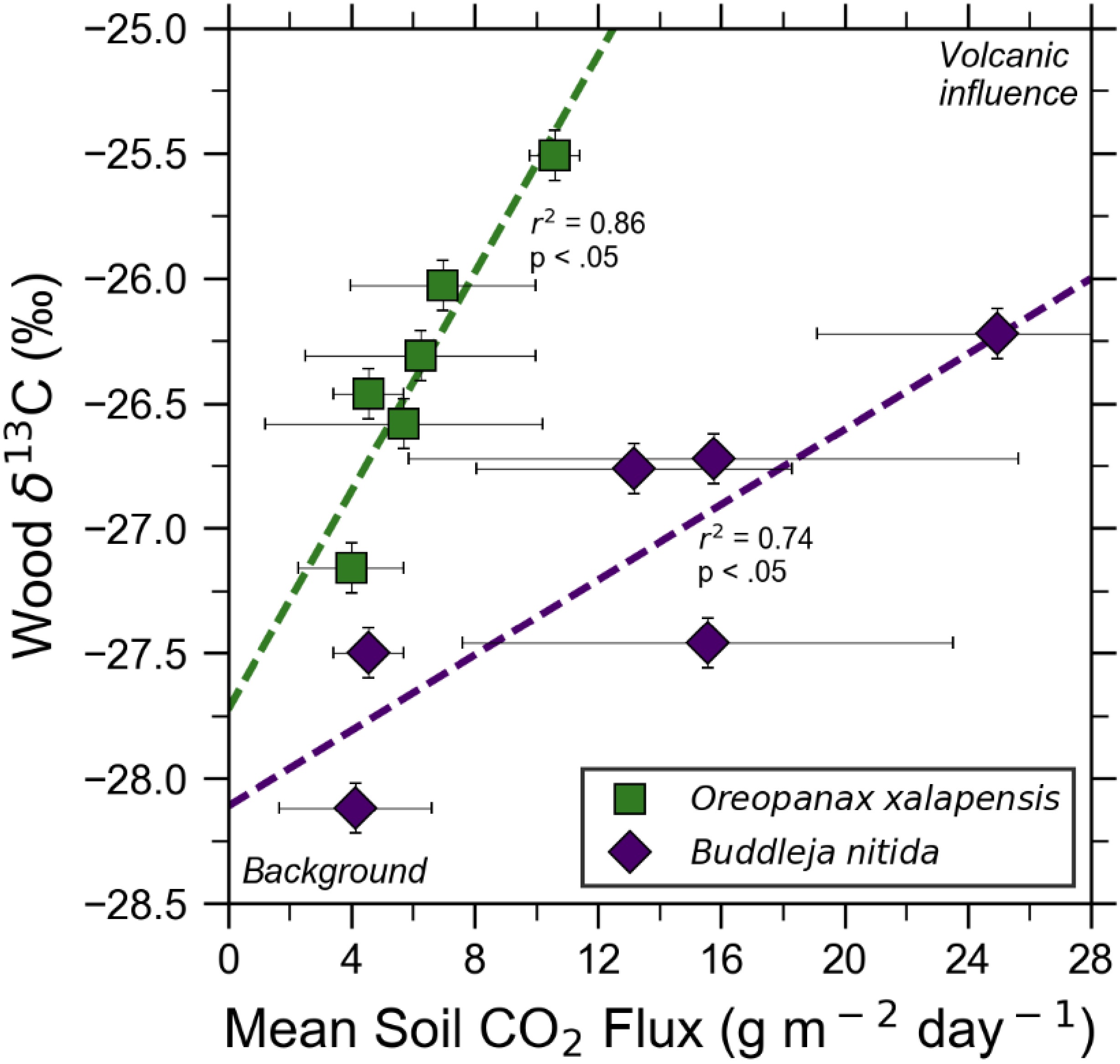

Fig 4: Bulk wood δ^{13}C of trees on Costa Rica's Turrialba volcano shows strong correlations with increasing volcanic CO_2 flux for two species, *O. xalapensis* and *B. nitida*, indicating long-term photosynthetic incorporation of isotopically heavy volcanic CO_2. Stable carbon isotope ratio (δ^{13}C)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

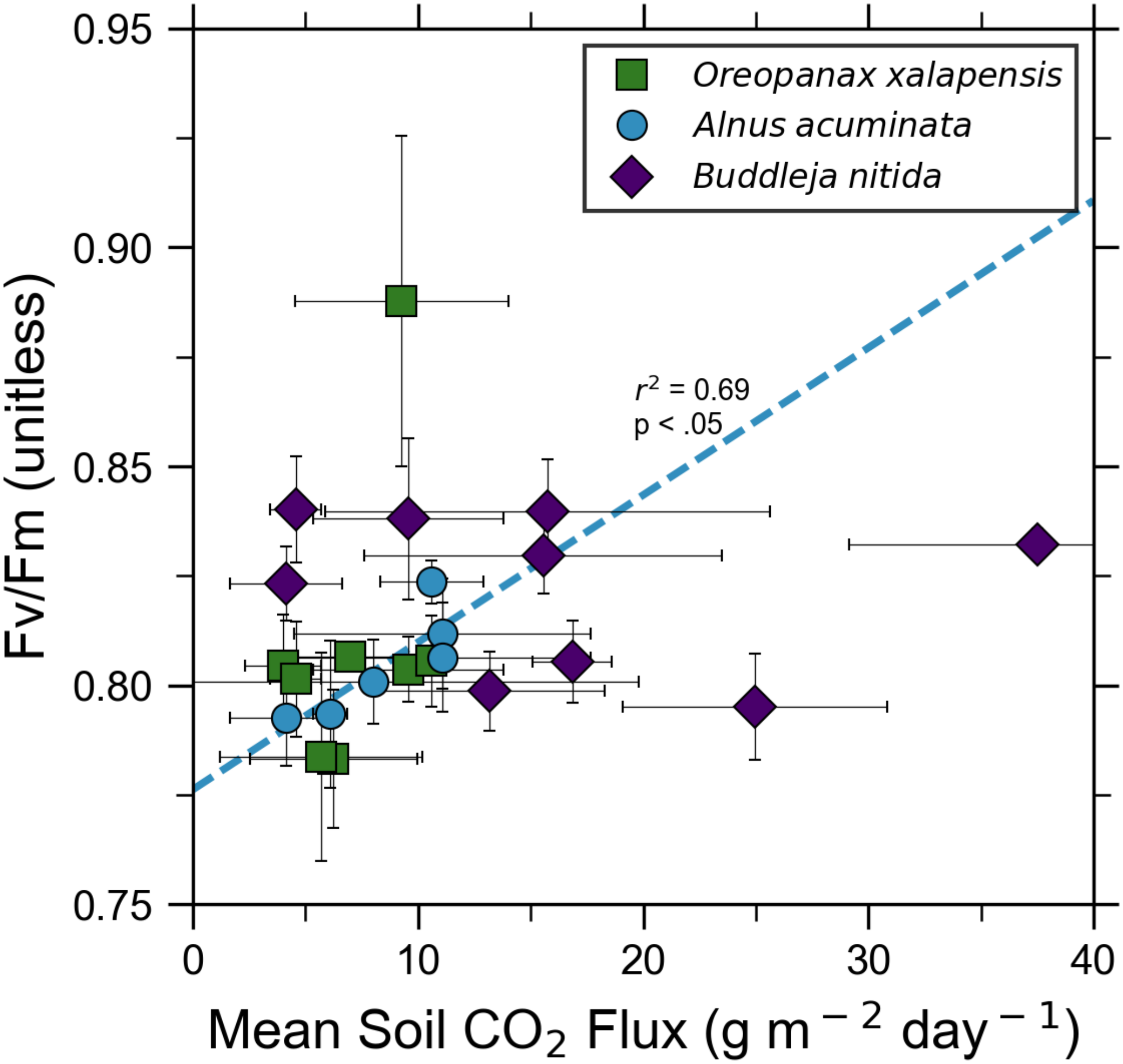

Fig. 5: Photosynthetic activity of some tree species in old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú, may show short-term response to volcanically elevated CO_2. Leaf fluorescence (Fv/Fm) and soil CO_2 flux were strongly correlated for *A. acuminata*,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

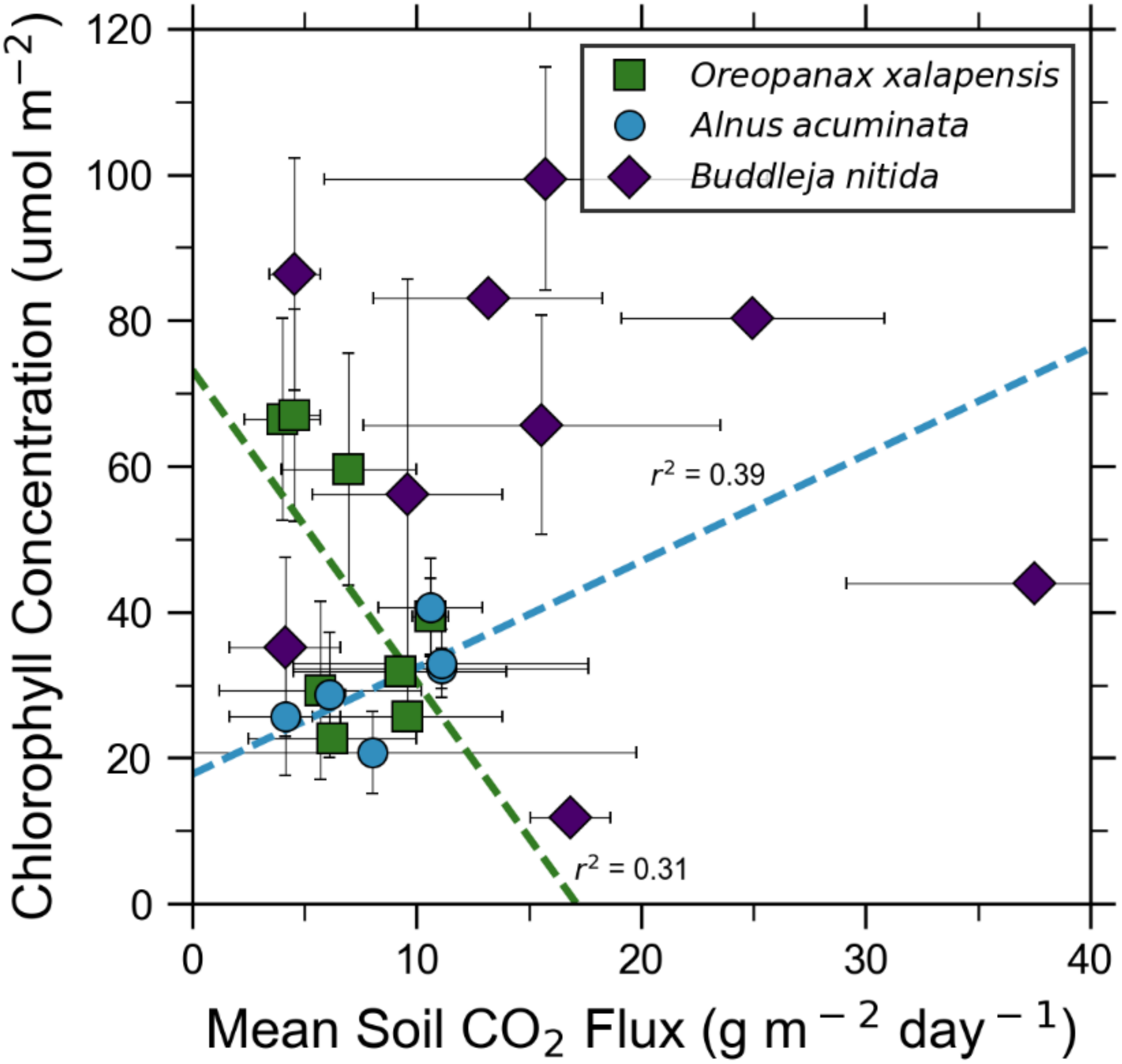

Fig. 6: Some tree species in old-growth forests on the upper flanks of two active volcanoes in Costa Rica, Turrialba and Irazú, may express their short-term response to volcanically elevated CO_2 by producing more chlorophyll. A species that showed strong short-term response (*A. Acuminata*, Fig. 5)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

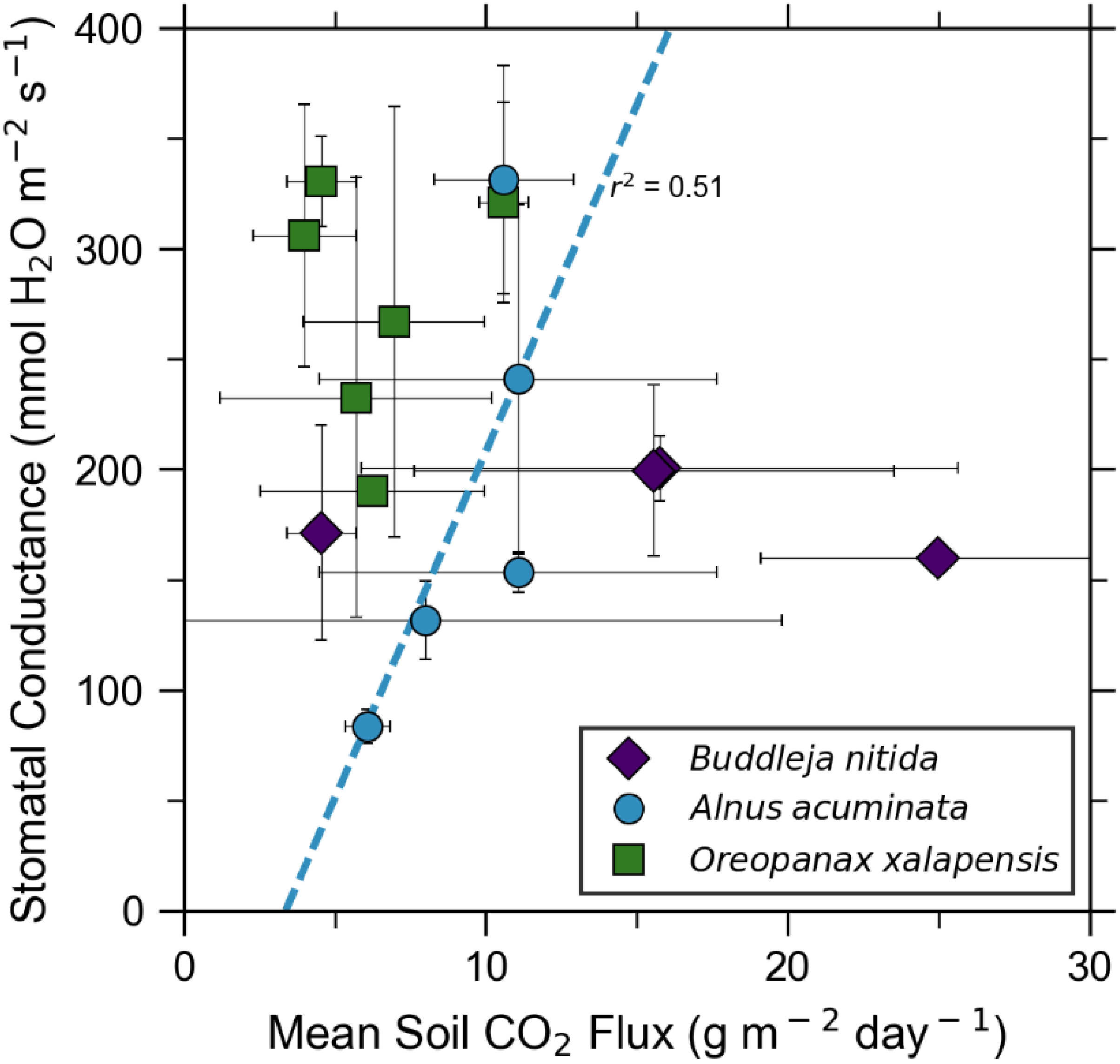

Fig. 7: Leaf stomatal conductance of a tree species that strongly responds to volcanically elevated CO_2 (Figs. 5, 6) has positive correlations with volcanic CO_2 flux, consistent with increased gas-exchange.

Supplementary Info

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.

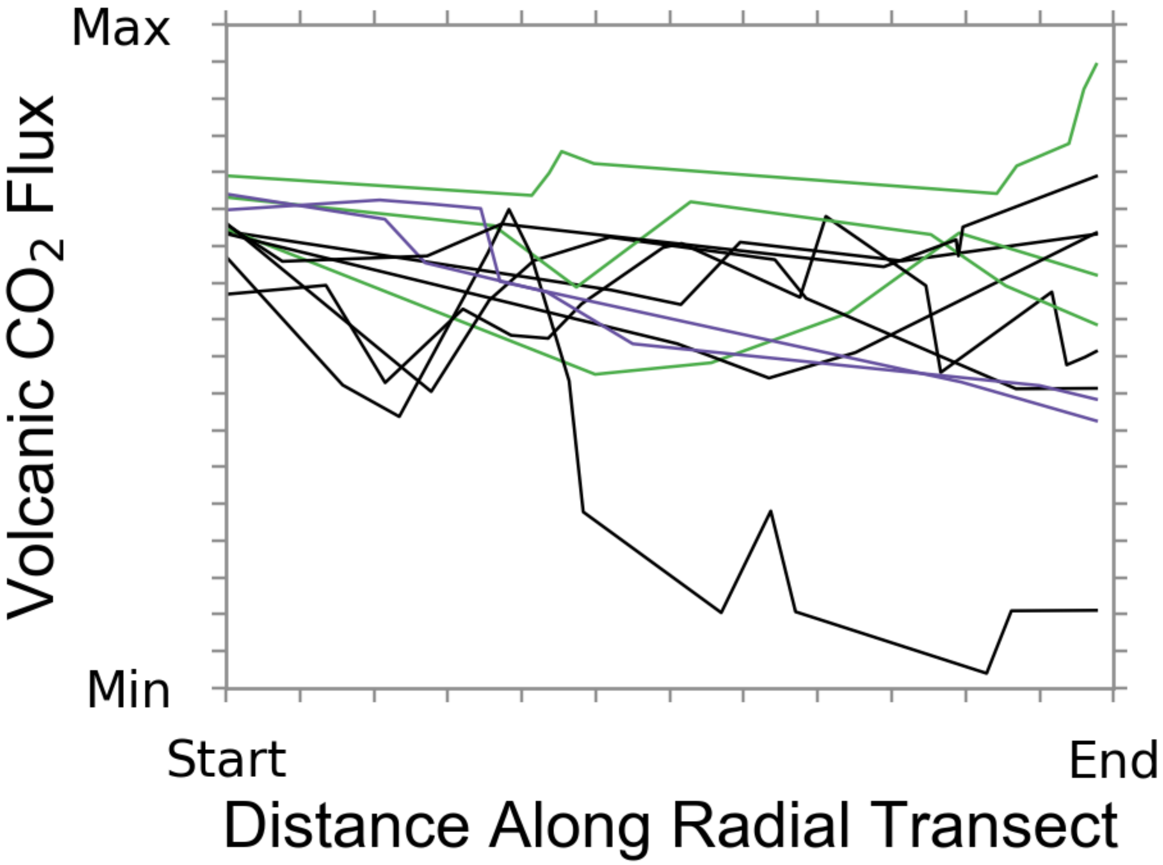

Fig. S1: CO_2 flux varies significantly along radial transects from 11 volcanoes around the world.

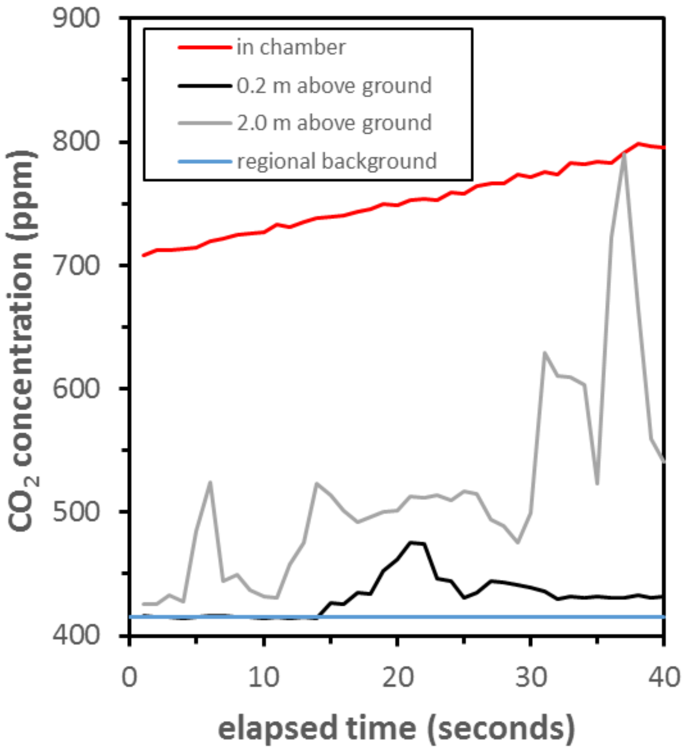

Fig. S2: CO_2 concentrations and fluxes in sub-canopy air are highly variable, while soil-to-atmosphere eCO_2 fluxes are stable representations of long-term eCO_2 addition (March 24, 2017, in a forest near the Ariete fault on Turrialba volcano).

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.