Response to reviewer #1

We thank the reviewer for comments and regret that he/she found our approach unclear. We have tried to clarify our thinking throughout the manuscript. In contrast to comments of the reviewer, we think the discussion of leaf-level results in the context of ecosystem scale is essential to placing the results in the context of the current understanding. We have addressed the stated concerns raised by reviewer #1 below. **Bold text** identifies the reviewer comments and our responses are in standard text. Line numbers in our responses refer to the revised manuscript.

General comments. First,"deposition velocities" measured in the lab are not the same as deposition velocities from a large scale model or estimated from an eddy covariance measurement, which represent the integrated uptake below a certain height, taking into account turbulent transport. I would prefer if the authors chose another term to represent leaf-level uptake, but more importantly, this has implications for the authors' large scale modeling and backhand calculations is it really appropriate to represent true deposition velocities with leaf-level uptake values? What about transport, leaf area, etc.?

The term "deposition velocities" is widely used in the leaf-level literature (e.g. Teklemariam and Sparks, 2006; Chaparro-Suarez et al., 2011; Breuninger et al., 2012 etc.). Canopy fluxes are calculated as $F = V_d \times LAI \times [NO_2]$, so these canopy-level deposition velocities represent average leaf deposition velocities, as in the Big-Leaf model. We agree that, of course, vertical transport, attenuation of above-canopy light, etc. complicates canopy-level V_d. However, our previously published (Delaria and Cohen, 2020) canopy scale model does take into account all of these effects. This previously published and peer-reviewed model was constructed for the purpose of scaling up leaf-level processes to the canopy scale, as is discussed extensively in Delaria and Cohen, 2020. Leaf-level processes will indeed affect canopy-scale processes. Our "backhand estimations" made in section 4.5, are intended to provide the reader with a qualitative suggestion of areas that may be influenced by large deposition fluxes of NO_2. As more sophisticated models have shown that leaf-level deposition is a dominant control, we believe this is a useful qualitative representation. We do not think any reader would mistake our estimate for a full quantitative model. Nevertheless, we add the following qualifier at line 475 on page 15:

"The estimations provided here are intended only to suggest qualitative indications of where NO_2 deposition may be important. Because we are ignoring effects of vertical transport and light attenuation through the canopy, and because we are using maximum measured deposition velocities, the deposition reported here is likely to be an upper-bound estimate. We recommend areas where this estimated deposition is highest as regions that should be the subject of future field and large-scale modelling studies. "

The authors make a series of assumptions about resistances to the leaf boundary layer and cuticles in their interpretation of their laboratory results that I think need to be discussed more.

We provide a complete disscussion of the methods used to determine the boundary layer conductance in Delaria et al., 2018, which is referred to in line 150 on page 5. We further discuss the boundary layer in lines 228—232 of page 8, in which we use previous laboratory leaf-level studies to argue that our measured R_b is an upper bound of the chamber R_b when a branch is present. We further discuss the error ($\sim 6\%$) that would be introduced by assuming negligible boundary resistance. On line 256 of page 9, we have added a line explaining our determination of negligible cuticular resistances:

"The deposition observed with the chamber lights turned off could be explained completely by the measured stomatal conductance. Fits of the resistance model (Eq. 10) typically resulted in cuticular resistances larger than 1000 s $cm^{-}1$, and represented cuticular deposition not significantly above zero."

Are the authors maintaining constant temperature, pressure and humidity in the chamber over their forty minute long experiments? How might temporal variations in these quantities, or spatial variations within the chamber, affect measurements?

We have added a sentence to line 131 of page 5 to clarify our temperature and humidity assumptions: " Over the course of a day the temperature and humidiy varied by a maximum of 2 °C and 5%, respectively. These deviations were not found to be significantly correlated with stomatal opening." We discuss how spatial variations in temperature throughout the chamber would affect our calculations in lines 139—142 page 5.

The canopy scale modeling and discussion in Section 4.1 is confusing. The authors do a fair amount of work in the lab to estimate Rm, and then say an increase from 0.1 s/cm to 0.6 s/cm in Rm doesn't matter based on canopy scale modeling. The paper could have just been "Rm could be off by an order of magnitude does this matter? Let's see with a model" I guess I'm asking the authors to more clearly articulate how their setup was designed to build on present knowledge. For example, is the increase much less than they expected based on previous work?

Our paper reports laboratory observations and their interpretations. These serve a number of purposes. Among these is our effort to understand Rm. The discrepancies existing in the literature on the role of the mesophyll are discussed in the introduction and to our thinking are important to assess. Even though Rm is shown to be unimportant to canopy scale fluxes, it is important to thinking about the fate of NO2 once it enters pore fluids in the leaf and to reconciling previous studies that report emission of NOx from leaves at low ambient NOx. Further, to our knowledge this is the first study assess whether the particular number for Rm included in most chemical tranport models is reasonable. A paragraph was added beginning line 310 on page 10 to further argue for the importance of our study:

"Our laboratory measurements of mesophyllic resistance address the uncertainty in the literature on whether reactions in the mesophyll may be consequential for NO_2 deposition velocities. To our knowledge, no previous study has explicitly calculated the mesophyllic resistance. Differences between leaf-level deposition velocities and stomatal conductances measured by Breuninger et al., 2013, and observations by Teklemmariam and Sparks, 2006, of the affects of leaf ascorbate on uptake rates have indicated mesophyllic reactions may be important. Additional studies (Gut et al., 2002; Eller et al., 2006; and Chaparro-Suarez et al., 2011) have also shown some evidence that between 20% and 40% of NO_2 deposition is under mesophyllic control. Our findings, however, suggest nearly 90% of uptake is controlled by the stomata."

Are there no boundary layer height products for California? I'd like to see at least some discussion of uncertainty in using only one PBL height for all of California for day or night

As we have stated previously, these calculations are meant to give a qualitative look at areas where deposition of NO_2 may be particularly important. Even so, we have adapted out figure to use a WRF-Chem output of boundary layer heights throughout the state. This updated figure does not change our conclusions.

The authors use “significant” to refer to statistical testing and to emphasize the implication of a finding. This is confusing and I ask that they choose another word for the latter. In some paragraphs multiple verb tenses are used. This is confusing.

We have gone through the manuscript and ensured that every instance that the word ”significant” is used, we mean statistical significance. A different word is chosen every time we are trying to emphasize the implication of a finding. We have also adjusted verb tense where appropriate.

Line 2: is it really absorption?

The word was changed to ”uptake”.

Line 11–12: what do the authors mean by effective?

This word was removed. The choice of ”effective” was used because, as we discussed elsewhere in the manuscript, there is some strong evidence in the literature of emission of NO. Because this emission is over an order of magnitude slower than NO_2 uptake, at atmospherically relevant conditions the net exchange of the chemical family NO_x will be uni-directional.

Line 17: references are needed for this sentence, and the authors should specify what importance is with respect to

References have been added. We have changed the sentence to read: ”The latter source is of particular importance in remote forested, and agricultural regions, where emission from soils is the primary source of NO_x.”

Line 19: “after” diffusion rather than “via”

The change has been made.

Line 28: are the processes really happening in the mesophyll?

Our understanding is that mesophyllic processes occur in the mesophyll. We have changed the sentence to read ”mesophyllic processes.”

Line 35: a paper from 2000 isn’t exactly recent

This citation has been removed from the sentence.

Line 43–44: “atmospherically relevant conditions” of what?

We mean under atmospherically relevant temperature, relative humidity, soil N levels, soil NO_x levels, pressure, and that no modifications were made to the plants. We feel that it would not be helpful to the reader to list all conditions that were maintained at atmospheric relevance for all above studies. We have, however, removed this phrase to avoid any further confusion.

Line 50: define compensation point briefly here

The phrase here has been changed to "NO_2 emissions".

Line 135: I think there needs to be a short description of Rb estimation here

We have moved a sentence from section 3.1. The sentences now read:

"The boundary layer resistance to water vapor was estimated to be negligible under our experimental conditions, with an upper bound of 0.6 s cm^{-1}. This was calculated by measuring the deposition of NO_2 to a 30 cm^2 tray of activated charcoal and confirmed by measuring the evaporation from a water-soaked Whatman No. 1 filter paper (Delaria et al., 2018). A detailed description of our assumption of negligible R_b can be found in section 3.1."

Line 215/219: Rb changes with leaf morphology, leaf movement and micrometeorology. I understand Rb is hard to estimate, but I think the authors need to discuss how uncertainty in Rb may play into their results more. For example, how might inferences about stomatal and mesophyll controls be impacted by Rb variations (the authors assume constant Rb)?

We have included a more extensive discussion of R_b. The paragraph now reads:

"We utilized two methods for analysing the importance of the mesophyllic resistance to the deposition of NO_2. Figure 2 shows the predicted stomatal-limited NO_2 deposition fluxes, assuming negligible R_b and R_m ($Flux = g_t[NO2]_{out}$) plotted vs. the measured NO_2 fluxes. Our upper bound measurement of R_b for NO_2 was 1 s cm^{-1} (0.6 s cm^{-1} for water vapor). Assuming $g_s = g_t$ would lead to a maximum of a 60% or 10% error in the calculated g_s with a g_t = 0.6 cm s^{-1} or g_t = 0.1 cm s^{-1}, respectively. However, R_b decreases with the enclosed leaf area according to Pape et al., 2009, which at a minimum was 200 cm^2. The maximum R_b in the chamber should have thus been $\approx$0.1 s cm^{-1}. Assuming $g_s = g_t$ would lead to a maximum of a 6% error at g_t = 0.6 cm s^{-1} in this case. Any deviation from unity in the observed slope of predicted vs. measured fluxes can thus be attributed to R_m. Any error in our assumption of negligible R_b may partially mask the affect of R_m. We do not expect that variation in R_b due to changes in leaf morphology, micrometeorology, and leaf movement would substantially change the affect of R_b, although we cannot rule out the possibility that this was partially responsible for day-to-day fluctuations in NO_2 fluxes. We confirmed the validity of our assumption of negligible R_b by comparing measurements of total conductance, g_t, in the chamber to measurements of stomatal conductance for the enclosed branch with a Licor-6800 instrument under identical environmental conditions of light irradiation, humidity, and temperature. This test was performed on one individual of three different tree species, and in all cases the chamber g_t measurements were found to be approximately equal to the Licor-6800 measurements of g_s within the range of uncertainty in g_t. "

Line 205: is the only evidence for "believing" this measurement is consistent with a zero compensation point that the concentration is below the limit of quantification? If so, will the authors make this more clear?

We believe our logic on this point is fully explained. We have slightly altered the phrasing of this sentence.

Line 206: I would be more careful in saying deposition of NO2 perhaps stomatal uptake of NO2 here deposition requires considering Rb,Ra, cuticular deposition

We do consider all of these in our chamber, which are stated and explained.

Line 207–209: might this be affected by a lack of a diurnal cycle in light in the lab? I know there is evidence for stomatal activity at night generally, but maybe there should be some discussion of uncertainty in moving between the lab and the real world.

There is a diurnal cycle of lights on and lights off on a 12 h light/dark period (section 2.1). Our results are also consistent with previous experiments in the field of leaf-level stomatal closure at night. We do observe slow closing and opening of the stomata when the lights are turned on or off, such that it takes approximately 1—2 hours for the stomata to reach minimum or maximum opening. We only considered data after the stomatal response had stabilized. We are not aware of any physiological evidence that there would be any differences between the lab and the real world due to sudden changes in light rather than gradual setting and rising of the sun, except during this transition time.

Line 210: It would be helpful if the authors explained what exactly to look for in Table 2

All results discussed are in table 2. Specifics of what to look for in table 2 are discussed thoughout the manuscript.

Line 211: the two methods don't seem that different to me they are relying on the same assumptions seems just like two ways of presenting one method.

The first discussed shows the overall deposition velocity stomatal scaling factor determined from all data points from all experiments. This method allows the reader to see the overall importance of the mesophyll. The second visualization method allows for a more explicit calculation of mesophyllic resistance. We believe both methods are helpful for communicating our conclusions even thought they are similar.

Line 213: and assuming zero cuticular uptake?

Yes, this has been added.

Line 230: First, "No significant cuticular resistances" implies cuticular uptake is happening. Second, how do the authors know that there is no cuticular deposition when the authors are also inferring Rm? How can the authors know that the residual is Rm and not Rc? Also, I think the authors should spell out here what exactly they are suggesting that the Vd/gt ratio means ("attribute to" is a bit vague) and the assumptions involved

We have changed the wording to be: ″No evidence of cuticular deposition was observed".

The description of V_d/g_t ratio has been changed for clarity. It now reads:

"Positive y-intercepts are indications of cuticular deposition and curvatures in the fit away from the 1:1 line are implications of mesophyllic resistance. "

Line 234: spelling error

This has been corrected.

Line 242-3: What do the authors mean "behave consistently"?

This sentence has been removed.

Line 255: It would be helpful if the authors described what is observed as changing in the relationship between gt and vd, instead of just saying that there are changes and referring to a supplemental figure

This sentence has been deleted to avoid further confusion and a reference to the figure is included in the previous sentence. This figure is similar to Figure 3 and was used to calculate R_m.

Line 263-6: I'm confused. My interpretation is that there is one slope for every plot in Figure 2. So how are the authors looking at a correlation between gt and the slope for each plot? The description of what the authors are doing on n Lines 219-221 could be improved ("slopes were calculated from . . . slopes. . .").

There is one slope for every plot, which often contains over 20 days of experiments. This slope is calculated as a weighted average of the slopes from each day of experiments.

Lines 219-221 now read (now beginning line 242 in the revised manuscript) :

"Figure 2 shows each flux measurement as a single data point. For each day of experiments a slope of predicted vs. measured fluxes was obtained from a least squares cubic weighted fit for the 8—12 fluxes measured at varying NO_2 concentrations. The reported slope for a given species (shown in blue in Fig. 2) was calculated using a weighted average of the slopes from all experiment days. This was done to minimize the contribution of systematic errors potentially introduced by the Licor 7000 instrument, which was calibrated daily. All data points for a given day were excluded (shown in red in Fig. 2) if the calculated slope on that day was determined to be an outlier by a generalized extreme studentized deviate test for outliers."

Lines 263-6 now read (beginning line 290 in revised manuscript):

"We also examined the potential impact of the mesophyllic processing of NO_2 by considering the Pearson's correlation coefficient between g_t and the slope for an individual experiment (1 day of light or dark data) of measured vs. predicted fluxes."

Line 284-6: Not sure what to do with this information.

We include this to compare our results to what atmospheric models currently include. We discuss the implications in the subsequent text.

Line 299-300: This seems like a rather broad conclusion based on the limited evidence that the authors have presented.

Our use of the word "suggest" rather than a stronger one is intended to encourage the reader to make their own judgement. We think the statement appropriate based on the evidence and analysis we present.
Nevertheless we have clarified the sentence to make our conclusions more specific to California forests (line 332 -335 in the revised manuscript):

"Contributions from mesophyllic processing, though mechanistically important at a cellular level, are likely to not matter at the canopy-scale in California forests. We therefore suggest that on canopy and regional scales, mesophyllic processes within leaves of trees represent a negligible contribution to NO_x budgets and lifetimes in California. More studies on crops, grasses, and North American tree species from outside of California are needed."

. Line 305-6: why is the fertilized group experiencing stress "supported by previous studies [finding] a negligible impact of N fertilization on NO2 uptake"? I think "these" should refer to the sentence before "We did observe. . ." but the writing is unclear.

Sentences have been rearranged for clarity:

"We observed no effects of soil nitrogen, in the form of NH_4^+ and NO_3^-, or the leaf nitrogen content on the ratio of V_d/g_t (Fig. 4) for either *Q. agrifolia* or *P. menziesii*. Changes in this ratio would indicate an effect on the mesophyllic resistance. We did observe declines in g_t in the fertilized group relative to the control group during the later stages of experimentation, which coincided with observable evidence of plant stress (e.g., browning, wilting, and beginning signs of embolism). All variation in the uptake rates (V_d) could be explained exclusively with deviations in g_t. These results are supported by previous studies which have also found a negligible impact of nitrogen fertilization on NO_2 uptake (Teklemmariam and Sparks 2006; Joensuu et al., 2014). "

Line 308: uptake can't ever be bidirectional

"bidirectional" has been changed to "reversible".

Line 309: how do the authors know that there is actually accumulation in NO3 and NO2 within the mesophyll after fertilization? Is this from the leaf N measurements?

Based on the leaf N measurements we can say that either we accumulated inorganic nitrogen in the leaves and it had no effect, or that we gave the an extreme amount of nitrogen fertilizer and it still did not cause accumulation. The sentence (line 343 in revised manuscript) has been adjusted to make this more clear:

"If the fertilizer results in increased NO_3^- and NO_2^- in the leaf, this suggests that the mechanism of NO_2 uptake via dissolution and subsequent reduction of NO_3^- and NO_2^- is likely not reversible and not influenced by accumulation of NO_3^- and NO_2^- within the mesophyll. Alternatively, if the increase in soil nitrogen leads only to an accumulation of organic nitrogen in the leaf, this increase has no effect on the uptake rates."

? Line 309: “neither . . . nor” (here and elsewhere)

Fixed.

Line 310: what does “disproportionation” mean?

Disproportionation is the chemical word for a reaction of the form 2A → A′ + A″, where substance A is simultaneously oxidized and reduced (See Lee and Schwarz 1981). Here $2NO_2$ → nitrate and nitrite.

Line 311: I’m not following why this “further supports. . .atmospheric unimportant”

The following has been added to replace the sentence previously on line 311 (347 in revised manuscript):

”Based on our current understanding of the mechanism of NO_2 mesophyllic processing, if reactions in the mesophyll indeed affect the rate of stomatal uptake, our fertilization experiments should have succeeded in changing NO_2 uptake rates, given that they succeeded in changing leaf nitrogen content. Because we observed no effect of nitrogen fertilization on NO_2 uptake, we believe that this finding further supports that reactions within the mesophyll may be atmospherically unimportant. It is also possible, that the disproportionation of NO_2 to form nitrate and nitrite, and scavenging by antioxidants (e.g. ascorbate) are the rate limiting steps in the mesophyllic processing of NO_2.”

Line 330: I have no idea what the authors mean “atmospherically relevant”. What is/where is this discussed above?

See sections 4.1, lines 315—325 in the revised manuscript. We revise the sentence as follows:

”Although there was a statistically significant impact of drought stress on R_m, this is unlikely to be important to the overall uptake rates of NO_2 an the canopy scale for reasons discussed in section 4.1.”

Line 340: The authors can’t move like this between lab and model “deposition velocities”

We do not use the term ”deposition velocities” here, or anywhere in this paragraph. The studies cited here all infer that deposition to leaves or soils are necessary to describe observed canopy fluxes and mixing ratios of NO_x. Leaf-level deposition does have an effect on canopy-scale processes.

Line 345: not true see 10.1002/2016JD025519

We thank the reviewer for pointing out this study. A citation to this reference has been added :

” Sparks et al., 2013 did not observe any evidence of non-stomatal deposition in the laboratory, but more recently Sun et al., 2016 implicated non-stomatal deposition in accounting for over 20% of PAN leaf-level deposition. Our PAN deposition experiments however, discussed in Place et al., EST in press, also did not identify any significant non-stomatal deposition. Despite the existing differences regarding the importance of non-stomatal PAN deposition, we suggest that a significant portion of the ″missing″ deposition sink of NO_2 and peroxyacyl nitrates at night may be due to non-total closure of the stomata. ″

Line 339: instead of saying the models assume this, it would be more appropriate to say Wesely scheme assumes this.

This has been adjusted.

Line 346: Is the box model validated for nighttime chemistry and transport in forests?

Yes. Delaria and Cohen, 2020 compared the box model to field measurements over a 24 hour period. In developing that model we went through additional validation processes where we ensured that the resulting lifetimes and loss rates calculated with the model at all times of day were reasonable when compared with field measurements.

Line 350: What do the authors mean at such a low degree of stomatal opening? What does "statistically equivalent" mean? That they are similar in magnitude?

The sentence has been edited to read: ″At such low stomatal conductances, we found these deposition velocities to be not significantly different ($\alpha = 0.05$) from the stomatal conductance to NO_2.″

Line 354: Is this a range in the NOx lifetime to deposition? Or the total lifetime? Also, it doesn't seem like the authors show anything about lifetime in Figure 6.

This has been corrected.

Line 358: reference needed for major chemical nighttime sink as PAN

References have been added.

360-380: this is a lot of info to take in; please consider a table or a figure.

A table has been added to the revised manuscript.

Line 382: what are the significant inconsistencies?

The inconsistencies were outlined in the previous paragraph. There are several contrasting gmax measured by the studies referenced.

Line 390: seems like the authors need to say in June somewhere in the text (it's only in the figure caption). Also, why June? What years are the authors looking at for LAI and NO2?

The information has been added to the text.

? Line 397: Why do the authors use maximum vd here? It seems like the implications of this need to be emphasized.

We have added additional discussion at this point in the manuscript. We use maximum because our purpose is to illustrate the importance of the deposition in a consistent way across the domain. Our intention is that this ”back of the envelope” calculation might be used by others to think about locations where deposition would be interesting to explore further.

Line 398: How does one multiply by “land cover”? What are the units of “land cover”?

This has been removed from the equation. Landcover was either nan for not forest, or 1 for forest, but this is covered by the sentence: ”Only forested sites were considered”.

Line 395: How big are the Forest Service plots? Do the authors define forests with less than 50% of the trees measured in the study as “nonforested”? Are they included in white space on the figure?

This information has been added to the manuscript. They would not be in the white space because the plots are interpolated to a 500 m grid.

Line 396: clarify what the effective vd is

The line has been corrected to:

”For each approximately 24 km^2 hexagonal plot (Bechtold et al., 2005) in the Forest Service Inventory that contained more than 50% of the trees measured in our study, an effective deposition velocity to NO_2 (V_d^{eff}) was calculated as a weighted (by tree species abundance) average from the V_d^{max} values listed in Table 2 (Fig. S3).”

Line 398: can one get midnight measurements of NO2 from OMI?

No. Our midnight measurements were from a WRF-CHEM simulation. We have corrected this in the manuscript, and re-calculated deposition fluxes during both the day and night using the NO_2 and PBL outputs from this simulation for consistency.

Line 400: what is chaparral?

It is a biome found in southern California, characterized by drought-resistant broad-leaved evergreen shrubs and trees (often oaks). The climate consists of hot dry summers and mild wet winters. There is also frequent drought and fire in these regions.

Line 406: what is significant?

This has been clarified in the marked-up manuscript.

Line 417: when do the authors look at vapor pressure deficit?

We alter the stomatal conductance by changing the chamber humidity under the same temperature conditions, which necessarily means we are changing the vapor pressure deficit. Nevertheless we have changed ”vapor pressure deficit” here to ”relative humidity” for consistency.

Line 419: what does “from an atmospheric perspective” mean?

This was added to contrast from a cellular and plant physiological perspective, where there might be indeed variations of internal processing of NO_2.

Line 420: I wouldn’t encourage others to overlook the role of transport through turbulence and molecular diffusion at the large scale though

We do not believe we are doing so. We have changed the sentence to:

”This opens the possibility of using direct measurements of stomatal conductance–coupled with models and measurements of chemical transport, known relationships of the effects of environmental conditions on stomatal opening, measurements of canopy conductance, as well as indirect measurements–such as satellite solar-induced fluorescence–to infer NO_x foliar exchange.”

Line 424: spelling error

This has been fixed.

Line 421-5: does this really merit discussion in the very short conclusion? The authors look at different species because they have different stomatal conductances. For example, the authors say: “To test this, we measured . . . over a range of stomatal conductances” in the introduction. In other words, I feel like this was the motivation in setting up the study, not a conclusion of it.

The differences in these species have not been shown before, and many of them–our six conifers, two broadleaf deciduous trees, and two broadleaf evergreen trees–would be treated the same in the widely utilized Wesely model. The range of stomatal conductance was achieved for each of the ten species by varying humidity, as is discussed in the methods sections, and demonstrated in Figure 3.

Line 436: can the authors briefly summarize here their evidence for “large and important”

We have changed the wording to:

”Our observations of stomatal opening in the absence of light also suggest foliar deposition may represent as much as 25% of the total NO_x loss at night, with stomatal deposition velocities as high as 0.038 cm s^{-1}. ”

Figures should be cleaned up to make them more appropriate for publication. The axis labels and tick marks should look better.

We will review the figures in the galleys to ensure that labels and tick marks are clear to the reader.

Figure 2: what data is included here? No N or drought perturbations right?

This figure does include N and drought data. The figure caption has been updated to clarify this.

Figure 3: specify acronyms used in caption; if the authors briefly described here what we are supposed to take away from helium/zero air differences that would be helpful

These corrections have been made in the revised figure caption.

Figure 4: if the authors said the meaning of Vd/gt ratio in their last sentence it would be even more helpful. Generally I'm not exactly sure how to interpret this figure what should I be looking at in terms of NH4 and NO3?

The conclusions based on this figure are discussed in the text. Ideally, the captions should not have interpretation of figures, just describe the content. Nevertheless, we add: "The amount of soil and leaf nitrogen has no significant impact on the V_d/g_t ratio." and revise the caption to read:

"The V_d/g_t ratio is plotted against soil nitrogen concentration in the form of NH_4^+ and NO_3^- for (a) *Q. agrifolia* and (c) *P. menziesii*. The dashed line shows a linear fit to NH_4^+ data. The relationship is not significantly different (α = 0.05) when fit to NO_3^- data. The V_d/g_t ratio is plotted against the leaf nitrogen:carbon ratio for (b) *Q. agrifolia* and (d) *P. menziesii*. V_d/g_t ratios less that 1 imply contributions from the mesophyll to the NO_2 uptake rate. On each pannel the Pearson's correlation coefficient and the p-value for the slope are shown. The amount of soil and leaf nitrogen has no significant impact on the V_d/g_t ratio."

Figure 5: spelling error; again helpful to say in plain language what a compensation point is

The error has been corrected and a definition added.

Table 2 - What does Rm (gt) vs. Rm (gs) mean? Are all compensation points statistically significant or just this one? There are two "e" in the footnotes.

Only the one identified is statistically significant. Clarifications have been made in the table footnotes.

Table 3 - Define acronym for IQR

The acronym has been defined.

Response to reviewer #2

We thank reviewer 2 for their constructive comments. We have addressed the stated concerns below. **Bold text** identifies the reviewer comments and our responses are in standard text. Line numbers in our responses refer to the revised manuscript.

General comments: Since the accurate determination of the flux of NO2 and the deposition velocity depends on the measurement of the concentration of the ingoing and outgoing air of the branch enclosure I miss a more detailed assessment how leak tight the chamber actually was. It is only stated that the chamber was operated at a slight over pressure to ensure lab air contamination. However what about leaks through which NO2 could escape? Additionally if you have higher relative humidity, how much water might condense on the Teflon wall? Might the potential water deposition on the walls depended of the mole fraction of water vapor in the chamber? What really would be beneficial to add measurements of an empty branch enclosure and measuring if and potentially how much NO2 and water vapor are lost due to leakage and/or wall losses.

We provide a more detailed description of our chamber setup in Delaria et al., 2018. With the dynamic chamber setup an equilibrium is reached where the rate of air entering and leaving the chamber is equal. Some of the air leaving the chamber is sampled in our system and some leaks out of the chamber. The leaking out of the chamber does not matter so long as there is positive pressure in the chamber to prevent laboratory air from entering the chamber. We calculate the deposition fluxes after the chamber has reached this equilibrium. We also maintain our chamber to below 90% relative humidity to minimize chamber condensation. To account for wall losses of both NO_2 and water vapor, we periodically ($\approx$ monthly) measure the wall loss of these compounds and use this to correct our calculations. With the lifetime in our chamber around 2 min, the wall loss of NO_2 is approximately 2%. We have added the following statements to the revised manuscript lines P3 83—85, P4, 92—95 and P5, 124—127, respectively. :

"where $[NO_2]_{in}$ and $[NO_2]_{out}$ are concentrations of NO_2 entering and exiting the chamber at chamber equilibrium, respectively. Chamber equilibrium is achieved when the flow rates in and out of the chamber are equal and can be identified by a constant concentration of $[NO_2]_{out}$."

"Experiments to an empty chamber were conducted approximately every two months during this study to calculate the deposition of NO_2 to the chamber walls. The wall loss was at maximum $\sim$2% of the $[NO_2]_in$ concentration and was background subtracted from our flux calculations."

"Measurements of an empty chamber were also used to calculate and correct for the water vapor deposition to the chamber at varying relative humidity. The difference between ω_a and ω_e for an empty chamber was not statistically significant and at all relative humidity levels was within instrumental uncertainty of the Licor-6262."

Line 221 and figure 2: "Some experiments were excluded (shown in red in Fig. 2),as they were determined to be outliers by a generalized extreme studentized deviate test for outliers." I am confused on how this approach was really applied to the data. While the data for P. contorta, P. menziesii, A. menziesii, A. macrophyllum, Q. agrifolia, and Q. douglasii show outliers which seem to have strangely also a linear correlation in themselves, no outliers could be found for C. decurrens and S. sempervirens. If the would a result of what the authors state "most likely

due to systematic error in calibration of the Licor-7000 instrument" then I would expect the outliers to be more random and found for all data sets since I guess the Licor data was taken on the same days for all plants with one calibration applied. The finding and excluding of the outliers (which would have quite an impact if taken into account for the fitting of the measured vs. predicted fluxes (e.g. strongly for P.contorte)) needs to be discussed in more detail as to why the outliers are not more randomly distributed and seem to have a correlation in themselves.

Following comments also from reviewer #1, we have made adjustments to our discussion of Figure 2 to clarify the methods used.

Figure 2 shows each flux measurement we made as a single data point. During each day of experiments we made a 8—12 different flux measurements at different NO_2 concentrations. The licor instruments were calibrated each day and a different water vapor concentration was delivered to the chamber. A slope was individually calculated for each day. Red outlier points are all the data points for a given day having a slope determined to be an outlier. We did it this way because we occasionally noticed issues with a daily Licor calibration.

Lines 239—247 :

"Figure 2 shows each flux measurement as a single data point. For each day of experiments a slope of predicted vs. measured fluxes was obtained from a least squares cubic weighted fit for the 8—12 fluxes measured at varying NO_2 concentrations. The reported slope for a given species (shown in blue in Fig. 2) was calculated using a weighted average of the slopes from all experiment days. This was done to minimize the contribution of systematic errors potentially introduced by the Licor instruments, which were calibrated daily. All data points for a given day were excluded (shown in red in Fig. 2) if the calculated slope on that day was determined to be an outlier by a generalized extreme studentized deviate test for outliers."

Line 264: you examine the correlation of the total conductance vs. the slope of measured vs predicted fluxes. Why do you not provide the correlation graphs (e.g. in the supplement) as well? Seeing the correlation graphs with the fits derived from it are more instructive than just giving the numbers.

Figures have been added to the supplement.

Line 268: "All tree species except for C. decurrens, Q. agrifolia, and Q. douglasii show statistically significant correlations (α = 0.05) (Table 2)." I have difficulties to reconcile this with Table 2. The footnote "c" indicates statistically relevant correlations however the marked values do not correspond with the tree species mentioned in the text. To restate my previous comment also to estimate this the reader would very much benefit from being able to see the correlation plots for g_t vs. slope themselves.

This was an error that has been corrected in the revised manuscript. Note that the listed correlations have changed. The correlations in the table were from a previous manuscript version from before an error in our code was found. The text was correct. Our conclusions are unaffected.

Line 410: In the discussion only the comparable lifetime is mentioned. However comparing Fig. 7 and Fig. 8 one also sees that the flux predicted by the model is significantly lower than

during the day. So the total loss even with similar lifetime during the day will not be as much as during day time. That should be also mentioned in the discussion as well and in general the modelling of the night time fluxes and NO2 lifetime is so shortly presented and discussed that it almost appear as if an addendum. The discussion should be extended.

Yes this is completely true. Our nighttime discussion is meant to suggest the deposition of NO2 is an import sink for NO2 at night that will compete with chemical loss. However, it is correct that the total flux from an ecosystem perspective would be small. Additional discussion has been added. We have also added the following to the revised manuscript line 465—470:

"The deposition fluxes and lifetimes to deposition during the night are shown in Fig. 8. With reduced deposition velocities at night, the nighttime deposition flux and the resulting total loss of NO2to deposition is small. However, with a reduced boundary layer during the night, the lifetime of NOx to deposition is on the same order as the deposition lifetime during the day (10—100 hr) and the overall NOx lifetime at night. This indicates this loss pathway may be an important nighttime sink of NOx from the atmosphere and may affect the nighttime chemical NOx sinks of alkyl nitrate formation and N2O5 chemistry."

Line 425: "large and important" form the comments mentioned before I don't see that yet this statement can be made without at least summing up what this is based on here again.

This statement has been edited to read: ". Our observations of stomatal opening in the absence of light also suggest foliar deposition may represent as much as 25% of the total NO_x loss at night, with stomatal deposition velocities as high as 0.038 cm s^1."

Line 27: The sentence "Although the role. . ." is very hard to follow. I would suggest splitting the sentence in two shorter ones.

We have replaced the sentence with: "Although the role of stomatal conductance (gs) in controlling the deposition of NO_2 is well-documented, the impact of mesophyllic processes remains poorly resolved. These mesophyllic mechanisms are complex and include any process taking place between the intercellular air space and the ultimate nitrogen assimilation site."

Line 159: I assume that in the sentence "100, 200, 100, and 500 µL of 0.2 M citrate, 5 mM nitroprusside,. . ." the second "100" is actually meant to be either 300 or 400? Otherwise is it not clear to me why the 100 is repeated.

The numbers in the list refer to respective listed reagents. We have editted this sentence to be more clear:

"100 μL of 0.2 M citrate , 200 μL of 5 mM nitroprusside, 100 μL of 0.3 M hypochlorite reagents, and 500 μL of milli-q water were then added sequentially into each cuvette."

Line 409: "The lifetimes to deposition during the day. . ." should read "night"

Yes it should have read "night". This has been corrected and the section has been updated following comments from reviewer 1. Please see the marked-up manuscript.

Laboratory measurements of stomatal NO_2 deposition to native California trees and the role of forests in the NO_x cycle

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Abstract.

Both canopy-level field measurements and laboratory studies suggest that ~~absorption~~ uptake of NO_2 through the leaf stomata of vegetation is a significant sink of atmospheric NO_x. However, the mechanisms of this foliar NO_2 uptake and their impact on NO_x lifetimes remains incompletely understood. To understand the leaf-level processes affecting ecosystem scale atmosphere-biosphere NO_x exchange, we have conducted laboratory experiments of branch-level NO_2 deposition fluxes to six coniferous and four broadleaf native California trees using a branch enclosure system with direct Laser Induced Fluorescence (LIF) detection of NO_2. We report NO_2 foliar deposition that demonstrates a large degree of inter-species variability, with maximum observed deposition velocities ranging from 0.15 – 0.51 cm s^{-1} during the daytime, as well as significant stomatal opening during the night. We also find that the contribution of mesophyllic processing to the overall deposition rate of NO_2 varies by tree species, but has an ultimately inconsequential impact on NO_x budgets and lifetimes. Additionally, we find no evidence of any emission of NO_2 from leaves, suggesting an effective uni-directional exchange of NO_x between the atmosphere and vegetation.

1 Introduction

Nitrogen oxides ($NO_x \equiv NO + NO_2$) are a form of reactive nitrogen that ~~plays~~ play a major role in the chemistry of the atmosphere. NO_x catalyzes tropospheric ozone formation, contributes to the production of photochemical smog, and influences the oxidative capacity of the atmosphere (Crutzen, 1979). NO_x is primarily emitted as NO through fossil fuel burning, lighting, and soil microbial activity (Seinfeld and Pandis, 2006). The latter source is of particular importance in remote ~~,~~ forested, and agricultural regions~~.~~, where emission from soils is the primary source of NO_x (e.g. Jacob and Wofsy, 1990; Lerdau et al., 2000; Seinfeld and Pa

Understanding the fate of atmospheric NO_x, in addition to its emission sources, is essential for interpreting the impact of NO_x on atmospheric chemistry. Prior studies have demonstrated that NO_2 can directly deposit to foliage ~~via~~ after diffusion through stomata (e.g., Teklemmariam and Sparks, 2006; Chaparro-Suarez et al., 2011; Breuninger et al., 2013; Delaria et al., 2018). The currently understood mechanism of this uptake process is as follows: NO_2 enters through the stomatal cavity and dissolves into the apoplastic fluid, forming nitrate, which then is reduced to ammonium by the enzyme nitrate reductase (Park and Lee, 1988; Ammann et al., 1995; Tischner, 2000; Lillo, 2008; Heidari et al., 2011). There is evidence that NO_2 may also be directly scavenged by antioxidants, most notably ascorbate (Ramge et al., 1993; Teklemmariam and Sparks, 2006). These processes may be impacted by the leaf pH, which is known to change under conditions of limited water availability (Bahrun et al., 2002). Experiments using ^{15}N as an isotopic tracer have demonstrated that absorbed NO_2 is eventually assimilated into amino acids (Rogers et al., 1979; Okano and Totsuka, 1986). Although the role of stomatal conductance (g_s) in controlling the deposition of NO_2 is well-documented, the impact of ~~the processes in the mesophyll–processes~~ mesophyllic processes remains poorly resolved. These mesophyllic mechanisms are complex and include any process taking place between the intercellular air space and the ultimate nitrogen assimilation ~~site–on the rate of uptake remains poorly resolved~~site. The question of whether and how much mesophyllic processes affect NO_x budgets at the canopy scale thus persists.

The most divisive example of the mesophyll quandry is the sometimes-reported emission of NO_x from plants, mostly in the form of NO, at low NO_x mixing ratios that would be relevant to remote forested regions (Johansson, 1987; Rondón and Granat, 1994; Hereid and Monson, 2001; Sparks et al., 2001; Teklemmariam and Sparks, 2006). This would, under many conditions, indicate that trees instead serve as a constant source, rather than sink, of NO_x. However, this idea has been called into question by a number of recent studies including ~~Lerdau et al. (2000),~~ Chaparro-Suarez et al. (2011), Breuninger et al. (2013) and Delaria et al. (2018). It is possible that the magnitude and direction of the NO_x flux to leaves may vary depending on the species and conditions. One such factor that has been suggested to impact foliar emission and deposition of NO_x is elevated soil nitrogen. Soil nitrate fertilization has been documented to lead to an increase in nitrate reductase activity in the needles of scots pine seedlings (Andrews, 1986; Pietilainen and Lahdesmaki, 1988; Sarjala, 1991). It is possible that as a result of abundant nitrate fertilization, nitrate accumulates in leaves, leading to emission or a reduction in uptake. For example, Chen et al. (2012) observed an increase in NO emission and Teklemmariam and Sparks (2006) detected an increase of NO_2 emission under conditions of elevated soil nitrate. *Per contra*, Joensuu et al. (2014) found no evidence of fertilization-induced NO_x emissions. No influence of soil nitrogen on either NO_2 or NO uptake has been documented ~~at atmospherically relevant conditions~~ (Okano and Totsuka, 1986; Teklemmariam and Sparks, 2006; Joensuu et al., 2014).

In this study we present results from laboratory measurements of NO_2 fluxes ~~on~~ of ten native California tree species–six conifers and four broadleaf trees–using a branch enclosure system and laser-induced fluorescence (LIF) detection of NO_2. Here we investigate the relative influence of stomatal and mesophyllic processes on the total uptake rate of NO_2 under atmospherically relevant conditions. Our aim is to assess the factors controlling NO_2 foliar deposition and their ultimate impact on the NO_x cycle. To test this, we measured the NO_2 deposition velocity over a range of stomatal conductances and considered evidence for additional limits on the uptake rate. We also conducted experiments under drought and elevated soil nitrogen and tested for indications of ~~an~~ NO_2 ~~compensation point~~ emission or changes in the apparent mesophyllic uptake limit.

2 Methods

2.1 Tree specimens

Foliar deposition of NO_2 was investigated in the laboratory using ten native California tree species–*Pinus sabiniana, Pinus ponderosa, Pinus contorta, Pseudotsuga menziesii, Calocedrus decurrens, Sequoia sempervirens, Arbutus menziesii, Acer macrophyllum, Quercus agrifolia, and Quercus douglasii.* Three to six individuals of each species were purchased from a local native California plant nursery (Native Here Nursery) or Forestfarm, where the plants were grown from seeds and cuttings. The tree specimens were grown in a nutrient-rich commercial soil mixture of Sun Gro Sunshine #4 and Supersoil potting soil in 20—40 liter pots in an outdoor section of the Oxford facility greenhouse at the University of California, Berkeley. The trees were 2—3 years old when measurements were taken. No additional fertilizers or pesticides were used on the plants. Trees were transported into the lab for experimentation, where they were exposed to a 12 h light/dark cycle. Trees were illuminated with an LED diode array of 430—475 and 620—670 nm lights (Apollo Horticulture). For the deciduous trees (*Q. douglassi, and A. macrophyllum*) experiments were run between May and September 2019. For all other species experiments were conducted year-round, between October 2018 and November 2019.

2.2 LIF measurement of NO_2 deposition fluxes

Measurements were made with a dynamic chamber and Laser-Induced Fluorescence (LIF) detection of NO_2. A full description of our apparatus can be found in Delaria et al. (2018). Briefly, an NO_2 standard was mixed with humidified zero air (air filtered to remove NO_x and reactive species) and delivered to a ~10 L chamber enclosing the branch of a tree at a total flow rate of ~6000 cm^3 min^{-1} (Fig.1). The lifetime of air within the chamber was $\sim$ 2 min. Humidity was adjusted by controlling the fraction of zero air that passed through a bubbler filled with distilled water. The mixing ratios of NO_2 entering the chamber were typically between 0—10 ppb. Some of the air entering the chamber was diverted to cell #1 of the NO_2 LIF analyzer and two Licor instruments (6262 and 7000) for measuring the mixing ratios of NO_2 and H_2O/CO_2, respectively in the in-flowing air stream, such that the flow rate of air directly into the chamber was ~5000 cm^3 min^{-1}. Air from the chamber was simultaneously pumped out to cell #2 of the NO_2 LIF analyzer and the Licor-7000 instrument for measuring the mixing ratio of NO_2 within the chamber and the change in CO_2 and water vapor between the in- and ~~outgoing~~ out-going air streams, respectively (Fig. 1). A slight positive pressure was maintained within the chamber to ensure lab air did not leak into the chamber.

Fluxes of NO_2 to leaves were calculated according to (Eq. 1—2):

$$Flux = \frac{Q}{A}([NO_2]_{in} - [NO_2]_{out}) \qquad (1)$$

$$Flux = V_d([NO_2]_{out} - [NO_2]_{comp}) \qquad (2)$$

where $[NO_2]_{in}$ and $[NO_2]_{out}$ are concentrations of NO_2 entering and exiting the chamber, respectively, at chamber equilibrium. Chamber equilibrium is achieved when the flow rates in and out of the chamber are equal and can be identified by a constant concentration of $[\mathrm{NO}_2]_{out}$. $[\mathrm{NO}_2]_{comp}$ is the compensation point concentration, Q is the flow rate (cm^3/s), A is the enclosed one-sided leaf area, and V_d is the deposition velocity. The leaf area was determined using the ImageJ software package (Schneider and Eliceiri, 2012) and the flow rate was measured at the beginning of each experimental run (Mesa Laboratories 510-M Bios Defender). Peroxyacetyl nitrate (PAN) and acetone were also delivered to the chamber for simultaneous measurements of PAN stomatal deposition. Negligible thermal production of NO_2 was observed. The results of PAN deposition experiments will be discussed elsewhere. The NO_2 mixing ratio was also corrected for the differences in collisional quenching of the excited state NO_2 by water vapor in cells #1 and #2, caused by transpiration of the tree within the chamber (Thornton et al., 2000).

$$[NO_2]_{out,actual} = [NO_2]_{out,measured} \times (1 + 5\Delta X_{H_2O}) \tag{3}$$

where ΔX_{H_2O} is the difference in the water vapor mole fraction between the chamber and the incoming air stream. Experiments to an empty chamber were conducted approximately every two months during this study to calculate the deposition of NO_2 to the chamber walls. The wall loss was at maximum $\sim$2% of the $[\mathrm{NO}_2]_{in}$ concentration and was background subtracted from our flux calculations.

Deposition velocities were determined using the method described in Delaria et al. (2018): a weighted orthogonal distance linear regression was performed on NO_2 fluxes (determined using Eq. 1) against $[\mathrm{NO}_2]_{out}$ to obtain a slope equal to V_d. A positive x-intercept was interpreted as evidence for a possible compensation point. During each day of experimentation we stepped through at least 8 different NO_2 concentrations, with each concentration step lasting for 40 minutes. Uncertainty in V_d was obtained through propagating uncertainty in measured NO_2 concentrations, Q, and A. The uncertainty in NO_2 concentrations was estimated as one standard deviation of variation in measurements during the last 10 minutes of each concentration step. The uncertainty in Q was estimated as <1 % and a 10% uncertainty was estimated for the enclosed one-sided leaf area.

The deposition velocities measured can be related to the resistance-model framework for deposition of trace gases developed by Baldocchi et al. (1987) (Eq.4—6).

$$V_d = \frac{1}{R} \tag{4}$$

$$R = R_a + R_b + R_{leaf} \tag{5}$$

$$\frac{1}{R_{leaf}} = \frac{1}{R_{cut}} + \frac{1}{R_s + R_m} \tag{6}$$

R is the total resistance to deposition, R_a is the aerodynamic resistance, R_b is the boundary layer resistance and R_{leaf} is resistance to uptake by the leaf. R_a was assumed to be negligible under our chamber conditions (Pape et al., 2009; Breuninger et al., 2012; Delaria et al., 2018). R_{leaf} is made up of R_{cut}, R_s, and R_m. Respectively, these refer to the cuticular resistance (resistance to deposition to the surface of the leaf), stomatal resistance ($1/g_s$), and mesophyllic resistance (resistance associated with all processes taking place within the leaf that limit uptake).

2.3 Measurement of stomatal conductance

CO_2 and water vapor exchanges were measured using the Licor 6262 and Licor 7000 instruments. Measurements of water vapor exchange were used to calculate the transpiration rate (E) and total conductance to water vapor (g_t^w) using Eq. 7 and Eq. 8, according to von Caemmerer and Farquhar (1981).

$$E = \frac{Q}{A}\frac{w_a - w_e}{1 - w_a} \tag{7}$$

$$g_t^w = \frac{E(1-(w_i + w_a)/2)}{w_i - w_a} \tag{8}$$

where w_a and w_e are the mole fractions of water vapor of the outgoing and incoming airstreams, respectively, and ω_i is the internal leaf water vapor mole fraction. ω_e was measured with the Licor-6262 with dry air as a reference and ~~$\Delta\omega(\omega_a - \omega_e)$~~ $\Delta\omega\ (\omega_a - \omega_e)$ was measured with the Licor-7000 with incoming air as the reference. ω_e was kept constant throughout a day of measurements and was varied between days. Measurements of an empty chamber were also used to calculate and correct for the water vapor deposition to the chamber at varying relative humidity. The difference between ω_a and ω_e for an empty chamber was not statistically significant and at all relative humidity levels was within instrumental uncertainty of the Licor-6262. ω_i was assumed to be the saturation vapor pressure at the leaf temperature, which was measured with a thermocouple at the surface of an enclosed leaf. The chamber temperature was measured with a second thermocouple and was typically 20±3°C. Over the course of a day the temperature and humidiy varied by a maximum of 2 °C and 5%, respectively. These deviations were not found to be significantly correlated with stomatal opening. The photosynthetic photon flux density (PPFD) was monitored outside the chamber with a LiCor quantum sensor (LiCor LI-190SA) and was 1190 μmol m^{-2} s^{-1}, approximately the PPFD for Berkeley, California, at noon during the month of October. We performed calculations based on von Caemmerer and Farquhar (1981) to confirm this is above the photon flux required to achieve maximal stomatal aperture for tree types relevant to this study. Total conductance was calculated as the average over the light or dark period of an experiment. The uncertainty in our calculation of total conductance to water vapor was primarily influenced by uncertainty in the leaf temperature and the assumption of leaf water vapor saturation. We observed fluctuations in the temperature of enclosed leaves of ±2°C. Total uncertainty in g_t^w was determined by propagating this uncertainty in leaf temperature, which resulted in larger estimated uncertainties at larger chamber humidities, usually coinciding with higher stomatal conductances. Chamber relative humidity was maintained at less than 90% to minimize this effect. Variations in stomatal conductance were achieved by varying the mole fraction of water vapor in the air delivered to the chamber. The Licor-6262 instrument was calibrated weekly using standard CO_2 cylinders and ~~the~~ a Licor-610 dewpoint generator. The Licor-7000 instrument was calibrated daily.

The stomatal conductance (g_s^w) could then be calculated from Eq. 9:

$$\frac{1}{g_s^w} = \frac{1}{g_t^w} - \frac{1}{g_b^w} \tag{9}$$

where $1/g_b^w$ is the boundary layer resistance to water vapor. The boundary layer resistance to water vapor was estimated to be negligible under our experimental conditions, with an upper bound of 0.6 s cm^{-1}~~determined using the methods described~~

~~by Delaria et al. (2018).~~ . This was calculated by measuring the deposition of NO_2 to a 30 cm^2 tray of activated charcoal and confirmed by measuring the evaporation from a water-soaked Whatman No. 1 filter paper. (Delaria et al., 2018). A detailed description of our assumption of negligible R_b can be found in section 3.1. Stomatal (g_s) and total (g_t) conductances to NO_2 were calculated by scaling the values for water vapor by the ratio of diffusivities in air (D_{NO_2}/D_{H_2O}) according to Massman (1998).

2.4 Nitrogen measurements

To test the influence of excess soil nitrogen on the ability of trees to take up nitrogen through their stomata in the form of NO_2, we fertilized three individuals of both *Quercus agrifolia* and *Pseudotsuga menziesii* with a 20 mM ammonium nitrate ~~soilution~~solution. The trees were watered with 250 ml of this ammonium nitrate solution three days per week. Three individuals of each species were watered with DI water as the control group. The trees underwent this fertilization treatment for 120 days before beginning dynamic chamber measurements on NO_2 foliar deposition. NO_2 deposition experiments were conducted for 70 days, during which time the soil fertilization treatments were continued.

2.4.1 Soil nitrogen

Approximately 5 mg of a soil core sample was taken each day from the individual on which we conducted an NO_2 deposition experiment. The soil was sifted through a mesh 2 mm sieve. Soil nitrate and ammonium were extracted by shaking $\approx$2.5 mg of the soil sample in 30 ml of $\approx$ 2M KCl for one hour, followed by filtering the samples through a Whatman No.1 filter paper. The other $\approx$2.5 mg was dried in a drying oven at 60°C for at least 48 hours. The mass of the soil after drying was measured to determine the percentage dry mass of the extracted soil sample. Six KCl blanks, 3 KCl samples spiked with 5 mL (low QC), and 3 KCl samples spiked with 10 mL KCl (high QC) were carried through the extraction process to serve as quality controls (QC samples). NH_4^+ and NO_3^- were measured using a colorimetric synthesis following the method of Sims et al. (1995) and Decina et al. (2017). Briefly, a standard 1 ppm stock solution of ammonium nitrate was made from ammonium nitrate solid dissolved in milli-q water, and was diluted to 0, 0.1, 0.2, 0.3, 0.4, and 0.5 mg/L in 1 cm, 2.5 mL cuvettes. These standard solutions served as the calibration standards; we made three sets of calibration standards for both ammonium and nitrate analysis. All glassware was acid washed in a 1M solution of HCl prior to all measurements and extractions to prevent contamination.

For ammonium analysis, 160 μL of each soil extraction sample from the control group, 10 μL from the fertilizer-treated group, and 1.6 mL of the QC samples were pipetted into individual cuvettes. 100 ~~, 200, 100, and 500~~ μL of 0.2 M citrate , 200 μL of 5 mM nitroprusside, 100 μL of 0.3 M hypochlorite reagents, and 500 μL of milli-q water ~~, respectively,~~ were then added sequentially into each cuvette. The cuvettes were filled to a final volume of 2.5 mL with KCl, and the samples were allowed to sit for 30 min. For nitrate measurements, 320 μL and 10 μL of soil samples from the the control and fertilized groups, respectively, and 1550 μL of the QC samples, were pipetted into separate cuvetts. 950 μL of a regent containing 1g/L vanadium chloride and 25 mg/L N-(1-Naphthyl)ethylenediamine (NEDD) was subsequently added to each cuvette, which were then filled to a final volume of 2.5 mL with KCl and allowed to sit for 24 hrs. 160 μL and 320 μL of a control *Q. agrifolia* soil extraction sample were added to one set of calibration standards for ammonium and nitrate analysis, respectively, to test the effects of the soil matrix on the calibration.

Concentrations of ammonium and nitrate in each sample were determined with colorimetric measurements using a custom built spectrophotometer. The spectrophotometer light source was a broad spectrum quartz tungsten-halogen lamp (QTH10 Thorlabs Inc.). The absorption of each sample and standard was measured with the light source passing through a 540 $\pm$ 2 nm bandpass filter (FB570-10 Thorlabs Inc.) for nitrate analysis or a 670 $\pm$ 2 nm bandpass filter (FB540-10 Thorlabs Inc.) for ammonium analysis.

2.4.2 Uncertainty analysis

Concentrations of ammonium and nitrate in the soil extraction samples were determined from the slope in their respective calibration curves. The calibrations for ammonium and nitrate analysis had respective uncertainties of 7% and 5%. The slopes of the calibration curves with added sample from a *Q. agrifolia* soil extraction were not statistically different from those containing only standards, allowing us to exclude the possibility of interference from the soil matrix.

The accuracy uncertainty in the high and low QC samples were 3% and 11%, respectively for anmmonium measurements, and 3% and 12% for nitrate measurements. We estimated the resulting uncertainty for cuvette samples with less than 0.15 mg/L NH_4^+ or NO_3^- (≈ 1.8 μg/mg soil NH_4^+ or NO_3^-) to be 15%. Samples with larger concentrations were estimated to have 5% uncertainty. The blank quality control standards contained 0.04 mg/L ammonium and nitrate. This was blank-subtracted from each sample.

2.4.3 Leaf nitrogen

After deposition experiments were completed the leaves were removed from the trees and dried for 48 hours in a drying oven. The leaves were then ground to a fine powder and the percent nitrogen, hydrogen, and carbon content were measured with a ICP Optima 7000 DV instrument.

2.5 Drought stress

Calocedrus decurrens and *Pinus ponderosa* were drought stressed to study the impact of drought on NO_2 deposition. Three individuals of each species were watered daily (control group) and three individuals of each species were watered with 250 mL once every four weeks (drought group). Limited-water treatment of the drought group was carried out for 60 days before conducting dynamic chamber experiments for NO_2 foliar deposition. NO_2 deposition experiments were run for 30-40 days. During the experiments, the control group was watered 50 mL daily and the experimental group was watered 50 mL once every two weeks. The *P. ponderosa* drought-stress experiments took place between March and June 2019. The *C. decurrens* drought stress spanned from August to December 2019.

The xylem water potential (Ψ_p) of the trees were monitored to measure the drought stress level of the trees using a Scholander pressure chamber (Model 670 PMS Instr. Comp.). Leaves were cut, wrapped in aluminum foil, and then inserted into the pressure bomb. The Ψ_p of cuttings were measured around 11:~~00AM~~ 00 AM each day. A Ψ_p measurement lower than -1.0 MPa indicated signs of drought stress in the *P. ponderosa*. The *C. decurrens* did not show evidence of drought stress in Ψ_p measurements while in the greenhouse, however, early signs of embolism were observed.

3 Results

V_d was calculated for each day of measurements with a weighted linear regression of measured fluxes and chamber NO_2 concentrations (Delaria et al., 2018). No statistically significant compensation point was observed under any experimental condition for the majority of the species studied, in agreement with previous work (Chaparro-Suarez et al., 2011; Breuninger et al., 2013; Delaria et al., 2018). Only *P. menziesii* was found to have a compensation point, estimated to be 20 ppt, but this concentration is below the limit of quantification for our instrument ~~and we believe~~ so we consider this measurement to be consistent with a compensation point of zero. V_d and g_s measurements allowed for consideration of whether the deposition of NO_2 is exclusively stomatally controlled, or is also affected by the internal processing in the mesophyll. We rarely observed total closing of the stomata when the chamber lights were turned off at night. All of the deposition observed at night could be explained by deposition to these partially open stomata. This is consistant with previous studies observing only partial closing of stomata at night in a variety of plant species (Dawson et al., 2007; Drake et al., 2013) . The results of experiments are ~~show~~ shown in (Table 2).

3.1 Measurements of mesophyllic resistance

We utilized two methods ~~of examining~~ for analysing the importance of the mesophyllic resistance on the deposition of NO_2. Figure 2 shows the predicted stomatal-limited NO_2 deposition fluxes, assuming negligible R_b, R_c, and R_m ($Flux = g_t[NO_2]_{out}$) plotted vs. the measured NO_2 fluxes. Our upper bound measurement of R_b for NO_2 ~~is~~ was 1 s cm^{-1} (0.6 s cm^{-1} for water vapor). ~~This was calculated by measuring the deposition of NO_2 to a 30 cm^2 tray of activated charcoal.~~ Assuming $g_s = g_t$ would lead to a maximum of a 60% or 10% error in the calculated g_s with a g_t = 0.6 cm s^{-1} or g_t = 0.1 cm s^{-1}, respectively. However, R_b decreases with the enclosed leaf area according to Pape et al. (2009), which at a minimum was 200 cm^2. The maximum R_b in the chamber should ~~thus be~~ have thus been $\approx$0.1 s cm^{-1}. Assuming $g_s = g_t$ would lead to a maximum of a 6% error ~~in the calculated g_s assuming a~~ at g_t ~~of~~ = 0.6 cm s^{-1} ~~and R_b of 0.1 s cm^{-1}~~ in this case. Any deviation from unity in the observed slope of predicted vs. measured fluxes can thus be attributed to R_m. Any error in our assumption of negligible R_b may partially mask the effect of R_m. We do not expect that variation in R_b due to changes in leaf morphology, micrometeorology, and leaf movement would substantially change the effect of R_b, although we cannot rule out the possibility that this was partially responsible for day-to-day fluctuations in NO_2 fluxes. We confirmed the validity of our assumption of negligible R_b by comparing measurements of total conductance to water vapor, g_t^w, in the chamber to measurements of stomatal conductance for the enclosed branch with a Licor-6800 instrument under identical environmental conditions of light irradiation, humidity, and temperature. This test was performed on one individual of three different tree species, and in all cases the chamber g_t^w measurements were found to be approximately equal to the Licor-6800 measurements of g_s^w within the range of uncertainty in g_t^w.

Significant deviations from unity ~~can~~ in the slope of $g_t[NO_2]_{out}$ vs measured fluxes could be seen in several species, most notably *S. sempervirens* (Table 2 and Fig. 2). ~~Slopes were calculated using a weighted average of the slopes~~ Figure 2 shows each flux measurement as a single data point. For each day of experiments a slope of predicted vs. measured fluxes was obtained from a least squares cubic weighted fit ~~of each individual experiment~~ on the 8—12 fluxes measured at varying NO_2 concentrations. The reported slope for a given species (Table 2~~). Some experiments~~ , shown in blue in Fig. 2) was calculated using a weighted average of the slopes from all experiment days. This was done to minimize the contribution of systematic errors potentially introduced by the Licor 7000 instrument, which was calibrated daily. All data points for a given day were excluded (shown in red in Fig. 2) ~~, as they were~~ if the calculated slope on that day was determined to be ~~outliers~~ an outlier by a generalized extreme studentized deviate test for outliers. Identified outliers were excluded both to account for potentially erroneous deviations in the V_d/g_t ratio (most likely due to systematic error in calibration of the Licor-7000 instrument), and to avoid over-weighting of days with abnormally large stomatal conductances. These latter instances normally coincided with low V_d/g_t ratios, and if these data were also subject to some systematic error, would bias our analysis of R_m.

R_m was also explicitly calculated using the relationship of V_d and g_t. Figure 3 shows V_d from each day of experiments plotted against the measured g_t. ~~Deviations~~ Positive y-intercepts are indications of cuticular deposition and curvatures in the fit away from the 1:1 line are ~~attributable to the~~ implications of mesophyllic resistance. R_m was calculated with a weighted fit of the resistance model:

$$V_d = \frac{1}{R_c} + \frac{1}{(\frac{1}{g_s} + R_m)} \tag{10}$$

No ~~significant cuticular resistances were~~ evidence of cuticular deposition was observed so only results of R_m are recorded (Table 2). The deposition observed with the chamber lights turned off could be explained completely by the measured stomatal conductance. Fits of the resistance model (Eq. 10) typically resulted in cuticular resistances on the order of 1000 s cm^{-1}. R_m was calculated both assuming negligible R_b ($g_s = g_t$) and R_b = 1 s cm^{-1}. There were no significant differences between these two calculations (Table 2).

3.2 Effects of excess soil nitrogen

The impact of soil ~~fertilzation~~ fertilization on the foliar uptake of NO_2 by two tree species, *Q. agrifolia* and *P. menziesii*, was examined by watering a control group of both species with deionized water and a fertilized group with 20 ppm ammonium nitrate. On average, the soil nitrogen concentrations of NH_4^+ and NO_3^- were 100x larger for the fertilized groups than the control groups (Table 1). The percentage of leaf nitrogen content approximately doubled between the control groups and the fertilized groups (Table 1).

The effect of soil nitrogen fertilization and leaf nitrogen content on the ratio of V_d/g_t is shown in Fig. 4. No significant relationship (α = 0.01) was observed for either *Q. agrifolia* ~~of~~ or *P. menziesii*, suggesting the mesophyllic processing of NO_2 is unaffected by soil or leaf nitrogen content . We also observe no increase in the compensation point of NO_2 as a result of higher leaf nitrogen content or elevated soil nitrogen (Fig. 5). ~~The trees on which we conducted these experiments were observed to behave consistently up to the point of embolism.~~

3.3 Drought stress measurements

The impact of drought stress on NO_2 foliar uptake for *C. decurrens* and *P. ponderosa* was observed by regularly watering a control group and watering an experimental, drought group at much lower frequency (once every 4 weeks in the greenhouse, and once every 2 weeks in lab). The median Ψ_p measured was lower for the drought groups than the control groups (Table 3)~~,~~. *C. decurrens* drought median Ψ_p was -0.80 MPa compared to control median of -0.30 MPa, and *P. ponderosa* drought median was -1.05 MPa compared to control median of -0.60 MPa. The first quartiles of the control groups and third quartiles of the drought groups ~~do~~ did not overlap, reflecting a significant difference between the Ψ_p measurements of the two groups. We also observed a strong correlation between measured Ψ_p and stomatal conductance. We ~~find~~ found a more substantial impact of drought on the water potentials, and of the water potentials on the stomatal conductance, in *P. ponderosa* trees than *C. decurrens*. Both these California conifer species are quite drought resistant (Pharis, 1966; Kolb and Robberecht, 1996; Maherali and DeLucia, 2000), but these results may indicate *C. decurrens* is particularly protected against water loss.

The mesophyllic resistance (R_m) calculated showed a statistically significant difference for both *C. decurrens* and *P. ponderosa* between drought-stressed and control groups. R_m in drought-stressed *C. decurrens* increased from 0.37 s cm^{-1} to 1.17 s cm^{-1}, while in *P. ponderosa* R_m decreased from 0.86 s cm^{-1} to 0 s cm^{-1} ~~. The effects on calculated R_m are also reflected in the relationship of measured conductance (g_t)and deposition velocity (V_d) (Figure S4)~~(Fig. S5).

4 Discussion

4.1 Effects of mesophyll resistance on the lifetime of NO_x

The mesophyllic resistances (R_m) for each of the ten tree species measured are calculated from Fig. 3 and Eq. 10 and are tabulated in Table 2, assuming either $g_s = g_t$ or the upper bound for R_b. The slopes of predicted fluxes vs. measured fluxes, calculated in Fig. 2, are also tabulated in Table 2. The importance of the mesophyllic resistance and internal processing of NO_2 can be evaluated by examining both R_m and the slope of measured vs. predicted fluxes. We also examined the potential impact of the mesophyllic processing of NO_2 by considering the Pearson's correlation coefficient between g_t and the slope ~~of~~ for an individual experiment (1 day of light or dark data) of measured vs. predicted fluxes ~~measured on each day an experiment was run.~~ (Fig. S3). These correlation coefficients can be found in Table 2. The more negative this correlation, the greater the deviation in the slope from unity for higher values of g_t, consistent with larger impact of the mesophyll on the NO_2 uptake rate. All tree species except for *C. decurrens*, *Q. agrifolia*, and *Q. douglasii* show statistically significant correlations ($\alpha = 0.05$) (Table 2). R_m becomes more important at larger stomatal conductances (lower stomatal resistances), as can be seen with the increasing deviations from 1:1 in some species at higher values of g_t in Fig.3. Thus, even for trees with higher calculated R_m, the impact of mesophyllic processing is unlikely to be large if the maximum stomatal conductance observed is relatively small, resulting in a slope in the measured vs predicted flux that does not deviate greatly from unity. This is the case for *Q. agrifolia* and *P. ponderosa*. Alternatively, *P. sabiniana* demonstrates a case of a relatively small R_m, but also a smaller slope in measured vs. predicted fluxes, driven by consistently larger stomatal conductances (lower R_s) (Fig. 3). The most sizable impacts of mesophyllic NO_2 processing ares seen in *S. sempervirens*, *P. sabiniana*, and *A. macrophyllum*. These species have the largest maximum observed g_t (Fig. 3, Talbe 2) and slopes of measured vs. predicted fluxes of 0.79 ± 0.04, 0.84 ± 0.03 and 0.84 ± 0.03, respectively. However, the greater uncertainty in measurements of stomatal conductance at a larger chamber humidity calls in to question the accuracy of many g_t measurements larger than approximately 0.4 cm s^{-1}.

To evaluate with greater certainty the relationship of V_d and g_t, we conducted a set of experiments in helium to raise the stomatal conductance by increasing the gas diffusivities while maintaining relatively lower chamber humidity. These experiments were conducted on four of the tree species: *P. sabiniana, S. sempervirens, Q. agrifolia*~~, *A. macrophyllum*~~, and *A. menziesii*. In these experiments the V_d/g_t ratio for ~~*A. menziesii* and~~ *P. sabiniana* remained close to 1:1 up to ~~0.4 and~~ 1.3 cm s^{-1} stomatal conductance ~~, respectively~~ (Fig. 3). ~~We therefore suspect negligible~~ Experiments in helium for this species thus suggest a smaller contribution of the mesophyll ~~to deposition to these two species. The only sizable impact of mesophyllic~~ (red dashed line in Fig. 3). R_m calculated including helium experiments was not statistically different for *S. sempervirens, Q. agrifolia*, nor *A. menziesii*.

Our laboratory-measurements of mesophyllic resistance address the uncertainty in the literature for whether reactions in the mesophyll may be consequential for NO_2 ~~processing is seen in *S. sempervirens*, with a large calculated R_m and a frequently high g_t (Fig. 3, resulting in a slope of measured vs. predicted fluxes of 0.6–considerably below unity.~~ deposition velocities. To our knowledge, no previous studies have explicitly calculated the mesophyllic resistance. Differences between leaf-level deposition velocities and stomatal conductances measured by Breuninger et al. (2013), and observations of leaf ascorbate impacts on uptake rates by Teklemmariam and Sparks (2006) have indicated mesophyllic reactions may be important. Additional studies (Gut et al., 2002; Eller and Sparks, 2006; Chaparro-Suarez et al., 2011) have also shown some evidence that between 20% and 40% of NO_2 deposition is under mesophyllic control. Our findings, however, suggest nearly 90% of uptake is controlled by the stomata.

Currently, atmospheric models incorporate a mesophyllic resistance to NO_2 of 0.1 s cm^{-1} (Zhang et al., 2002). This would result in slope of measured vs. predicted fluxes of 0.94, even with a relatively large average g_t of 0.6 cm s^{-1}. The median slope measured in our study was 0.89. Using the multibox canopy model presented in Delaria and Cohen (2020), we investigated whether our results could possibly imply a more important impact of the mesophyllic resistance on the atmospheric fate of NO_x at the canopy level. This model takes into account in-canopy processes (e.g. vertical transport, chemistry, etc.) to scale leaf-level processes to the canopy-level. The model was run using meteorological conditions for June measured during the BEARPEX-2009 campaign, located at a ponderosa pine forest in the western foothills of the Sierra Nevada mountain range (38°58’42.9"N, 120°57’57.9”W, elevation 1315 m). The model was initialized over two days and data from the third day was analyzed. We conducted two model runs at a stomatal conductance (g_s) to NO_2 deposition of 0.3 cm s^{-1}–the median measured maximum stomatal conductance excluding *P.sabiniana*–with an R_m of either 0.1 or 0.6 s cm^{-1}–the median measured R_m excluding *P. sabiniana*. For a stomatal conductance to NO_2 of 0.3 cm s^{-1} ($\approx$ 0.5 cm s^{-1} to water vapor) the model predicts only a 2.5%

decrease in NO_x lost to deposition with an R_m of 0.6 compared with an R_m of 0.1 s cm^{-1}. The lifetime to deposition with an R_m of 0.1 and 0.6 s cm^{-1} was 30.5 hr and 32.2 hr, respectively, representing only a 6% difference. The total atmospheric lifetime of NO_x in the boundary layer with an R_m of 0.1 and 0.6 s cm^{-1} was 4.86 hr and 4.89 hr, respectively, representing only a 0.6% difference. Even the observed seemingly ~~significant~~ substantial mesophyllic resistance of *S. sempervirens* is therefore likely to be irrelevant at the canopy-scale. Contributions from mesophyllic processing, though mechanistically important at a cellular level, are likely to not matter at the canopy-scale in California forests. We therefore suggest that on canopy ~~, regional, and global~~ and regional scales, mesophyllic processes within leaves of trees represent a negligible contribution to NO_x budgets and lifetimes ~~.~~ in California. More studies on crops, grasses, and North American tree species from outside of California are needed.

4.2 Effects of excess soil nitrogen

We observed no effects of soil nitrogen, in the form of NH_4^+ and NO_3^-, or the leaf nitrogen content on the ratio of V_d/g_t (Fig. 4) for either *Q. agrifolia* or *P. menziesii*. Changes in this ratio would indicate an effect on the mesophyllic resistance. ~~All variation in the uptake rates (V_d) could be explained exclusively with deviations in g_t.~~ We did observe declines in g_t in the fertilized group relative to the control group during the later stages of experimentation, which coincided with observable evidence of plant stress (e.g., browning, wilting, and beginning signs of embolism). All variation in the uptake rates (V_d) could be explained exclusively with deviations in g_t. These results are supported by previous studies which have also found a negligible impact of nitrogen fertilization on NO_2 uptake (Teklemmariam and Sparks, 2006; Joensuu et al., 2014). ~~This~~ If the fertilizer results in increased NO_3^- and NO_2^- in the leaf, this suggests that the mechanism of NO_2 uptake via dissolution and subsequent reduction of NO_3^- and NO_2^- is likely not ~~bidirectional, nor~~ reversible and not influenced by accumulation of NO_3^- and NO_2^- within the mesophyll. ~~It seems likely that either the disproportionation step and~~ Alternatively, if the increase in soil nitrogen leads only to an accumulation of organic nitrogen in the leaf, this increase has no effect on the uptake rates. Numerous studies indicate nitrate reductase activity is affected by the presence of ammonium, nitrate and organic nitrogen in the form of amino acids in a variety of plant species (e.g. Datta et al., 1981; McCarty and Bremner, 1992; Woodin et al., 2006). Based on our current understanding of the mechanism of NO_2 mesophyllic processing, if reactions in the mesophyll indeed affect the rate of stomatal uptake, our fertilization experiments should have succeeded in changing NO_2 uptake rates, given that they succeeded in changing leaf nitrogen content. Because we observed no effect of nitrogen fertilization on NO_2 uptake, we believe that this finding further supports that reactions within the mesophyll may be atmospherically unimportant. It is also possible that the disproportionation of NO_2 to form nitrate and nitrite and scavenging by antioxidants (e.g. ascorbate) are the rate limiting steps in the mesophyllic processing of NO_2, ~~or that under biologically relevant conditions nitrate reductase is not saturated. This finding further supports that reactions within the mesophyll are atmospherically unimportant~~rather than enzyme activity. More leaf and cellular-level studies are needed to elucidate the uptake mechanism.

We also did not observe any evidence for a relationship between the NO_2 compensation point and the soil nitrogen content nor the leaf nitrogen content (Fig 5) for either *Q. agrifolia* or *P. menziesii*. In general, we only observed uptake and no emission of NO_2. We also conducted measurements of NO uptake and emission, but the fluxes measured were so small they were below the limit of quantifcation for our instrument. Chen et al. (2012) observed a strong relationship between NO emissions from stomata and soil nitrate fertilization. However, the maximum NO emissions they measured were a factor of 50 lower than the deposition of NO_2 measured here. NO emission from leaves is therefore not likely to be ~~a significant~~ an important source of atmospheric NO_x. *P. menziessi* was the only tree examined in our experiments that demonstrated any evidence for emission of NO_2 at low mixing ratios, with a compensation point of $\approx$ 20 ppt. This concentration is much lower than has been observed in previous studies that have detected an NO_2 compensation point (Hereid and Monson, 2001; Teklemmariam and Sparks, 2006). However, this concentration is near the limit of detection for our instrument (Delaria et al., 2018) so should be taken *cum grano salis*. A possible cause for discrepancy between our study and those that have measured significant NO_2 compensation points is that our experiments are conducted only using photosynthetically active radiation. Some past work has demonstrated that UV light may cause photolysis of nitrate at the leaf surface and subsequent emission of NO_x (Hari et al., 2003; Raivonen et al., 2006). The lack of a relationship between NO_x emission and soil N fertilization contrasts with the results of Teklemmariam and Sparks (2006), but is consistent with the nitrogen fertilization experiments conducted by Joensuu et al. (2014).

4.3 Effects of drought stress

Although there was a statistically significant impact of drought stress on R_m, this is unlikely to be ~~atmospherically relevant for reasons stated above. Additionally,~~ important to the overall uptake rates of NO_2 an the canopy scale for reasons discussed in section 4.1. The differing effects of drought on R_m between *P. ponderosa* and *C. decurrens* is surprising, with the drought group having a smaller R_m in *P. ponderosa* and larger R_m in *C. decurrens*. However, in the case of *P. ponderosa*, the lack of measurements at larger g_t is likely to mask any existing mesophyllic effects, leading to minimal deviation in ~~V_d/g_t~~ the total slope of predicted vs. measured fluxes from unity (Fig. ~~S4~~S5). Despite a calculation of significant mesophyllic resistance in both drought and control *C. decurrens* individuals, the lack of a statistically significant (α = 0.05) correlation between g_t and ~~V_d/g_t~~ the slopes of predicted vs. measured fluxes casts doubt on this relationship. The control group of *P. ponderosa* is the only for which this correlation is significant. The impact of drought on NO_2 uptake at the leaf-level is thus ~~exclusively its affect~~ primarily its effect on the stomatal conductance. At the canopy-level, documented ~~affects~~ effects of drought on leaf area also requires consideration (Pharis, 1966; Kolb and Robberecht, 1996; Maherali and DeLucia, 2000).

4.4 Effects of nighttime stomatal deposition

Most atmospheric chemical transport models, such as the abundantly utilized WRF-Chem and GEOS-Chem, use the Wesley model for parameterizing dry deposition of gaseous species (e.g., Skamarock and Powers, 2008; Fast et al., 2014; Amnuaylojaroen et al., 2014; Ng et al., 2017). ~~These models implicitly assume~~ The Wesley model implicitly assumes the stomata are fully closed at night, despite more recent studies demonstrating many species of vegetation maintain partially open stomata at night (Musselman and Minnick, 2000; Dawson et al., 2007; Fisher et al., 2007; Drake et al., 2013). We find minimal cuticular deposition of NO_2, in agreement with several other studies (Sparks et al., 2001; Chaparro-Suarez et al., 2011). However, field observations have shown that substantial leaf-level nighttime deposition of NO_2 is necessary to explain nighttime levels of NO_x (Jacob and Wofsy, 1990). The same phenomenon has been seen with other gaseous molecules, most notably PAN, which has also been ~~observed to have a non-zero~~ suggested by a number of field observations to have significant non-stomatal deposition at night ~~(Wolfe et al., 2009; Crowley et al., 2018). Laboratory studies have measured zero PAN cuticular deposition(Sparks et al., 2003).~~ (Turnipseed et al., 2006; Wolfe et al., 2009; Crowley et al., 2018). Sparks et al. (2003) did not observe any evidence of non-stomatal deposition in the laboratory, but more recently Sun et al. (2016), implicated non-stomatal deposition in accounting for over 20% of PAN leaf-level deposition. Our PAN deposition experiments however, discussed in Place et al. ES&T in press, also did not identify any significant non-stomatal deposition. Despite the existing differences regarding the importance of non-stomatal PAN deposition, we suggest that a significant portion of the "missing" deposition sink of NO$_2$ and peroxyacyl nitrates at night may be due to non-total closure of the stomata.

To assess the impact of nighttime stomatal opening on the atmospheric fates and lifetimes of NO$_x$ at night, we ran our 1-D multibox canopy model, under the conditions described above, at the minimum, maximum, 25th percentile, and 75th percentile of the median nighttime deposition velocities measured in this study (0.004, 0.087, 0.009, and 0.038 cm s $^{-1}$, respectively). At such ~~a low degree of stomatal opening~~low stomatal conductances, we found these deposition velocities to be ~~statistically equivalent to~~ not significantly different ($\alpha = 0.05$) from the stomatal conductance to NO$_2$. The fractions of NO$_x$ loss to deposition and chemistry to these levels of stomatal opening at night are shown in Fig. 6. Here chemistry represents loss to HNO$_3$, RONO$_2$, and PAN, and nighttime is defined from 20:00 — 05:00. The range between the first and third quartile of the nighttime deposition observed results in a range in the fraction of NO$_x$ loss to deposition from 13% to 25% (Fig 6) and a range in total NO$_x$ lifetime from ≈ 7.5—5 hrs~~(Fig 6)~~.

The relatively large impact of the nighttime stomatal conductance on the fate of NO$_x$, coupled with the large degree of inter-species variation in nighttime stomatal opening, indicates a need for more extensive studies of the nighttime deposition of NO$_2$. Deposition is a permanent sink of atmospheric NO$_x$, contrasting with ~~the major~~ chemical nighttime sink of NO$_x$ to ~~PAN formation~~ peroxyacyl nitrates (Russell et al., 1986; Cantrell et al., 1986; Perring et al., 2009). Heterogenous reactions at aerosol surfaces involving the NO$_x$ reservior N$_2$O$_5$ and alkyl nitrate formation are among the other major nighttime chemical NO$_x$ sinks (Perring et al., 2009; Stavrakou et al., 2013; Kenagy et al., 2018). The relative fractions of nighttime NO$_x$ loss to deposition and ~~PAN formation would thus be~~ chemistry is likely to have a substantial impact on the fate of atmospheric NO$_x$ and the cycling of ~~NO$_x$~~reactive nitrogen.

4.5 Impacts on the nitrogen cycle in California

To our knowledge, this is the first study conducted on NO$_2$ stomatal deposition to native California tree species, except for *Q. agrifolia* (Delaria et al., 2018). However, there are many measurements of the stomatal conductance of ~~Californian trees~~ California trees (Table 4) with which to compare our maximum total conductance to water vapor measurements (max g_t^w). Murray et al. (2019) examined patterns in maximum ~~g_s^w (max~~ stomatal conductance to water vapor (max g_s^w) across bioclimatic zones. Among the species they looked at were *A. menziesii*, *A. macrophyllum* and *Q. agrifolia*, for which they measured an average ~~max~~ max g_s^w of 550 mmol m^{-2} s^{-1}, 420 mmol m^{-2} s^{-1}, and 390 mmol m^{-2} s^{-1}, respectively. In comparison, our measurements of ~~max g_s^w~~ max g_t^w for these species were, respectively, 210 ± 10 mmol m^{-2} s^{-1}, 400 ± 100 mmol m^{-2} s^{-1}, and 90 ± 20 mmol m^{-2} s^{-1}. Our estimates of ~~max g_s^w~~ max g_t^w for *A. menziesii* and *Q. agrifolia* are substantially lower. Matzner et al. (2003) report larger conductances than we do for *Q. douglasii* as well (Table 4). Maire et al. (2015) determined a maximum stomatal conductance for *A. menziesii* of 150 mmol m^{-2} s^{-1}~~. For *Quercus* and *Acer* species in similar climate regions, Maire et al. (2015) calculated $max\ g_s^w$ ranging from 103—890 mmol m^{-2} s^{-1} and 112—320 mmol m^{-2} s^{-1}, respectively~~, in better agreement with our measurements. Henry et al. (2019) measured a similar maximum stomatal conductance of *Q. agrifolia* to our study of 95 mmol m^{-2} s^{-1}~~. Maire et al. (2015) also~~ , also in better agreement with our results than Murray et al. (2019). Maire et al. (2015) measured a maximum stomatal conductance to water vapor for *P. ponderosa* and *S. sempervirens* of 124 mmol m^{-2} s^{-1} and ~91 mmol m^{-2} s^{-1}, respectively–considerably smaller than the values measured in this study. Ambrose et al. (2010) measured a ~~max~~ max g_s^w for *S. sempervirens* of 240 m^{-2} s^{-1}, in better agreement with our measurements. ~~*P*~~*C*. ~~*ponderosa*~~*decurrens* ~~stomatal conductance measurements reported in this study were in very~~ max g_t^w reported here are in good agreement with ~~the stomatal conductance measured during the BEARPEX-2009 campaign in a ponderosa pine dominated forest during a wet year (Min et al., 2014; Delaria and Cohen, 2020)~~previous measurements of max g_s^w(Grantz et al., 2019). For *Quercus* and *Acer* species in similar climate regions to California, Maire et al. (2015) calculated max g_s^w ranging from 103—890 mmol m^{-2} s^{-1} and 112—320 mmol m^{-2} s^{-1}, respectively. The median of ~~$max\ g_s^w$~~ max g_t^w for all four angiosperms we measured was 200 mmol m^{-2} s^{-1} , in good agreement with the 250 mmol m^{-2} s^{-1} median of all angiosperms in Mediterranean climate regions found by Murray et al. (2019) and the 215 m^{-2} s^{-1} median found by Maire et al. (2015). Our median for the six gymnosperms measured was 230 m^{-2} s^{-1}, considerably larger than the median 100 m^{-2} s^{-1} ~~max~~ max g_s^w found by Maire et al. (2015) in Meditteranean climate regions (defined as warm temperature steppe regions as classified by Kottek et al. (2006)).

Overall, the ~~stomatal~~ total conductances to water vapor measured in our laboratory experiments ~~falls~~ fall within the ranges of ~~$max\ g_s^w$~~ maximum stomatal conductances measured in previous studies–although ~~significant~~ inconsistencies exist in the current literature. (We also consider this to further support our conclusion that the boundary layer resistance in our chamber is negligible). Possible discrepancies may have resulted from the location each species were measured, growing conditions, ages of the trees, etc. Nevertheless, our NO$_2$ deposition results–and their applicability to California forests–are bolstered by the fact that our ~~$max\ g_s^w$ measurements fall with in the ranges~~ max g_t^w measurements fall within the ranges of max g_s^w measured for for mature trees in the field. To assess the impact of the lab-measured deposition velocities on the NO$_x$ cycle in California, we used our measurements of ~~$maxV_d$ and $medV_d$(night)~~ maximum V_d during the day and median V_d at night (V_d^{max} and V_d^{med}(night), respectively) to estimate the flux and lifetime of NO$_x$ to deposition in forests throughout the state during the day and night, respectively (Fig. 7, Fig.8).

The average deposition flux to trees in California was calculated via Eq.11

$$F_{dep} = [NO_2] \times V_d\underline{eff}^{eff} \times LAI \underline{\times \text{land cover}} \tag{11}$$

Leaf area index (LAI) data for June 2018 was obtained from MCD15A2H Version 6 Moderate Resolution Imaging Spectroradiometer (MODIS) Level 4 product (Myneni et al., 2015) (Fig. ~~S3~~S6). The NO$_2$ surface ~~concentration over California was obtained from the OMI satelite using the BEHR product (Laughner et al., 2018)~~ concentrations and planetary boundary layer heights over California were obtained from a WRF-CHEM simulation for June 2014 (Fig. ~~S3) .~~ S6) (Laughner et al., 2019).

The month of June was chosen because in California this is when forests have a large LAI, large GPP, the greatest sunlight availability, and ecosystems often experience water limitations in the later summer (Turner et al., 2020). Land cover data was obtained from NLCD Land Cover (CONUS) for 2016 (Yang et al., 2018) (Fig. S1). ~~The land cover data set was modified such that there were only two land categories: forest and not forest.~~ Only forested sites were considered. Although the use of products from different years may introduce some error into our calculations, this will not qualitatively change our conclusion. Tree counts were obtained from the USDA Forest Service Forestry Inventory Analysis Database (for, 2014) (Fig. S2). For each ~~plot~~ approximately 24 km^2 hexagonal plot (Bechtold, 2005) in the Forest Service Inventory that contained more than 50% of the trees measured in our study, ~~a weighted averaged~~ an effective deposition velocity to NO_2 (~~V_deff~~V_d^{eff}) was calculated ~~from the max V_d~~ as a weighted (by tree species abundance) average from the V_d^{max} values listed in Table 2 (Fig. ~~S3).~~ S6). Plots that contained less than 50% of the trees measured were not considered. Data was interpolated to a 500m grid. The resulting midday fluxes throughout California are shown in Fig. 7 and midnight fluxes are shown in Fig. 8. The greatest fluxes predicted are ~~near~~ south of the San Francisco Bay Area, where there are high NO_x concentrations, and also a relatively high forest LAI for an urban region (Fig. ~~S3~~S6). Similar hotspots can be seen near Los Angeles in the inland chaparral regions. Large fluxes are also predicted in the foothill forest region of the Sierra Nevada mountain range, where there is a a large LAI, and frequent occurances of *P. sabiniana*, the tree having the largest V_d (Fig. S2, Fig. ~~S3~~S6). Relatively large fluxes occur in this region particularly during the nighttime.

The resulting lifetime of NO_2 to deposition ~~is~~ was calculated via Eq. 12

$$\tau_{dep} = PBL\left(V_d\underline{eff}^{eff} \times LAI\underline{\times \text{land cover}}\right)^{-1} \tag{12}$$

where PBL is the planetary boundary layer height. The lifetimes to deposition during the day ~~for a uniform PBL height of 1 km~~ are shown in Fig. 7. In forested regions the lifetime to deposition is approximately 10 hrs. This ~~is especially significant in the near-urban~~ relatively short lifetime may be especially consequential in south of San Francisco Bay, where deposition ~~is~~ could be competitive with the chemical sinks of HNO_3 and $RONO_2$ formation, which typically represent a lifetime to NO_x loss of 2-11 hrs (e.g., Nunnermacker et al., 2000; Dillon et al., 2002; Alvarado et al., 2010; Valin et al., 2013; Romer et al., 2016; Laughner and Cohen, 2019). ~~The~~

The deposition fluxes and lifetimes to deposition during the ~~day for a uniform PBL height of 100 m~~ night are shown in Fig. 8. With reduced deposition velocities at night, the nighttime deposition flux and the resulting total loss of NO_2 to deposition is small. However, with a reduced boundary layer during the night, the lifetime ~~to~~ of NO_x to deposition at night is on the same order as the deposition lifetime during the day (~~10—100 hr) , representing a very significant permanent loss~~ 10—100 hr) and the overall NO_x lifetime at night. This indicates this loss pathway may be an important nighttime sink of NO_x from the atmosphere ~~when compared with the overall~~ and may affect the nighttime chemical NO_x ~~lifetime at night~~ sinks of alkyl nitrate formation and N_2O_5 chemistry (Brown et al., 2004, 2006; Crowley et al., 2010).

The estimations provided here are intended only to suggest qualitative indications of where NO_x deposition may be important. Because we are ignoring effects of vertical transport and light attenuation through the canopy, and because we are using maximum measured deposition velocities, the deposition reported here is likely to be an upper-bound estimate. We recommend areas where this estimated deposition is highest as regions that should be the subject of future field and large-scale modelling studies.

5 Conclusions

We present measurements assessing the relative effects of stomatal diffusion and mesophyllic processing of NO_2 on the uptake rate of NO_2. We find that the deposition velocity of NO_2 is essentially equal to the stomatal conductance to NO_2 under conditions of drought, excess soil nitrogen, variations in ~~vapor pressure deficit~~relative humidity, and in both the day and night. We find no evidence of any emission of NO_2 from leaves. NO_2 foliar exchange is thus uni-directional and variations are driven–from an atmospheric perspective–nearly entirely by the rate of diffusion through open stomata. This opens the possibility of using direct measurements of stomatal ~~conductance~~conductance–coupled with models and measurements of chemical transport, known relationships of the effects of environmental conditions on stomatal opening, measurements of canopy conductance, as well as indirect ~~measurements, such~~ measurements–such as satellite solar-induced fluorescence ~~data to~~ data–to infer NO_x foliar exchange. Additionally, we find significant differences in deposition velocities between species, reflecting differences in maximum stomatal conductance measurements that have been found by a number of previous studies (e.g., Ambrose et al., 2010; Maire et al., 2015; Henry et al., 2019; Murray et al., 2019). This diversity is not reflected in current ~~atmospehric~~ atmospheric models, and may have a meaningful impact on estimates of regional NO_x fluxes and lifetimes. Our observations of stomatal opening in the absence of light also ~~suggests foliar deposition serves as a large and important sink of~~ suggest foliar deposition may represent as much as 25% of the total NO_x ~~during the night~~loss at night, with stomatal deposition velocities as high as 0.038 cm s^{-1}. These findings not only have important implications for NO_x chemistry, but are also relevant for the atmosphere-biosphere exchange of other gasses, such as CO_2 and biogenic volatile organic compounds.

Author contributions. ERD and BKP designed the experimental setup and ERD, BKP, and AXL collected all NO_2 exchange data. BKP and ERD designed methods and collected data for nitrogen fertilization experiments. ERD and AXL designed methods and collected data for drought stress experiments. ERD performed data analysis, with assistance from AXL. ERD prepared the manuscript in consultation with RCC. RCC supervised the project.

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

Data availability. The data collected in this study can be obtained from the authors upon request.

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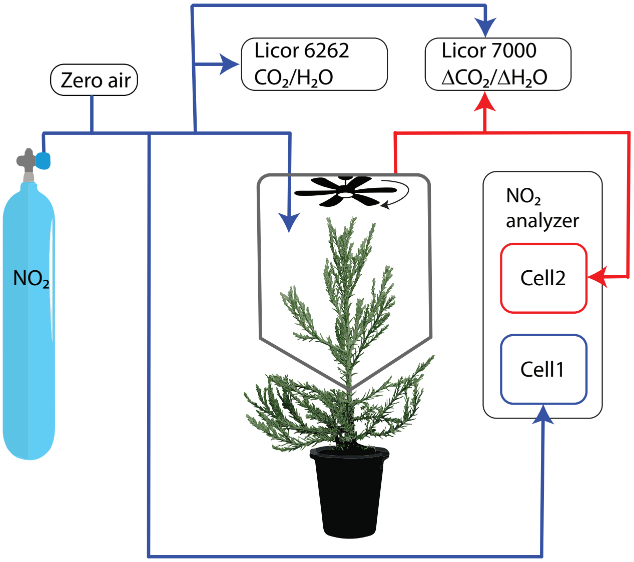

Figure 1. Figure of instrumental setup. Blue lines show the flow of gas that enters the chamber and red lines show the flow of gas sampled from the chamber.

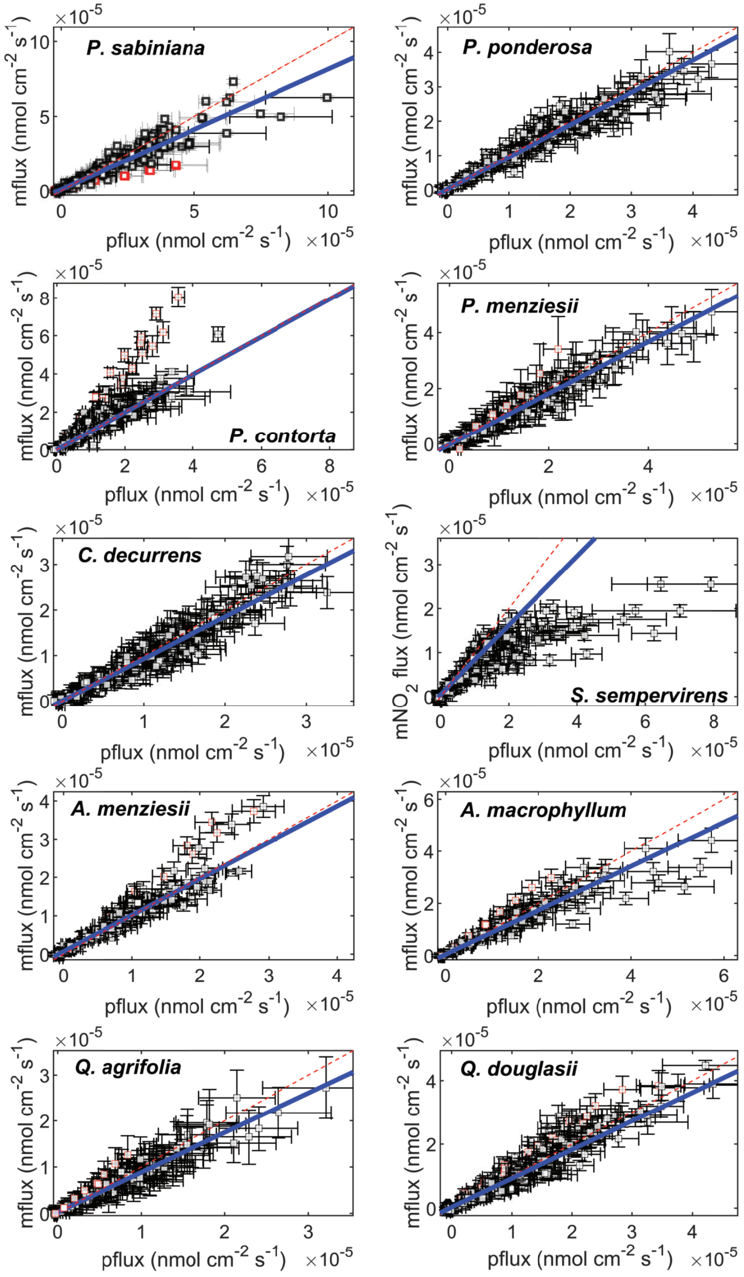

Figure 2. Measured fluxes (mflux) plotted against stomatal-limited predicted fluxes (pflux = $g_t[NO_2]_{out}$). Drought data and nitrogen fertilization data are included. Blue solid lines are the linear fit to data. Red lines are the 1:1 line. Error bars for the measured fluxes are calculated by propagating uncertainty in the measured NO_2 mixing ratios, the flow rate, and the leaf area (Eq. 1). Error bars for the predicted fluxes are calculated by propagating uncertainties in the measured NO_2 mixing ratios and the total conductance (Eq. 8). Red markers indicate data determined to be outliers by a generalized extreme studentized deviate test for outliers.

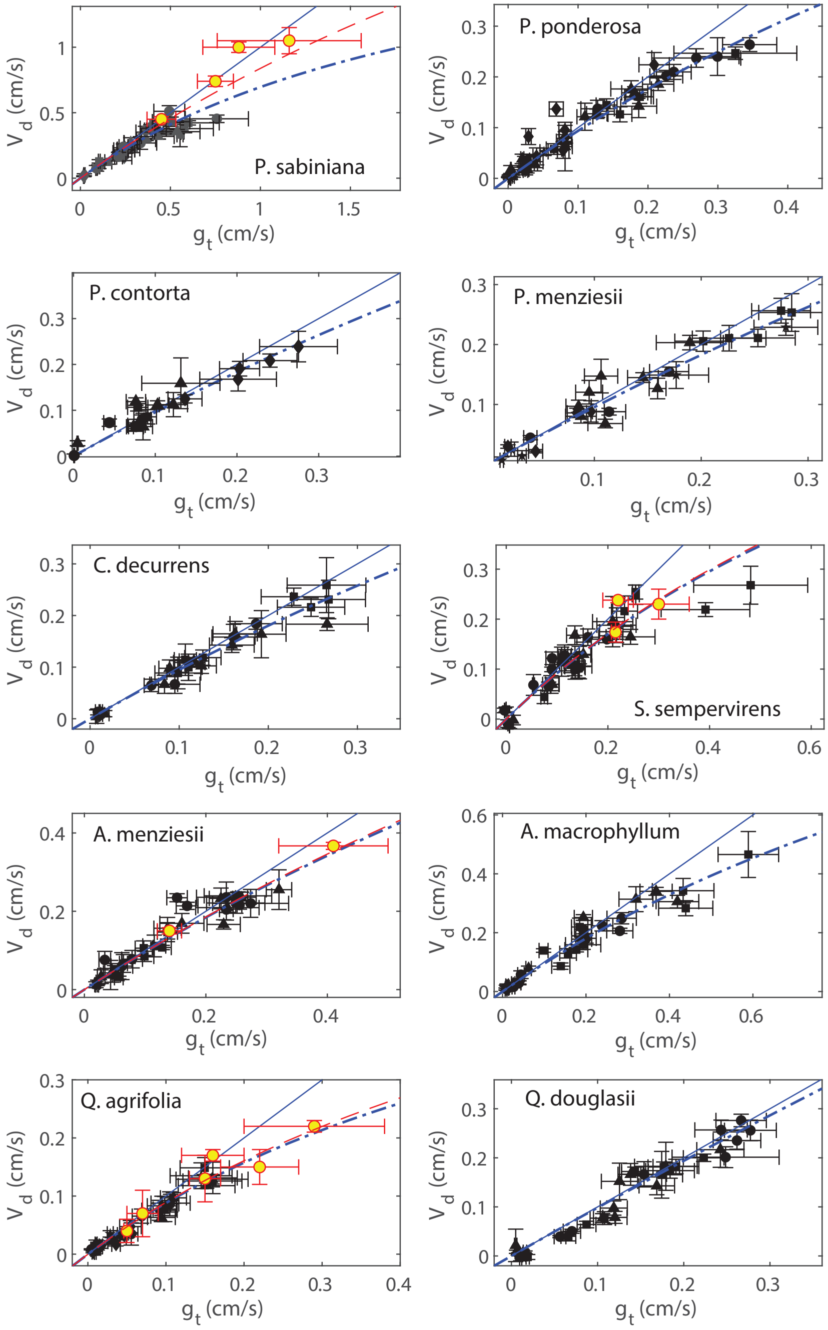

Figure 3. Deposition velocities (V_d) plotted against measured ~~stomatal~~ total conductances to NO$_2$ (g_t). Black markers represent measurements in zero air and red-yellow markers are measurements in helium. Measurements in helium are subject to less uncertainty introduced by potential systematic error in the leaf temperature. Solid blue lines are the 1:1 line and dashed blue lines are error weighted fits to the resistance model using only measurements in zero air, assuming the boundary layer resistance is negligible (Eq. 4). Fits to the resistance model including data from helium measurements are shown as dashed red lines.

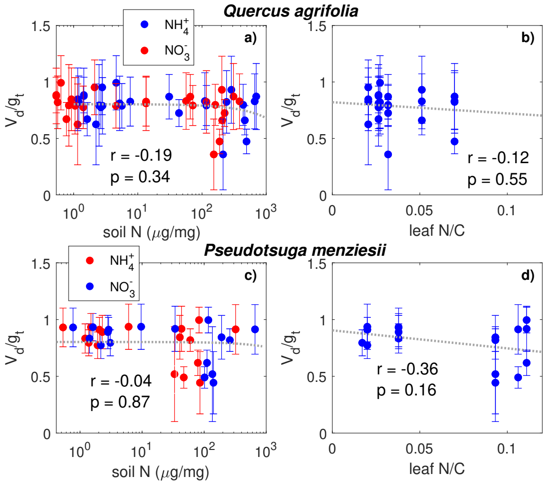

Figure 4. The V_d/g_t ratio is plotted against soil nitrogen concentration in the form of NH_4^+ and NO_3^- for (a) *Q. agrifolia* and (c) *P. menziesii*. The dashed line shows a linear fit to NH_4 data. The relationship is not significantly different (α = 0.05) when fit to NO_3^- data. The V_d/g_t ratio is plotted against the leaf nitrogen:carbon ratio for (b) *Q. agrifolia* and (d) *P. menziesii*. V_d/g_t ratios less that 1 imply contributions from the mesophyll to the NO_2 uptake rate. On each pannel the Pearson's correlation coefficient and the p-value for the slope are shown. The amount of soil and leaf nitrogen has no significant impact on the V_d/g_t ratio.

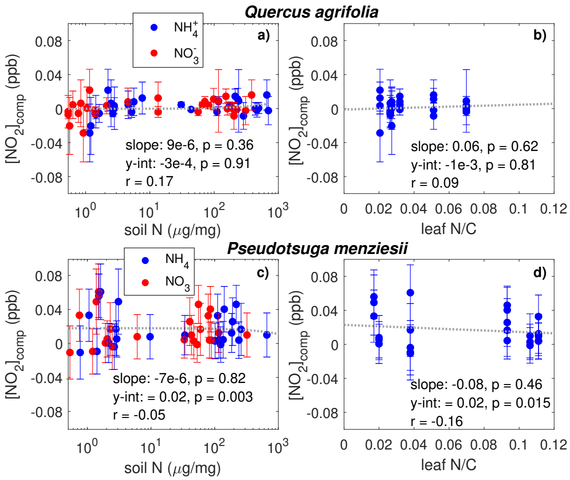

Figure 5. The concentration below which leaves emit NO$_2$ is the compensation point ([NO$_2$]$_{comp}$). [NO$_2$]$_{comp}$ is plotted against the soil nitrogen concentration in the form of NH$_4^+$ and NO$_3^-$ for (a) *Q. agrifolia* and (c) *P. menziesii*. The dashed line shows a linear fit to NH$_4$ data. The relationship is not significantly different ($\alpha = 0.05$) when fit to NO$_3^-$ data. [NO$_2$]$_{comp}$ is plotted against the leaf nitrogen:carbon ratio for (b) *Q. agrifolia* and (d) *P. menziesii*. On each ~~pannel~~ panel the Pearson's correlation coefficient, the slope, the intercept, and their p-values are shown. The amount of soil and leaf nitrogen has no significant impact on the compensation point.

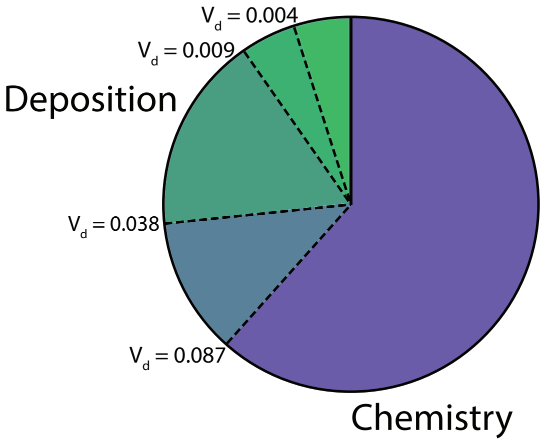

Figure 6. Fraction of NO_x loss to deposition and chemistry (nitric acid, alkyl nitrate, and peroxyacyl nitrate) at night (20:00—05:00). The four dashed lines between the deposition and chemistry fractions show NO_x loss with a nighttime NO_2 deposition velocity of 0.004, 0.009, 0.038, and 0.087 cm s^{-1}. These deposition velocities respectively represent the minimum, first quartile, third quartile, and maximum of the median nighttime deposition velocities measured for the native California trees examined in this study.

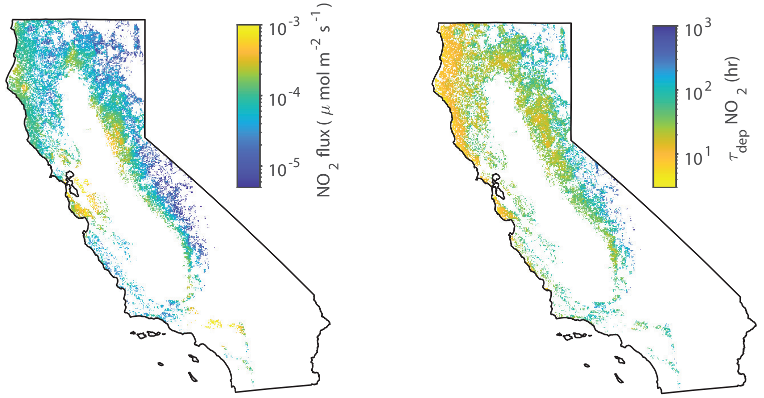

Figure 7. (left) Average midday deposition fluxes of NO$_2$ to forests in June throughout California. (right) Average midday deposition lifetimes of NO$_x$ ~~assuming a uniform 1 km boundary layer height~~ in June throughout California. White areas are non-forested areas.

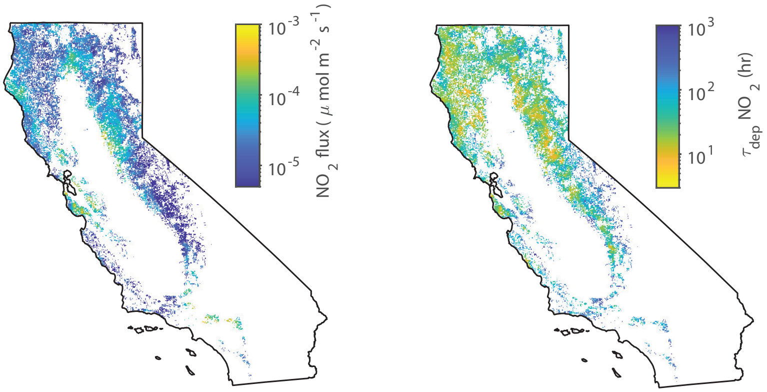

Figure 8. (left) Average midnight deposition fluxes of NO_2 to forests in June throughout California. (right) Average midnight deposition lifetimes of NO_x ~~assuming a uniform 100 m boundary layer height~~ in June throughout California. White areas are non-forested areas.

Table 1. Average soil and leaf nitrogen

tree[a]	soil NH_4^+ μg/mg	soil NO_3^- μg/mg	leaf N %	leaf C %
QA control	3.0± 0.5	3 ± 1	1.1 ± 0.1	47.7 ± 0.2
QA high N	300± 60	170 ± 30	2.4 ± 0.5	48.1 ± 0.2
PM control	2.7 ± 0.8	2.0 ± 0.5	1.3 ± 0.2	56 ± 9
PM high N	190± 43	80 ± 20	4.7 ± 0.2	45.9 ± 0.4

a. QA is *Q. agrifolia* and PM is *Pseudotsuga menziesii*.

Table 2. Summary of species-dependent foliar deposition results

species	R_m (g_t)	R_m (g_s)[a]	max[d] V_d	max[e] g_t^w	median dark V_d	slope~~[a]~~[f]	r	$[NO_2]_{comp}$
	s cm^{-1}	s cm^{-1}	cm s^{-1}	~~cm s^{-1}~~ mmol m^{-2}s^{-1}	cm s^{-1}		g_t vs. slope[g]	ppb
P. sabiniana	0.43± 0.06[h]	0.46± 0.06	0.51 ± 0.04	500 ± 100	0.087	0.79±0.04	~~-0.37~~-0.58[c]	-0.03 ±0.03
P.ponderosa	0.7 ± 0.1	0.69 ± 0.09	0.26 ± 0.01	230 ± 25	0.038	0.91 ± 0.05	~~-0.72~~-0.43[c]	0.00±0.02
P.contorta	0.5 ± 0.2	0.5 ± 0.2	0.24 ± 0.03	180 ± 30	0.018	0.99 ± 0.03	~~-0.36~~-0.31[c]	0.00±0.01
P. menziesii	0.30 ± 0.07	0.30 ± 0.06	0.26 ± 0.02	230 ± 20	0.044	0.91 ± 0.04	~~-0.26~~-0.30[c]	0.02±0.02[b]
C. decurrens	0.4 ± 0.1	0.4 ± 0.1	0.21 ± 0.03	160 ± 20	0.009	0.91 ± 0.02	~~-0.36[c]~~-0.01	0.00±0.02
S. sempervirens	0.9 ± 0.1	0.9 ± 0.1	0.27 ± 0.04	330 ± 80	0.009	~~0.60~~0.84 ± ~~0.04~~0.03	~~-0.43~~-0.56[c]	-0.01±0.02
A. menziesii	0.4 ± 0.1	0.4 ± 0.1	0.26 ± 0.05	210 ± 10	0.037	0.93 ± 0.03	~~-0.38~~-0.44[c]	-0.02±0.01
A. macrophyllum	0.5 ± 0.1	0.54 ± 0.09	0.47 ± 0.08	400 ± 100	0.017	0.84 ± 0.03	~~-0.21~~-0.42[c]	-0.02±0.01
Q.agrifolia	1.3 ± 0.3	1.3 ± 0.2	0.15± 0.01	90 ±20	0.008	0.89 ± 0.04	~~-0.22~~-0.14	0.00±0.01
Q. douglasii	0.2 ± 0.1	0.2 ± 0.1	0.30 ± 0.03	180 ± 20	0.004	0.89 ± 0.04	~~0.23~~-0.24	-0.01±0.02

a. R_m calculated assuming R_b = 1 s cm^{-}1.

b. Statistically significant (α = 0.01) compensation point. Compensation point listed is at limit of detection for the instrument. All other compensation points are not statistically significant (α = 0.05).

c. Statistically significant (α = 0.05) correlation. Correlations not indicated are not statistically significant (α = 0.05).

d. Maximum stomatal conductance that was observed during our experiments and the error associated with that measurement.

e. Listed maximum g_t^w the maximum stomatal conductance to water vapor that was observed during our experiments and the error associated with that measurement. Units in mmol m^{-2}s^{-1} for ease of comparison with other stomatal conductance studies.

f. Total slope of measured vs. predicted fluxes (Fig. 2).

g. Individual slopes of predicted vs. measured fluxes from each day an experiment was run.

h. Calculated including data in helium.

Table 3. Summary of drought stress results

tree[a]	med Ψ_p (IQR)[b] MPa	med g_t (IQR) cm s^{-1}	med V_d (IQR) cm s^{-1}	R_m s cm^{-1}	slope~~[b]~~[c]	~~r[c]~~r[d] g_t vs ~~V_d/g_t~~slope	~~r[c]~~r[e] Ψ_p vs g_t
PP control	-0.60 (0.35)	0.23 (0.17)	0.21 (0.13)	0.69 ± 0.09	0.89 ± 0.02	-0.59~~[d]~~[e]	0.651~~[d]~~[e]
PP drought	-1.05 (0.53)	0.07 (0.12)	0.06 (0.12)	0.0 ± 0.3	1.0 ± 0.1	-0.10	
CD control	-0.30 (0.30)	0.13 (0.09)	0.12 (0.09)	0.37 ± 0.15	0.95 ± 0.02	-0.11	0.357~~[d]~~[e]
CD drought	-0.80 (0.45)	0.06 (0.05)	0.06 (0.05)	1.17 ± 0.38	0.88 ± 0.03	-0.23	

a. PP is *Pinus ponderosa* and CD is *Calocedrus decurrens*

b. IQR is the interquartile range.

c. Slope of measured vs. predicted fluxes.

d. Pearson correlation coefficients.

e. Statistically significant ($\alpha = 0.05$ correlation).

Table 4. Comparison of total conductance measurements with previous works

tree[a]	max g_t^w (this study) mmol m^{-2} s^{-1}	reported max g_s^w mmol m^{-2} s^{-1}	reference[a]
P.ponderosa	230 ± 25	124	Maire et al., (2015)
P.contorta	180 ± 30	230 ± 30	Arango-Velez et al. (2016)[b]
P. menziesii	230 ± 20	140± 10; 250	Manter et al. (2000); Manter and Kavanagh (2003)[c]
C. decurrens	160 ± 20	150	Grantz et al. (2019)[b]
S. sempervirens	330 ± 80	91; 240	Maire et al., (2015); Ambrose et al., (2010)
A. menziesii	210± 10	150; 550	Maire et al., (2015); Murray et al., (2019)
A. macrophyllum	400 ± 100	420	Murray et al., (2019)
Q.agrifolia	90 ± 20	95; 390	Henry et al. (2019); Murray et al., (2019)
Q. douglasii	180 ± 20	325 ± 30	Matzner et al. (2003)

a. References respectively refer to values in the reported max g_s^w column.

b. Study did not report value as a maximum stomatal conductance. The conductances shown are the maximum of the stomatal conductances reported in the cited study.

c. Theoretical calculation.