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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Laboratory measurements of stomatal NO_2 deposition to native California trees and the role of forests in the NO_x cycle" *by* Erin R. Delaria et al.

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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.