Author response to Anonymous Referee #3 of ACP-2020-149: "Measurement report: Leaf-scale gas exchange of atmospheric reactive trace species (NO2, NO, O3) at a northern hardwood forest in Michigan"

We greatly appreciate the thoughtful feedback provided by Anonymous Referee #3. The questions and comments have helped to improve and enhance the manuscript. Below, we address each comment individually. Referee comments are given in **Bold**, author responses are given in normal font, changes made to the text in the manuscript are given in blue. The revised manuscript includes all the changes listed below.

Line 96, misspelled foliar

It's corrected.

Line 170, What is the conversion efficiency for the photolysis? If it was different from 100% that would show up as a difference in calibration factor for NO and NO2. Those calibrations ought to depend on ambient O3 and light. Can you include some comment on how calibrations depend on ambient condition. I don't doubt you have done it all correctly, but this information might give some additional insight on interpreting the data.

The reactive trace gases in ambient air were scrubbed prior to the purge air entering the enclosure. So, measurements of the NO_x added to the enclosure were not subject to O_3 interference.

For the calibrations, UHP zero air, an NO standard, and UHP O_2 (for making O_3) were used. These steps did not involve ambient air.

During the calibrations, NO was calibrated directly using an NO standard diluted with the UHP zero air. For the NO_2 calibration, the same diluted NO standard was titrated with some O_3 to form a mixture of NO_2 and NO, then the NO was measured, which gave **the expected NO_2** counts (NO_2 = NO_original_amount – NO_after_adding_O_3). Afterward, NO_2 was photolyzed to NO using the LED, and the total NO was measured, yielding **the measured NO_2** counts. The ratio: (**measured_NO_2 /expected_NO_2**), is the conversion efficiency. It was fairly steady throughout the campaign at ~0.68. The instrument was calibrated every 7 hours.

We added in the manuscript, P6:

"…with a conversion efficiency of ~0.68. Because the ambient air was scrubbed to remove O_3 (and other trace gases) before entering the enclosures, the effect of ambient O_3 on NO_x measurements was negligible."

Line 245; The discussion about quantifying the impact of NO2 photolysis could be clarified a little more. Is your point that because the amount of NO emitted is poorly constrained you cannot just compute the uptake of NOx by adding together NO and NO2? Are there enough calibrations at different times of day to examine how the apparent NO2 conversion efficiency varies with light level and account for conversion? What about conversion of NO to NO2 by ambient O3? This ought to be apparent by evaluating the variation in NO calibration constant as a function of O_3.

We have modified the text to explain the background correction using the empty enclosure better. Regarding photolysis, the two enclosures could not be measured simultaneously with one instrument, and they were in mid-canopy instead of under direct sunlight without branches above. So, the light exposure of the two chambers was not identical, however close, making the correction of NO_2 photolysis an approximation.

Conversion of NO_2 to NO was done in the instrument using an LED light source. The calibration was done every 7 hours.

The ambient air was scrubbed free from O_3 before it was sent to the enclosures. If there's any residual O_3, it's below the detection limit of the O_3 detector (<0.5 ppb). This is not enough O_3 to significantly convert NO to NO_2 within the residence time in the enclosure and the sample line (total ~96 sec).

(Please also see response to RC#1, P8 L246.)

The text in the manuscript is modified as follows, on page 8:

"There are a couple of factors that complicated the NO_2 gas exchange experiment. First, the NO_2 standard used for delivering NO_2 to the enclosure contains about 5% NO that was unavoidably added to the enclosure. Secondly, when there was intense direct sunlight, some NO_2 in the enclosure was photolyzed. While corrections for these interferences were done using the measurements from the reference enclosure, it is difficult to perfectly remove the artifact caused by NO_2 photolysis. This is because the sunlight exposure of the two enclosures, although situated side-by-side, was often uneven, and the measurements of the enclosures were done not simultaneously but sequentially. This problem is particularly pronounced when it was cloudless with a strong contrast of light and shade inside the canopy. The branch enclosure was always placed for better sun exposure than the reference enclosure if choices needed to be made. Therefore, the branch enclosure likely received more sunlight overall, even though it might be more shaded during some measurement cycles. Generally, for the periods of strong sunlight, there is residual NO after the correction against the reference enclosure is made. If we assume all this is due to an underestimation of NO_2 photolysis and make a further correction by combining the changes of NO and NO_2, the data quality is not improved while more noise is introduced to the data. Because of this and because we are not absolutely certain about all possible sources of NO_x from the branch enclosures, we prefer to adhere with the correction using only the reference enclosure measurements and view the resulting NO_2 flux as an upper bound, with possibly as much as 20% overestimation under direct sunlight conditions, which accounts for ~16% of all data during the NO_2 exchange experiments. "

Line 310, Can you go the next step after concluding that there is some mesophyll resistance? The effect of having a non-zero mesophyllic resistance is a non-zero concentration inside the leaf. Using equation 2 and 3 you could solve for NO2 concentrations internal to leaf. Similarly, for situations with excess deposition you could compute a value for cuticular deposition from the residual after subtracting the stomatal uptake.

Granted you wouldn't get a unique solution if there were both cuticular uptake and non-stomatal deposition. But you can make this section stronger by quantifying some values for the other processes

you point to. At the end of paragraph, having some values for range of mesophyllic conductance would be better than just stating further investigation is needed.

The concentration of NO_2 in the leaf internal air space indeed can be calculated using equations 2 and 3. However, I am not sure if the numbers can be put into a meaningful context because the mesophyll resistance was inferred from data where the deposition rate was lower than the theoretical value from g_{H2O}, but not systematically investigated. Also, if both cuticular uptake and mesophyll resistance exist, their effects would be in the opposite direction. NO_2 goes through disproportionation when it dissolves in water, thus the NO_2 pressure in the internal air space needs to be in steady state with the solution. These make it difficult to interpret the apparent internal NO_2 pressure.

Line 318 In addition to there being a possibility cuticular adsorption accounts for extra NO2 deposition you might also note that stomatal enclosure might not be complete. Discussion about whether stomatal conductance goes to zero shows up mostly in discussions seeking to explain sap flow or water flux that doesn't go to zero at night. It might not be as much of an issue for daytime periods, but could be noted just for completeness.

We did observe some water flux at nighttime, especially in the white pine enclosure. Correspondingly there was nighttime deposition of NO_2 to pine needles. The additional deposition attributed to cuticular or other non-stomatal processes was inferred by extrapolating the deposition velocity to zero stomatal conductance. The nighttime stomatal conductance of other trees was very small or close to zero.

Can you also comment on how much of the data are for conditions that the vapor pressure differences between leaf and ambient air are quite small so that stomatal conductance computation has larger uncertainty. At the limit when ambient air approached saturation and leaf and air temperature were equal the stomatal conductance couldn't be determined from water flux. You have noted in that leaf temperature always exceeded dewpoint in the context of discounting possibility of dew, but it is also relevant for evaluating how well stomatal conductance is defined.

About 10% of the data show small VPD (< 1 standard deviation from zero) under the conditions you mentioned. It usually happened in the early morning just before and around sunrise. The trace gas fluxes were relatively small during these times.

The above is added to the manuscript, P9:

"When the conditions are such that the difference between the leaf and air temperatures is small and the enclosure humidity is high, the difference between $C_{H_2O\_leaf}$ and $C_{H_2O_{enclosure}}$ is also reduced, increasing the uncertainty in g_{H_2O} . In our measurements, this happened mostly from dawn to sunrise, accounting ~10% of the total data points, where the $(C_{H_2O\_leaf} - C_{H_2O\_enclosure})$ was within one standard deviation from zero. "

Can you comment more on O3 uptake. I agree that reaction with VOC could be an important loss process for O3 in addition to reaction with foliage. Your point would be stronger, however, by providing the rate constants for the VOC typically associated with white pine not just pointing out one with the highest reaction rate as well as noting that the oak and aspen are known isoprene emitters.

The part regarding gas-phase reactions has been modified to use emission rates and speciation from literature to give a more realistic estimation.

(Please also see RC#1 P12 L363.)

In the manuscript, page 12:

"Estimation of the possible contribution from gas-phase reactions with BVOCs was made as follows. The upper bounds of typical emission rates at 30°C and PAR level at 1000 μmol m^{-2} s^{-1} for monoterpenes and other BVOCs (excluding isoprene) are 3 and 5 μg C g^{-1} h^{-1}, respectively (Guenther et al., 1994). The speciation of major BVOCs emitted by white pine at UMBS is based on Kim et al. (2011), including α- and β-pinene, limonene, linalool, α-humulene, and β-caryophyllene. Using the rate constants of the BVOCs with ozone reactions (Burkholder et al., 2015), and the residence time of 1.5 min in the enclosure plus ~6 sec in the sample line before reaching the detector, the estimated ozone loss due to gas-phase chemical reactions was less than 1%. Even with optimal light and temperature conditions for BVOC emission, the estimated gas-phase chemical removal would only be on the order of a few percent."

Line 392 Say something more about the difference in chamber temperature for the aspen branch compared to the other species. Is this because the outside air temperature was cooler also, or on account differences in radiation? Large differences in conditions between the species make comparisons among them more difficult. Can you say anything about whether the chamber conditions relative to outside conditions were different for the species. Finally, the point that aspen have stomata on both sides of leaf ought to come first, and rather than speculate that they have more stomata per unit area find some data in the literature about this. There is no need for several lines of explanation about why the conductance is higher before this point about double sided stomata. The explanation only needs to explain the additional enhancement beyond twice. Likewise the other differences should come first. Does the extra water flux account for reduced temperatures in apsen enclosures?

The text has been modified based on the suggestions. The daily *average* temperatures inside and outside the chamber were similar. The air temperature was cooler on the days when aspen was sampled. The VPD during this time was smaller than in other enclosures when it was warmer.

We could not find in the literature specific records on the stoma distribution of aspen except populus in general. The part regarding stomata on both sides of aspen leaves was moved to the beginning of this part of the discussion as suggested.

In the manuscript, P13:

"Biological features may have contributed to this difference. Compared with the other three trees in this work, the aspen was younger and smaller. The enclosed branch was in the upper part of the crown containing developing new leaves. Past measurements, albeit on different species, have shown that for the same species under similar environmental conditions, leaves of young trees generally have higher stomatal conductance than old ones (Fredericksen et al., 1995; Hubbard et al., 1999; Niinemets, 2002; Yoder et al., 1994). Another possible reason for the observed high g_{H_2O} , while direct evidence has yet to be found, is the number of stomata. Many trees have stomata on only the lower (abaxial) leaf surface; however, trees that belong to the genus Populus, which includes aspen, are an exception. They have stomata on both sides (amphistomatous), a feature that allows increased photosynthetic rate and fast growth (Kirkham, 2014). If the bigtooth aspen leaves are indeed amphistomatous, a relatively high

g_{H_2O} can be expected. We compared the environmental conditions of the enclosures. The integrated PAR exposure levels were similar. The daily variation of the relative humidity in the bigtooth aspen enclosure was not significantly different from the others. In contrast, the average daily temperature was 19.2°C, cooler than the temperatures (23.9°C, 22.6°C, and 21.6°C) in the other enclosures, similar to the average ambient air temperature outside the enclosure during the same time, 19.1°C, and 23.6°C, 22.4°C, and 21.3°C. The combined conditions of moisture and temperature led to a relatively low vapor pressure deficit (VPD) in the aspen enclosure, 0.8 kPa, compared to 1.2 kPa (white pine), 1.0 kPa (red maple), and 1.4 kPa (red oak) in the others. Generally, VPD and g_{H2O} are inversely correlated and a low VPD corresponds to a relatively high g_{H2O} (Hubbard et al., 1999; Urban et al., 2017a, 2017b). However, because here we are comparing different tree species, we consider the observed results to stem from the combination of biological and environmental factors. Further examination of these factors is beyond the scope of this paper, nevertheless, it would be beneficial to take this temporal and spatial variability and inhomogeneity into account in model parameterizations of trace gas dynamics since plant stomata are the main conduit of NO_x and O_3 deposition over vegetation."

Line 510: It would be preferable to have data availability point to an existing data set already available rather than just making it available on request. It easier for the investigator to just prepare the files once and submit to a data server (doesn't UMBS have this for work at the site). Additionally, if the investigators move or retire then data on request gets hard to find years from now.

Yes, the data will be archived at https://umich.box.com/v/PROPHETAMOS2016.