Author response to Anonymous Referee #1 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 #1. 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 to make in the manuscript are given in blue.

P2 L60: The citation of Delaria et al., 2018 and reported estimation of 15-30% removal of soil-emitted NOx is correctâ ˇAˇToak woodlands have a very low LAI. However, in Delaria and Cohen 2020 (now published and not in discussion), they report much larger canopy reductions for forests with more typical LAI, in line with the 25-55% loss previously reported.

The latest publication of Delaria and Cohen (2020) has been cited.

In the manuscript, P2:
"Implementing these results in a multi-layer single-column model, it was calculated that California oak woodland canopy removes 15-30% of soil-emitted NO_x, and other forests in California and Michigan, close to 60% (Delaria and Cohen, 2020)."

P3 L64: Extra parenthesis

It is removed.

P3 L83: Would be nice if the instrument were stated explicitly.

That information has been added to the text on P3. It was a chemiluminescent NOx detector equipped with a highly NO_2 specific blue light converter.

P3 L96: Correct "folia" to "foliar"

Corrected.

P7 L205: Several studies have observed significant stomatal opening during the night (e.g. Dawson et al., 2007–10.1093/treephys/27.4.561). Consider adding a discussion of how, if this was occurring in your chamber, this assumption would have affected your results (if at all).

We have modified the manuscript text to address this point:

In the manuscript, P7:
"Nighttime transpiration in trees and shrubs has been measured in prior work, with reports of nighttime transpiration rates ranging from 0 to as much as 25% of the daytime value (Dawson et al., 2007), suggesting that leaf stomata may remain open at night for some plants. However, this possibility did not affect the above results as there was no evidence of a consistent concentration difference above zero between the enclosure outlet and inlet measurements."

P8 L246: A more detailed description of your empty chamber photolysis corrections would be useful.

We have modified the paragraph to give a more specific and detailed description on the corrections based on the empty chamber measurements.

(Please also see response to RC#3, L245.)

In the manuscript, P8:

"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 completely 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 for clear sky conditions with strong contrasts in sunlit and shaded conditions inside the canopy. The branch enclosure was always positioned to get more 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."

P10 L314: Units for the intercept should be added. Additionally, under the resistance model framework you discuss, the relationship of Vd to gH2O is non-linear. How might this affect your inferences of cuticular uptake?

We have added the units (mm s^{-1}) to the intercept.

For the second question:
In the resistance model framework at the leaf scale, the cuticular, stomatal, and mesophyll resistances are the main factors to determine the deposition velocity. Putting them together, the overall conductance (i.e. the inverse of the total resistance) to deposition is:

$1/R_{total} = 1/R_{cut} + 1/(R_{sto} + R_{meso})$.

Thus, if $R_{cut} >> (R_{sto} + R_{meso})$ or R_{cut} is constant and $R_{meso} << R_{sto}$, the deposition velocity vs. stomatal conductance will be linear. If R_{meso} is significant compared to R_{sto}, the deposition velocity will be limited by R_{meso} as stomatal conductance increases. Of course, we don't know if and how R_{cut} and R_{meso} vary with environmental factors, which would potentially complicate the V_d to g_{H2O} relationship.

We added the following in the manuscript, P14:

"When extrapolated to zero stomatal conductance, the deposition velocity of NO_2 to white pine was 0.43 mm s^{-1} (Figure 6a), implying deposition unrelated to leaf stomata, possibly to wet leaf surfaces and/or to leaf cuticula. This observation does not exclude the possible existence of these pathways when the stomata are open. A deposition velocity higher than expected based on the stomatal conductance would result if there is significant non-stomatal deposition. On the other hand, mesophyll resistance renders a lower deposition velocity than the expected value. There is no mechanistic reason why the deposition velocity associated with either a non-stomatal pathway or mesophyll resistance should remain constant or vary linearly with stomatal conductance. The relationship of deposition velocity, $v_{d\_NO_2}$, and stomatal conductance, g_{H_2O} , would remain essentially linear as long as stomatal deposition dominates or the non-stomatal deposition term is constant while mesophyll resistance is small. However, if mesophyll resistance is significant, it would limit the increase of $v_{d\_NO_2}$ with stomatal conductance. "

P12 L363: How high of emission rates would this require? Is it outside the range reported for trees of the species considered?

Yes, it does require an unreasonably high emission rate to match the amount of ozone removed.

Prompted by this comment, we have modified this argument using literature values of BVOC emission rates and speciation to give a more realistic estimation of the amount of ozone loss due to chemical reactions. It is < 1%.

(Please also see RC#3, p 3-4, "Can you comment more on O3 uptake…".)

In the manuscript, P12:

"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."

P13 L395-396: should this be VPD?

Yes. It is fixed now.

P13 L403: "In the future,"? "In future work,"?

Suggestion is taken.

P14 L437: This was also a conclusion of Delaria et al., 2018.

We added this information in the text.

In the manuscript, P15:

"Delaria et al (2018) reached the same conclusion from their study on *Quercus agrifolia*."

O3 deposition: There are a number of recent references discussing ozone deposition that are not included. The paper would be stronger if it placed itself in the context of these and other recent papers on the subject (e.g. Silva and Heald GRL 2018 https://doi.org/10.1002/2017JD027278, Kavassalis and Murphy GRL 2017 https://doi.org/10.1002/2016GL071791 and Clifton et al. in Reviews of Geophysics 2020 https://doi.org/10.1029/2019RG000670).

We took the suggestion and added the references and relevant context in the manuscript.

In the manuscript, P2:

"Similarly, vegetation and plant surfaces also affect ozone levels through dry deposition (Clifton et al., 2019, 2020; Kavassalis and Murphy, 2017; Silva and Heald, 2018). In forested areas, ozone dry deposition occurs through leaf stomata as well as non-stomatal pathways including cuticular uptake, and wet or dry leaf surface reactions, while some O_3 is also removed by gas-phase chemical reactions e.g. with biogenic volatile organic compounds (BVOCs) and NO. Though these processes have been identified, the exact partitioning between the dry deposition pathways (and in-canopy chemical destruction) has not been unequivocally determined, hindering the ability to correctly assess ground-level ozone."