

**Author response to Anonymous Referee #2 of ACP-2020-149: “Measurement report: Leaf-scale gas exchange of atmospheric reactive trace species (NO<sub>2</sub>, NO, O<sub>3</sub>) at a northern hardwood forest in Michigan”**

We greatly appreciate the thoughtful feedback provided by Anonymous Referee #2. 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.

**L45: Maybe rather state “the air layers above the forest” instead of “free troposphere” as the air will first encounter the roughness sublayer or at nighttime the stable nocturnal boundary layer, then the mixed layer (daytime) or residual layer (nighttime) before reaching the free troposphere.**

We have changed the phrase and now the text (page 2) reads:

“The relative differences in the time scales of the turbulent mixing and the chemical and physical sink processes determine the amount of NO<sub>x</sub> removed within the canopy, with the remaining NO<sub>x</sub> being released into the boundary layer.”

**L96: folia => foliar**

It’s corrected.

**L132: To be able to judge potential surface effects and light absorption behavior (cutoff wavelength) of the enclosure please provide information about the material the bags were made of.**

The material was Tedlar, polyvinyl fluoride. This info is now in the manuscript.

**L140: Which material were the lines made of?**

It’s polytetrafluoroethylene (PTFE), also added to the manuscript.

**L147 and Fig. 2: Was there any special reasoning for putting the activated charcoal in front of the Purafil NO<sub>x</sub> scrubber? Different to NO<sub>2</sub>, NO is not well captured by charcoal, and therefore normally the Purafil is put in front of the charcoal as it not only adsorbs NO<sub>2</sub>, but also oxidizes NO to NO<sub>2</sub> which is finally captured by the Purafil and the charcoal. At low ambient NO it might make no difference, but for higher NO this setup normally works better.**

There was no specific reason to put the Charcoal before Purafil. Fortunately, during our work, the ambient NO concentrations were generally low in the relatively remote forest. Thank you very much for the information!

**L163: Leaf wetness measurements are mentioned here but not presented or discussed in the manuscript. Could you please add these results? Alternatively, at least mention why they were not used.**

Thank you for this point. We only used the leaf wetness results for qualitative/diagnostic purposes. Therefore, it was not mentioned in the data analysis. We added a short explanation in the text.

In the manuscript, P6:

“leaf wetness (for qualitative assessment of leaf conditions only) (S-LWA, Onset)”

**L168: 1 min zero air measurement plus 2.5 min NO and 2.5 min NO<sub>2</sub> results in a 6 min cycle? Please clarify.**

It was a mistake. It should be “1 min zero air measurement plus 2 min NO and 2 min NO<sub>2</sub>”. Thank you for catching it.

**L171: To have higher NO<sub>2</sub> absorption and less HONO photolysis the light emissions of the diode should be > 390 nm. The 365 nm is close to the HONO absorption band at 368 nm (Stutz et al., 2000). Nevertheless, even at the peak absorption of HONO the absorption cross section of HONO is about a factor of 1.5 smaller and under environmental conditions the HONO to NO<sub>2</sub> ratio is normally below 10 % (some cases up to 30 %). Therefore, the HONO interference in ambient air should be small. Due to the high surface to Volume ratio of the chambers, the HONO to NO<sub>2</sub> ratio could be higher and might depend on the chamber material. So please also provide information on the chamber material (see above comment).**

We apologize for this mistake. We used Hamamatsu L11921-500 LED light sources. The peak wavelength was 385+/-5 nm.

**L300: “Unknown measurement issue for water concentration”. As stated in the paper in line 315 the chamber air was not condensing according to the calculated dew points. Could the reason be instead evaporation of surface water films that form at a RH > 50% due to the deliquescence of deposited salts and other processes (e.g. Burkhardt and Eiden, 1994), Burkhardt and Hunsche, 2013).**

Please see the response after the comment for L353.

**L317: Liquid surface films can be formed by processes other than condensation (see esp. Burkhardt and Hunsche, 2013). Furthermore, a recent laboratory chamber study investigated the influence of liquid films (at RH below condensation) on deposition of Peroxyacetyl nitrate and O<sub>3</sub> to plants ((Sun et al., 2016) in detail.**

Please see the response below.

**L353: As mentioned in the above comments there are processes other than pure condensation that lead to the formation of liquid films. What about the surface wetness measurements? Do they show any changes at RH between 50 and 100 % that could be associated to enhanced O<sub>3</sub> uptake?**

Regarding the last three comments, we thank the reviewer for bringing this to our attention. We do not have observational results to address the point about microscopic water film but it certainly is an aspect to investigate in future experiments. We have modified the text to reflect the possibility of microscopic

water film on the leaf surface. The leaf wetness sensor likely did not have similar deposits to aid the formation of water film because the sensor was cleaned before being placed in the enclosure. (The leaves were not). The wetness sensor showed relatively dry conditions, i. e. lower readings during the O<sub>3</sub> experiment compared to those at early morning hours, and the RH was between 70-80%.

We modified the manuscript text to reflect this possibility. On page 14:

“To assess the role of wet leaf surfaces to non-stomatal deposition, we calculated the white pine enclosure dew point using the temperature and relative humidity data and compared it to the measured leaf temperature. The leaf temperature was always higher than the dew point during the experiments, excluding the possibility of a wet leaf surface from the condensation of pure water. However, a microscopic water film may nevertheless form at a relative humidity as low as 50% if there are hygroscopic deposits on the leaf surface (Burkhardt and Eiden, 1994; Burkhardt and Hunsche, 2013; Sun, 2016). The microscopic water film could potentially modify gas exchange rates of water-soluble trace gases in the air. Data from this work do not contain information that can be used to delineate the possibilities of trace gas dissolution into microscopic water films or cuticular uptake. Further investigations with appropriately designed experiments, better measurement precisions, longer observation time, and under different environmental conditions are necessary to delineate the various possible deposition pathways and their dependencies.”

**L361: As the reactions will not stop at the chamber outlet please provide the total residence time from within the chamber (1.5 min) to the analyzer as well?**

The residence time in the sample line was about 6 seconds. (1/4" OD, 1/8" ID, 100 feet). This info is now added to the manuscript.

**L365: A very good description of the relevant loss processes for O<sub>3</sub> is provided by a recent review (Clifton et al., 2020).**

Yes. We have now cited this reference in the revised text.

**L464: Please revisit this statement in the light of the above comments that liquid films can form at RH > 50 % and therefore contribute to enhanced O<sub>3</sub> surface deposition (esp. Sun et al., 2016).**

Yes, this statement was modified to include the possibility of a thin water film at low RH and above the dew point.

In the manuscript, P16:

“A brief survey of the foliar O<sub>3</sub> loss found that uptake by the deciduous trees also closely followed stomatal conductance, while the O<sub>3</sub> foliar deposition velocity for white pine was much larger than expected from leaf stomatal uptake alone. Removal via gas-phase chemical reactions was calculated to be negligible based on estimates of known BVOC emission rates and speciation, implying other non-stomatal pathways - cuticular uptake, dissolution to wet leaf surfaces, and/or chemical reactions at the leaf surface – are responsible for the additional ozone deposition, with their relative importance to be determined. “