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Interactive comment on "Influence of meteorology and anthropogenic pollution on chemical flux divergence of the NO-NO2$-O_3$ triad above and within a natural grassland canopy" *by* D. Plake et al.

D. Plake et al.

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Reply to anonymous Referee #2

General comments:

In general, this is a very interesting paper that focuses on the relative timescales of transport and chemistry of NO-NO_2-O_3 within grassland. The measurements appear to have been performed very carefully, and the insight that transport timescales within grassland canopies can be as slow as within tall forests is important. I recommend

publication after the authors address the following comments.

Reply: The authors would like to thank the referee for the positive evaluation of the manuscript and for his suggestions to further improve the paper.

Comment: P 10739, L5-8 is the ozone production discussed here ozone production from differing rates of NO_2 photolysis above and within the canopy (e.g. a redistribution of Ox), or new Ox formation from RO_2 + NO?

Reply: It is written in the paper (page 10760, lines 23-24): "The O_3 production in our study was attributed to a deviation from the NO-NO_2-O_3 photo-stationary state by a surplus of NO_2 as a result of the oxidation of NO by HO_2 and RO_2.

Comment: Section 2.3.1 The form of Eq 2 is not obvious, and the reader would benefit from more context into how this is derived. At the end of Section 4.2, you suggest that O_3+VOC reactions can be discounted, however that the impact of RO_2 + NO cannot be quantified. This would be easier to assess if we could see how these terms would play out in a more generalized version of Equation 1. For example, if peroxy radicals were responsible for an equivalent amount of NO oxidation, would the chemical lifetime decrease by half (or more, or less)?

Reply: This question was partly addressed in the reply to referee 1. Eq. 2 was derived from mass conservation of the NO_2-O_3-NO triad. Although the influence of HO_2 + RO_2 may be significant, this evaluation is beyond the scope of this paper due to the variety of compounds and reaction rates involved in the complex RO_2 chemistry that would require numerical modelling and more measurements. Additional information will be included in the text regarding this topic.

Comment: Section 4.1.2 It was not intuitive to me that R_{ac} for the whole canopy was intermediate to $R_{ac}(L_1)$ and $R_{ac}(L_2)$. I would have thought that it includes resistance across L_1 and L_2. Why is this not the case?

Reply: We agree with the referee that for resistances in series the total resistance

is the sum of the two individual ones. This means, R_{ac} for the whole canopy should be equal to $R_{ac}(L_1)$ + $R_{ac}(L_2)$, which is not the case in Figure 5. The value for R_{ac} in Figure 5 reflects the sum of all transport times divided by the entire layer thickness. This corresponds to a weighted average of $R_{ac}(L_1)$ + $R_{ac}(L_2)$. The text and Figure 5 will be clarified accordingly in the revised version.

Comment: Section 4.2 I have a hard time following the logic in lines 15-25. Are you saying that the variability in chemical timescales was influenced most strongly by variability in O_3? And that this is because the absolute variability in O_3 was larger than for the other species (as opposed to the relative variability)?

Reply: The chemical timescale is dominated by the influence of O_3 as long as O_3 is present in excess compared to the other compounds. This section will be clarified.

Comment: Section 4.4.1 Can you explain more clearly why the timescale of NO_2 uptake was much longer during the night? Which of the terms in Equation 7 changed substantially?

Reply: The uptake of NO_2 by plants is lower during nighttime because plant stomata are closed. This uptake pathway only exists during daytime. This implies that the stomata resistance (R_s) increases substantially during nighttime causing a longer time scale (see Eq. 8, R_{Lx} is dominated by R_s).

Comment: Section 4.4.2 While the analysis in this section is interesting, how robust are the conclusions given that peroxy radicals are not included? It seems like your statement on P10760, L18-19, that this is an interesting result that goes against other studies may not hold.

Reply: We do not agree with the referee in this case. We quantified the net production of O_3 integrated over the air column using our vertical profile measurements (Eq. 11) regardless of the reactions involved in the O_3 production process. From PSS calculations we estimate that the O_3 production (above the canopy) is attributed to HO_2

+ RO_2. The O_3 loss (line 18-19) in previous studies was attributed to high soil NO emissions (and conversion to NO_2), which are absent in our case. Hence, our findings regarding O_3 production are certainly only relevant for grasslands with negligible soil NO emissions and cannot be generalized. This is discussed on Page 10761 (lines 7-9).

Comment: P 10749, L19 – It would be useful to have a formal definition of deltaT(Ln).

Reply: The authors are not sure what the referee means with this statement. The values simply reflect the measured vertical temperature differences, which is stated in the manuscript.

Technical corrections:

Comment: P10738, L22 “found especially distinct” should read “found to be especially distinct”

Reply: This will be changed.

Comment: P10738, L24 does “3-4 times higher as in forests” mean “3-4 times higher than in forests”

Reply: This will be changed.

Comment: P10745, L16, 20, 21 and throughout the manuscript ‘ws’ should be ‘wind speed’.

Reply: This will be changed.

Comment: P10751, L9-10 The phrase “the diurnal course of R_{ac} was inversed in the layers above” is confusing. Do you mean that it’s the mirror image?

Reply: This will be clarified.

Comment: P10755, L 11, wording is unclear here ‘the nighttime DA of all and the high NOx periods data’

Reply: This will be clarified.

Interactive comment on Biogeosciences Discuss., 11, 10737, 2014.