Influence of meteorology and anthropogenic pollution on chemical flux divergence of the NO-NO_2-O_3 triad above and within a natural grassland canopy” by D. Plake et al., 2014

Dear Editor,

please find enclosed our replies to the referee comments and the revised manuscript with track changes. We have clarified all questions raised by the referees, in particular:

See document with Track changes

Lines 136-145: Details on the applied instrumentation.

Lines 178-189: Details about Equation 2.

Lines 379-382: Clarification of total in-canopy resistance.

Lines 433-489: Influence of peroxy radicals on chemical divergence.

Please note that we have also improved the readability of the paper and rephrased some parts of the text. Additionally, some typos were detected in Equation 2, which were corrected (the calculations were correctly made).

We hope that the manuscript can be accepted for publication in *Biogeosciences*.

Best regards,

Ivonne Trebs

Ivonne Trebs

Reply to referee comments:

Reply to anonymous Referee #1

General comments:

Plake et al present the results of a short campaign to observe concentration profiles of NO, NO_2 and O_3 within and above a grass canopy. The data set is interesting and relevant and fills a gap in understanding an important land class for which we have relatively less information about exchange of reactive trace gases. Besides noting that grasslands are a globally important surface type it may be worth mentioning that they are in particular very abundant adjacent to major sources of NOx emission. Roads are lined by grass and not by forest.

Overall, this is a well-executed measurement campaign and good presentation of the data. There are some places where minor additions to clarify missing details would be to improve the manuscript and some additional points to consider in the data interpretation.

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.

Specific comments:

Comment: Page 10742 It would help to say just a little more about the main instrument methods here. Consider adding a few sentences that summarize the most important features of the primary measurements and refer to prior papers for the details. The measurement time scales are especially important for the analysis in this paper so there should be some mention about integration times for the various analyzers. It would only add a little text to list the main features of the measurements. Refer to prior papers for the details of how they were done.

Reply: The suggested information will be added to the manuscript.

Comment: Page 10743 Equation 2 that defines the chemical time scale needs to be explained a little better. A sentence identifying what the underlying assumptions and basis for the time constant would be helpful here. The Lenschow reference does not provide sufficient explanation for the calculation of time scale in equation 2. Furthermore, readers may be left to wonder whether it is valid to consider only the NO-NO_2-O_3 triad, of if the level of peroxy radicals that recycle NO should be considered in calculating the timescales.

Reply: Equation 2 gives the chemical time scale of reactions R1 and R3, i.e., considering only the reactions between O_3, NO and NO_2 not considering reactions of other compounds (e.g., peroxy radicals and VOCs). It is the time at which the mixing ratio of one of the compounds significantly changes from its initial value when reacting with the other ones. It can also be seen as the time required for reaching a new photo-stationary state following a change in NO, NO_2 or O_3 mixing ratios, or the reaction constants jNO_2 and k_3 (see Ganzeveld et al., 2012). The underlying assumptions for the formulation of the O_3-chemical-budget equation are:

- → only source and sink terms of the "triad" are considered, which means other reactions (e.g. RO_2 +NO) are not included
- → covariance terms and other budget terms i.e. horizontal and vertical advection, flux divergence and change in O_3 concentration $d[O_3]dt$ are neglected

Ideally, the peroxy radical (HO_2+RO_2) level should be also considered for this calculation. However, vertical profiles of HO_2 and RO_2 were not measured inside and above the grassland canopy. Measurements of radicals inside canopies are still quite sparse and are typically not included when estimating chemical flux divergences. This is certainly desired for future experiments. However, no straightforward analytical framework exists to calculate their influence on chemical timescales due to the variety of compounds and reaction rates involved in the complex HO_2/RO_2 chemistry, which would require numeral modeling (see Heal et al., 2001). We will add some more remarks about this topic to the manuscript.

Comment: Page 10745, line 14 The discussion about high vs low NOx levels and correspondence with wind speeds ought to be more explicit about the role of emissions. Earlier section indicates the site is 9km SW of city center. High NOx from the NE then probably comes from local emissions and it would be a coincidence that wind speeds differ in that sector. Also, it is a little confusing to be identifying the cases as high and low NOx when actually the basis for separation is wind direction and wind speed.

Reply: The occurrence of low and high NOx situations during the field experiment was indeed directly coupled to the wind direction and could be attributed to two contrasting synoptic conditions that were characterized by different wind speeds (see Moravek et al., 2014). Certainly, the wind direction caused high or low NOx mixing ratios. However, since NOx chemistry is the major topic of the paper we would like to use this quantity to distinguish between the different regimes. We will be more explicit about this issue in the revised version.

Comment: Page: 10, line 1 Can you clarify what fraction of the data were actually analyzed. Are the conclusions based only on the 20 clearly high or low NOx days and the remaining 18 days of data just ignored, or are those still used in some way? Are these data used in the plotted values that are identified as “all data”?

Line 8 If wind speed is criteria for identifying the cases then of course the mean wind speeds for the two cases are different. Overall the data binning needs to be presented more clearly.

Reply: The overall conclusions are based on all data from 19 August to 26 September 2011 (this is referred to in each Figure caption). Conclusions addressing only high or low NOx episodes are based on the 20 days. This will be clarified in the revised version.

Comment: Page: 10753 Discussion of chemical time scales should make some mention at the outset that influence of RO_2 is unknown. This point is acknowledged later in the section but it should come sooner and include an effort to quantify its influence, perhaps by estimating its magnitude relative to reaction with O_3 based on literature values. Is it reasonable to ignore the contribution of peroxides to the NOx chemical lifetime?

Reply: As mentioned above, the inclusion of $HO_2 + RO_2$ in the NOx chemical lifetime is highly desirable. However, since measurements of HO_2 and RO_2 are not available inside the canopy and no straightforward analytical framework exists to retrieve their timescales; such an estimate is somewhat speculative. The reaction rate constant of NO + HO_2/RO_2 is about 500 times higher than that of the reaction NO + O_3. Assuming relatively high average $HO_2 + RO_2$ daytime mixing ratios of 60 ppt inside the canopy (see Wolfe et al., 2014) the oxidation of NO to NO_2 would be as fast as with 30 ppb of O_3 inside the canopy. This implies that the chemical divergence by $HO_2 + RO_2$ could be as significant as that introduced by NO + O_3. In case no chemical divergence exists for NO + O_3 it can be expected that another one may exist due to the reaction NO + HO_2/RO_2. However, it should be noted that peroxides have a high affinity to be lost at surfaces, which may reduce their presence in dense grassland canopies. We will add some more statements about this important topic to the paper.

Comment: Page: 10754, line 28 At a site that is clearly influenced by local anthropogenic emissions the contribution from anthropogenic VOC that are emitted together with NOx-should be noted. It is not enough to just note that biogenic VOC concentrations are small.

Reply: Unfortunately, measurements of anthropogenic VOCs within and above the canopy were not made.

Comment: Page: 10757, line 15 In the absence of significant soil NO sources I don't think it is justified to make conclusions about what the strength of NOx canopy reduction would be. The influence of soil NO emission on the vertical profile of O_3 and other oxidants needs to be evaluated in order to show that the reaction time scale is not changed. I agree that conversion to NO_2 and plant uptake could take place as long as there is adequate penetration of O_3 , but what happens if the NO efflux overwhelms transport of O_3 into the canopy layer and most of the NO oxidation occurs above the canopy? The conclusion is careful to note that this work cannot provide improved estimates of canopy retention for grasslands because the site did not have enough soil NO emission. I agree that is valid to point out the potential importance, and the need to do similar measurement where NO emissions from soil are higher.

Reply: We agree with the referee that our statements regarding the canopy reduction potential could be moderated. However, we have written in the text "for a similar canopy with significant soil NO emission", i.e., for natural grassland. It is very unlikely that soil NO emissions for unmanaged grassland will overwhelm O_3 transport into the canopy. Moreover, as reported in Fig. 2 during daytime for the high NOx regime we can assume O_3 = 20 ppb and NO_2 = 3ppb. In case the NO mixing ratio inside the canopy changes from 0.2 ppb to 10 ppb, the chemical timescale would only increase by 8s, which implies that chemistry inside the canopy could still be faster than transport.

Literature:

Ganzeveld, L., Ammann, C., Loubet, B.: Review on modelling atmosphere biosphere exchange of Ozone and Nitrogen oxides. Background document for the joint ÉCLAIRE/COST ES0804 Expert Workshop "From process scale to global scale: integrating our knowledge on biosphere / atmosphere exchange modelling of trace gases and volatile aerosols", 2012 (available online at https://colloque.inra.fr/cost_eclaire/Background document).

Heal, M. R., Booth, B. B. B., Cape, J. N. and Hargreaves, K. J.: The influence of simplified peroxy radical chemistry on the interpretation of NO_2 -NO-O_3 surface exchange, Atmospheric Environment 35, 1687-1696, 2001.

Moravek, A., Stella, P., Foken, T., and Trebs, I.: Influence of local air pollution on the deposition of peroxyacteyl nitrate to a nutrient-poor natural grassland ecosystem, Atmos. Chem. Phys. Discuss., 14, 20383-20416, doi:10.5194/acpd-14-20383-2014, 2014.

Wolfe, G. M., Cantrell, C., Kim, S., Mauldin III, R. L., Karl, T., Harley, P., Turnipseed, A., Zheng, W., Flocke, F., Apel, E. C., Hornbrook, R. S., Hall, S. R., Ullmann, K., Henry, S. B., DiGangi, J. P., Boyle, E. S., Kaser, L., Schnitzhofer, R., Hansel, A., Graus, M., Nakashima, Y., Kajii, Y., Guenther, A., and Keutsch, F. N.: Missing per-oxy radical sources within a summertime ponderosa pine forest, Atmos. Chem. Phys., 14, 4715-4732, doi:10.5194/acp-14-4715-2014, 2014.

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.