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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 #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

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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 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 fea-tures 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 photostationary 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 sec-tor. 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

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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 NOxshould 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 = 3 ppb. In case the NO mixing ratio inside the canopy changes from 0.2 ppb to 10 ppb, the chemical timescale would only increase by 8 seconds, which implies that chemistry inside the canopy could still be faster than transport.

Literature:

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Moravek, A., Stella, P., Foken, T., and Trebs, I.: Influence of local air pollution on the deposi-tion 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.

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