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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of local air pollution on the deposition of peroxyacteyl nitrate to a nutrient-poor natural grassland ecosystem" *by* A. Moravek et al.

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Response to interactive comments of anonymous referee #2 (received and published on 16 November 2014)

The authors thank anonymous referee #2 for the detailed review and positive evaluation of the manuscript. Also, we are grateful for the valuable comments and suggestions.

Comment: *The authors describe as one of their goals to understand the role of PAN in the deposition of reactive nitrogen (defined by them as Nr) to ecosystems. It is a bit unclear what is meant by Nr. The atmospheric chemistry community uses the term NOy to denote total odd-nitrogen, and that has an operational and chemical basis, being the sum of NOx and NOx oxidation products, as measured by a thermal converter. PAN is clearly in this category. Ecosystem folks are often interested in the nitrogen available for biological activity and so this also includes NH3, and NH4+ particles. The authors should put in a few sentences to clarify which they are referring to here, and if it is only NOy, could they comment on the NH3/NH4+ component of the budget?*

Response: We thank the referee #2 for the remark on the different use of N_r in the different scientific communities. Since the impact of additional nitrogen to the ecosystem is discussed we refer here to all nitrogen available for both oxidized and reduced nitrogen species (i.e. including NH_3 and NH_4^+). We added a brief definition of N_r in the revised manuscript.

Comment: *The discussion of PAN thermal decomposition is a bit incomplete, as it does not consider the possibility of removal of PA radicals on particles and surfaces. This effect has been seen in ambient measurements in the presence of fog [Roberts et al., 1996], and the uptake coefficient of PA radicals to aqueous surfaces has been measured in the laboratory [Villalta et al., 1996]. This may not be an important effect in the absence of fog water, or high aerosol particle surface area, but the paper did not discuss whether or not those conditions exist. Ground fog is not uncommon at night in the humid summertime. This process (PA radical uptake) should be given some consideration here.*

Response: We thank referee #2 for pointing out this additional removal pathway of PA. Although we did not detect fog events, we cannot exclude that at some nights fog may have developed. As we do not have measurements of PA available, we cannot quantify the effect explicitly. However, in our opinion it is unlikely that radical uptake of

PA by fog would have had a substantial influence on the PAN removal, also because thermochemical decomposition of PAN was very limited due to the low temperatures at night. As shown in Fig. 4a, the effect of PAN decomposition ($F_{chem_{surf}}$) on the measured PAN fluxes is negligible without considering fog events and it is unlikely that partially occurring fog events would have had a substantial influence on the mean diurnal values shown here. The same applies when considering the total PAN removal from the boundary layer ($F_{chem_{BL}}$ in Fig. 5), especially as fog (if present) most likely only occurred in the lowest meters of the nocturnal boundary layer. As the discussion on the effect of radical PA removal on the overall thermochemical decomposition of PAN still might be important for other studies on PAN fluxes, we added a remark in Sect. 2.5 of the manuscript.

Comment: *The analysis of NOx-O3 chemistry neglects the formation of NO3 and N2O5, the deposition of which will count as a loss of O3 and is part of the Nr deposition budget. This chemistry will certainly occur in the nocturnal boundary layer when NO is absent, and I would not be surprised if this effect is responsible for the lower O3 at night during the higher NOx periods. This needs to be considered here.*

Response: The reaction of O_3 with NO_2 is the major source of NO_3 at night. As we noted in Sect. 2.3 we find that its impact on the overall O_3 flux was negligible at our site because the reaction rate coefficient is about one order of magnitude lower than of the reaction of O_3 with NO, for which only a small contribution to the O_3 deposition flux was observed during nighttime (see. term "L" in Fig. 4b). This suggests that the flux loss due to the reaction of O_3 with NO_2 was insignificant for our study. During conditions when $NO_2 \gg O_3$ (< 1% of nighttime data of the MBR measurements) we can assume a pseudo-first order reaction for O_3 with NO_2 and determine an upper estimate of the O_3 flux loss according to Eq. 6 (adjusted for O_3). However, even for these exceptionally high NO_x cases the calculated O_3 flux loss due to the reaction with NO_2 was negligible (< 1% of the total O_3 flux). Hence, our estimates confirm that the

effect of the nighttime NO_3 removal pathway on the O_3 flux was negligible at our site.

Comment: *Title: The title has a typographical error, it should read "peroxyacetyl"*

Response: The error was corrected in the revised manuscript.

Comment: *Intro: The Sparks et al., and Telemarkian and Sparks studies were leaf-level studies, in contrast with Okano et al., in which whole plants were exposed in chambers.*

Response: Although both types of studies were based on chamber measurements, we added this distinction to the revised manuscript.

Comment: *Page 20390, Line 10: What is meant by non-stationarity?*

Response: Non-stationarity refers in general to periods where the statistical values vary with time. The stationarity test by Foken and Wichura (1996), which is typically used in the post-processing of eddy covariance data, compares the covariance of the whole averaging period (30 min) to the average covariance of six data subsets ($\grave{a}$ 5 min) to define periods of non-stationarity.

Comment: *Eq 3 and associated discussion. This assumes stomatal conductance is the limiting factor, Sparks et al., show that mesophyllic resistance can be limiting at higher conductances. The authors discuss later in the results section why they don't think the mesophyllic resistance plays a role, but it should be included here for completeness.*

Response: We thank referee #2 for the comment. We included the mesophyllic component in the Eq. 3 and adjusted the text accordingly in the revised manuscript.

Comment: *Section 3.1. PAN photochemical production is also possible, especially in the high NOx air masses. This should be considered in this section.*

Response: In Sect. 3.1 only the main characteristics of the low and high NO_x periods are described, while in Sect. 3.2 we discuss the PAN mixing ratios under both pollution regimes. As stated in the latter, we assume that most PAN originated from advected PA than was formed in situ from emitted VOCs. It is assumed that PAN is produced photochemically either close to the pollution sources or during the transport of NO_x rich air masses to the site. However, as we do not have direct measurements of PA and PAN at multiple locations available, we cannot estimate where exactly most PAN was formed.

Comment: *Figures – some legends and tags are too small and can't be read very easily.*

Response: The font size of tags, legends and labels is the same for all figures and was already adjusted for publication in the column format in ACP.

Reference

Foken, T., and Wichura, B.: Tools for quality assessment of surface-based flux measurements, Agr Forest Meteorol, 78, 83-105, 10.1016/0168-1923(95)02248-1, 1996.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 20383, 2014.