Atmos. Chem. Phys. Discuss., 14, C9236–C9238, 2014
www.atmos-chem-phys-discuss.net/14/C9236/2014/


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.

**Anonymous Referee #2**

Received and published: 16 November 2014

This paper reports measurements of PAN vertical gradients and estimates of PAN deposition fluxes by correlation with measured O3 gradients and fluxes. The conclusions were that PAN deposition occurs via both stomatal and non-stomatal pathways and that the overall nitrogen source to the ecosystems of these kinds, due to this pathway, is much smaller than the total nitrogen deposition measured in other studies. In principle this is a useful paper that describes some careful measurements and analysis, however there are some general comments and some specific issues and questions that need to be dealt with before it is acceptable for publication.

General Comments



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?

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.

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.

Specific Comments Title: The title has a typographical error, it should read "peroxyacetyl"

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.

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

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.

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

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

References

Roberts, J. M., et al. (1996), Episodic removal of NOy species from the marine boundary-layer over the North Atlantic, J. Geophys. Res., 101(D22), 28947-28960.

Villalta, P. W., E. R. Lovejoy, and D. R. Hanson (1996), Reaction probability of peroxyacetyl radical on aqueous surfaces., Geophys. Res. Lett., 23, doi:10.1029/96GL01286.

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