Interactive comment on “Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO₂ over a ponderosa pine ecosystem: observational evidence for within canopy removal of NOₓ” by K.-E. Min et al.

Anonymous Referee #3
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Review of paper acp-2013-313: Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO₂ over a ponderosa pine ecosystem: observational evidence for within canopy removal of NOₓ by K.-E. Min et al.

The paper describes an interesting dataset of extensive NOₓ and other reactive exchange measurements including gradient and direct flux measurements. A large part of the paper describes the details of the measurements and have to admit that this is not my field of expertise and consequently refrain from providing detailed comments on that component of the paper. Regarding the analysis of the data, assuming that the quality of those observations is good enough to indeed infer the details about the temporal variability in vertical sources and sinks of NOₓ inside and above the canopy, the paper makes as the main point the role of chemistry in affecting the efficient canopy top NOₓ fluxes. These fluxes are commonly represented in large-scale models, that do not contain explicit multi-layer canopy model, using the canopy reduction factor concept that does not account for this chemical component. As such the paper is relevant also for the large-scale atmospheric chemistry community. This actually is not clearly reflected by the title and would suggest that you could consider to modify the title to more clearly express this. Regarding the relevance for the atmosphere-biosphere exchange community; it would be actually interesting to demonstrate more clearly how some of this alkyl and multifunctional nitrate chemistry affects the effective NOₓ fluxes compared to NOₓ fluxes only considering basic NOₓ-O₃-BVOC chemistry as generally being done in a number of multi-layer canopy exchange systems (Jacob and Wofsy, 1990, Wolfe et al. 2011, Forkel et al., Ganzeveld et al., 2002) also being used to study the representation of the CRF in large scale models.

Below you can find a list of additional comments;

Pp 12441: “This parameter functions non-mechanistically to remove soil NOₓ emission before it escapes the canopy, thus preventing its contribution to atmospheric ozone formation”. It is always an interesting debate about what is a mechanistic model and a non-mechanistic model, parameterization or empirical function. The CRF appears to be a little of everything. The CRF proposed by Jacob and Wofsy/Yienger and Levy contains some parameters that reflect the actual mechanism involved in the removal of NOₓ with the LAI/SAI expressing to some extent the removal by deposition but, on the other hand, the role of chemistry in removing NOₓ is missing as well as the differences in the role nocturnal versus daytime turbulent transport is also not there. For that we need to use the more explicit representations in the multi-layer exchange model approaches.
turbulent mixing is strongest and dry soils result in NO emissions that are at their daily minimum. Emissions at their daily minimum? Don’t think so. It is generally seen that emissions increase with temperature giving a diurnal cycle and you would expect the soils to reach a maximum temperature in the afternoon. Does the moisture conditions relevant to soil NO emissions change so quickly? I could imagine that it might simply maximum dilution by the efficient mixing conditions.

While there have been a number of indirect lines of evidence for the idea of that processes other than soil NO emission and NO/NO2 photochemical partitioning affect NOx fluxes (Jacob and Wofsy, 1990; Yienger and Levy, 1995; Wang and Leuning, 1998; Lerdau et al., 2000; Wolfe et al., 2011; Min et al., 2012a), to our knowledge these observations provide the first direct observational evidence. Here you could add a reference to the recent work by Seok et al. (ACPD 2013) “Dynamics of nitrogen oxides and ozone within and above a mixed hardwood forest in northern Michigan”. This paper shows an analysis of the observed temporal variability in NOx (and O3) canopy gradients suggesting the potentially important role of the existence of a compensation point versus the role of foliar NOx emissions due to nitrate photolysis.

In this whole discussion on the role of the contributions by the chemistry to the NOx conversion that affects the effective canopy top NOx flux; I see your point that you would like to come across on the role of chemistry that is not considered in this CRF term commonly applied in large-scale models. As such the CRF might not give a reasonable estimate of the effective flux and this point should come across. However, recognizing the fact that multi-layer canopy exchange models that consider the role of chemistry in canopy top NOx fluxes, but ignoring this alkyl and nitrate chemistry, are available and be used would call for a comparison of the role of this other chemistry relative to the role of the basic photochemistry of these multi-layer exchange models.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 12437, 2013.