

### Response to Reviewer#3

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Title: Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO<sub>2</sub> over a ponderosa pine ecosystem: observational evidence for within canopy removal of NO<sub>x</sub>

We would like to thank reviewer#3 for their thoughtful comments. Our responses to the comments are shown in bold as below.

#### General comments and suggestions

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.

→ We have tried to think of a title that would be recognized by the large scale modeling community without losing the process based emphasis of the current title. If the referee has a specific suggestion of a full title or useful phrase we would appreciate the advice.

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 NO<sub>x</sub> fluxes compared to NO<sub>x</sub> fluxes only considering basic NO<sub>x</sub>-O<sub>3</sub>-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.

→ We agree. Here we take a small step of showing such chemistry is consistent with observed fluxes and gradients. It would make sense to initiate a parallel modelling study—perhaps building on the CAFÉ model of Wolfe et al., 2011 who have done some modeling of this site. That is beyond the scope of this paper.

#### General comments and suggestions

Pp 12441: “This parameter functions non-mechanistically to remove soil NO<sub>x</sub> 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 NO<sub>x</sub> with the LAI/SAI expressing to some extent the removal by deposition but, on the other hand, the role of chemistry in removing NO<sub>x</sub> 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.

→ We will rephrase the description of CRF and add more explanation. Our main objection is that the CRF is somehow able to work only on NO<sub>x</sub> emitted by soils and we are unable to think of any mechanism that would be able to distinguish soil NO<sub>x</sub> from other NO<sub>x</sub> once the NO is in the atmosphere.

Pp12452: “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.

→ The soil moisture content near the surface at this site does drop significantly during the day. With our admittedly limited soil chamber measurements, we observed NO soil emissions to decrease throughout the day. We will add some text to describe this unusual situation in more detail.

Pp 12453: “While there have been a number of indirect lines of evidence for the idea of that processes other than soil NO emission and NO/NO<sub>2</sub> photochemical partitioning affect NO<sub>x</sub> fluxes (Jacob and Wofsy, 1990; Yienger and Levy, 1995; Wang and Leuning, 1998; Lerda 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 NO<sub>x</sub> (and O<sub>3</sub>) canopy gradients suggesting the potentially important role of the existence of a compensation point versus the role of foliar NO<sub>x</sub> emissions due to nitrate photolysis.

→ We appreciate the suggestion and referred reference has been added.

Pp 12460; in this whole discussion on the role of the contributions by the chemistry to the NO<sub>x</sub> conversion that affects the effective canopy top NO<sub>x</sub> 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 NO<sub>x</sub> 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.

**→ We would like to make two separate points, first that we should revisit the idea of a CRF and figure out a mechanistic explanation for the process that is being represented by the CRF in large scale models. In our opinion that process has to work on all NO<sub>x</sub>, not only on soil NO<sub>x</sub>. Second chemistry might be a partial explanation for some aspects of what CRFs have accounted for. We agree that additional research in modeling and observation in this area would be useful and will add some text to clarify our point and represent the referees as well.**