Response to Reviewer#4
Author(s): K.-E. Min et al.
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Title: Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO_2 over a ponderosa pine ecosystem: observational evidence for within canopy removal of NO_X

We would like to thank reviewer#4 for the constructive and thoughtful comments. Our responses to the comments are shown in bold as below.

Major comments

(1) Page x41, line 15-19: This statement is not correct or at least strongly misleading. The canopy reduction factor by Yienger and Levy (1995), which is used in many CTM models, is not just an empirical factor to match observed ozone concentrations. Although quite simple, the parameterization on LAI and SAI is a mechanistic concept taking into account in-canopy conversion of soil emitted NO to NO2 and consecutive stomatal uptake (depending on the canopy residence time influenced by LAI and on stomatal area index SAI).
→ **We note that a stomatal mechanism should not be capable of recognizing that NO_2 is derived from soil emissions—rather it should act uniformly on all NO_x in the canopy. Our understanding is that CRF factors do not set up in this way. We will revise the statement to present a more nuanced description of the issue.**

(2) Page x45, line 18-22: Obviously, the normal NO measurement was interrupted twice per minute by a 6 s measurement of the so-called "background-signal". The authors should explain in detail, how the EC flux was calculated from the resulting noncontinuous time series. This is especially a problem for spectral analysis as presented in Fig. 4.
→**In the section of the paper describing our flux measurements and the associated error analysis we describe our approach to the non-continuous time series and compare the analysis to the flux of sensible heat calculated using only those points coincident with the NO or NO_2 observations. We will add text to elaborate on these issues in a revised manuscript and explain our approach to gap filling in the spectral analysis more clearly.**

(3) Page x48, line 23ff.: It is not clear whether the lag time was determined individually for each flux time interval or only from the average midday cross covariance function as displayed in Fig. 3. Please explain in more detail. The use of an average lag time for the entire measurement campaign may be problematic, since the lag can vary with time due to various reasons (especially when different computers are used for sonic and trace gas data acquisition). Even a small error in the lag time can lead to considerable systematic errors in the flux. Comment about the temporal stability and the detectability of individual lag times. In addition, Fig. 3 is not very useful for illustrating the lag time for the NO and NO2 EC systems, because the x-axis scale is much too large. Moreover, according to the text the plots represent the average midday covariance function, which may not be representative for time lags of individual intervals, if the latters are not fully constant.
→ **In the revised text we will describe the lag time determination in more detail. We tested for drifts in the lag time of the sort suggested by the referee and found no evidence for them. As the majority of the flux is carried by eddies with time scales of 10-100 sec, we do not believe that small drifts can much affect the flux—at least at the level required for this analysis. If we were studying CO_2 flux such small errors would be important because the questions being addressed are so much more subtle.**

(4) Page x49, line 14-25 (and Table 1): The authors list many error sources for the EC fluxes and corresponding relative uncertainties. Yet for the relatively low concentration and fluxes encountered in the present study, not the relative but the absolute uncertainties (absolute detection limit) are most probably the limiting factor. The latter is only mentioned for the photon counting statistics, but should also be quantified for the other error sources. Especially for NO, which is determined as a difference between sample and "background" signal (P. x45), the uncertainty and potential correlated variation of the background signal should be assessed. Also for the standard deviation of the covariance function (P. x50, line 6), an absolute flux detection limit should be derived rather than a relative uncertainty.
→ **As the background is taken as an average and is smoothed over long time periods, it doesn't contribute to the variance used in the flux calculation and the relative uncertainties remain appropriate. The description about flux difference using non-continuous data vs continuous data can be found in error analysis part. We also add additional text describing issues of flux detection limit to try to clarify our perspective on the issue in the light if the referee comments.**

(5) Spectral analysis (Page x50/51 and Fig. 4): The entire presentation of spectral analysis is not scientifically sound and completely unsatisfying. The authors argue, that it "provides additional evidence that our instruments for NO and NO2 observe the full range of flux carrying eddies at this site." In my view the displayed cospectrum rather shows the

opposite (see following details)!
5a) If the authors want to show that their separate NO and NO2 instruments both can observe all relevant eddy sizes, they have to show (co-)spectra for NO and NO2 separately, because the two instruments may not have not the same response characteristics!
→ **We will show both cospectra for NO and NO_2 as well as NO_X in the revised manuscript.**

5b) It is not clear whether Fig. 4 shows average midday cospectra over the entire study period or cospectra for an individual day. This has to be clearly specified in the Figure caption. Analysing average cospectra is very problematic because the shape and position of each cospectrum depends on stability and wind speed.
→ **We updated figure caption to clarify the time window. As described in the section on the site and meteorology, there is an extremely regular pattern in meteorology at this site, such that stability, wind speed and direction are essentially identical at a given time of day throughout the study period. Our main point in this figure the comparison the cospectra between NO_2 and temperature. We treat the averaged cospectra of sensible heat flux and NO_2 flux identically and in our opinion the similarity is a useful diagnostic.**

5c) The authors argue that the spectral analysis indicates that there is no problem with their EC data sampling and processing procedure. In my opinion the opposite is the case. The change in sign at higher frequencies of the cospectrum possibly indicates severe problems in the EC data sampling and/or processing (e.g. non-constant lag, different response times for NO and NO2, averaging of spectra under different conditions, or other issues).
→ **We disagree. Changes in sign of flux direction as a function of frequency are common feature of observations at this location as reported in our work by Park et al, 2014; Digangi et al, 2011; and Wolfe et al., 2009.**

5d) A systematic sign change in the cospectrum would violate pre-requisites of the EC methodology and may mask the true lag time of the measurement system. If the authors really want to argue that this spectral sign change is a real effect and not a measurement or data processing artifact, they would have to analyse and discuss this issue in due detail and in a scientifically sound way. The reference to another manuscript "in preparation" is clearly not enough here, because the quality of the EC fluxes is crucial for the conclusions in the present paper.
→ **We will reference other studies using different instrumentation that report the sign changes as a function of eddy size. For example, Figure 5 in Park et al., 2013 shows different cospectral features among different chemical species using one instrument (PTR-ToF-MS).**

5e) In Fig. 4c, the positive counting of negative cospectral contributions makes no sense and is strongly misleading to the reader (even if the sign change is declared in the caption). Negative flux contributions should be counted negatively in the ogive plot!
→ **Our purpose was to test for completeness of the spectrum not to assess the total flux. For bi-directional eddies, the absolute magnitude needs to be considered in a test of whether the flux from that scale of eddy is captured or not, rather than the direction.**

(6) Page x53, line 9-13: This assumption is not correct or at least misleading. Even for non-reactive scalars, the gradient between the forest floor and the above canopy concentration is never a straight line, because the turbulence intensity may never be expected to be constant with height (even not in the boundary layer above the canopy as illustrated by the Monin-Obukhov logarithmic profiles!). On the other hand, if extremely strong mixing would exist, than the concentration would be almost constant with height and a significant gradient would only exist close to the ground.
→ **We are aware of the issue described by the referee and find that strong mixing is an appropriate description for scalars at this site. The analysis of sensible heat flux, H_2O and CO_2 indicates that the flux-gradient similarity holds even in canopy. See the response below for more details. We will adjust our language to reflect the nuances more accurately.**

(7) Page x55, line 23-26: This statement is clearly erroneous! The LNF theory says that the vertical concentration profile inside and directly above the canopy is a function of the respective vertical source/sink distribution. This means that only scalars with the same source/sink distribution have similar profiles (flux-profile similarity). Therefore a deviation from profile similarity (as observed in this study between NOx and temperature/ H2O) does not necessarily point towards additional chemical reactions, but may also be due to different biological source/sink distribution in the canopy. Such a discrepancy in the biological source/sink distribution has to be expected between temperature/ H2O (with the main source in the crown layer) and NOx (with the main source at the ground. Therefore the approach used in Section 5 is not valid for quantifying chemical consumption of NOx!
→ **The referee is correct. However, BEARPEX forest is an open canopy, so the temperature and heat flux has a source primarily at the ground where it is collocated with the NO source. The temperature profiles are consistent with this analysis. On the other hand the source/sink of water is stomata in the canopy. If the effect of a difference in location of the source and sink as described by the referee were large enough to detect, we**

would expect to see the difference in flux gradient relationships between temperature and H_2O. We do not. We also tested Ks derived in BVOC measurements (Park et al., 2014) which draw similar result with H_2O/temperature analysis. However, the difference in NO_X gradients and fluxes is not negligible which is an indication of the existence of NO_X loss mechanism within canopy. From our work presented in Min et al, 2012, which describes the active XPN formation within canopy, we postulate the chemical conversion from NO_X to NOy is a within canopy chemical process affecting the flux.

(8) Fig. 6c: The authors assume a continuous NOx source from soil NO emission as detected by nearby chamber measurements. However the vertical NOx gradients at midday in the lower part of the canopy (down to 0.5 m above ground) do not give any indication for a NOx source at the ground, while the hypothesized chemical NOx sink (smaller than the soil NOx source) produces large gradients near the canopy top. This discrepancy needs to be explained since it either indicates a small local NO soil emission or a decoupling between observed gradients and fluxes.

→ **Our inference of a soil NO_x source is primarily based on observations and mechanisms reported in the literature and the shape of our vertical profiles. The few soil chamber measurements we made are consistent with this interpretation but are not the prime source of our inference. The reviewer is correct that the gradients provide some hint about the relative magnitudes of the soil source and canopy sinks. Our limited observations suggest the soil source is strongest in the AM when dew forms on the ground and the soil first warms. NO fluxes from the soils are then lower in the hot dry afternoons.**

Minor comments and language corrections

Page x40, line 22: The study by Dorsey et al. (Q.J.R.Meteorol.Soc., 130, 1941-1955, 2004) may be added to the references here.

→ **Reference added**

Page x43, line 25: I am a bit astonished that the air masses at the site really represent an "urban plume" because the NOx concentrations are always quite low (< 0.5 ppb) and thus seem to be more typical for remoter areas!?

→ **There is an extensive literature on the transport of the Sacramento urban plume and even the low NO_x we report is higher than the background as a result of the urban plume (Dillon et al. 2002; Day et al., 2003; Murphy et al., 2007; Choi et al., 2011; LaFranchi et al, 2011). We will add some text to orient the reader to the relevant literature.**

Page x44, line 16-18: The sentence about NO chamber measurements does not fit into the logical text flow.

→ **We moved the description for better flow.**

Page x48, line 26: Correct to "by the same instrument"

→ **Corrected**

Page x50, line 2: Correct to "smaller than the precision"

→ **Corrected**

Page x51, line 25-29: This sentence is difficult to understand and needs to be rephrased. Give more information about the temporal variation of the sign change in the cospectrum.

→ **Few more sentences are added in previous graph for additional explanation why we use absolute value of negative cosepctra.**

Page x54, line 2-3: "molecular movement" is not an adequate term here.

→ **We reword the phrase.**

Page x83, Fig. 11 Caption: Replace "xx" in the last line.

→ **We add corresponding number of concentration.**