

Response to Reviewer#1

Author(s): K.-E. Min et al.

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Title: Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO₂ over a ponderosa pine ecosystem: observational evidence for within canopy removal of NO_x

We would like to thank reviewer#1 for the constructive and thoughtful comments. Our responses to the comments are shown in bold as below.

General comments and suggestions

1) My overarching concerns are that uncertainties are not adequately treated and that the data analysis is applied to aggregated data without demonstrating that the same patterns would be observed for an individual observation point. A more thorough treatment of uncertainties is essential because the measurements are in many cases close to detection limits, and the influence of approximations and assumptions are not adequately explored. The concern about using data aggregates comes down to a question of order of operations and demonstrating that the same result would be derived by analyzing individual data points and averaging the results as was obtained by aggregating the data and analyzing the averages.

→ We have done our best to present a complete and thorough discussion of the systematic and random errors. In response to reviewer comments we have added some detail to the discussion of measurement uncertainty in the text. The bottom line is that we can identify no scenario where our basic conclusions are invalidated because they are not significant compared to the uncertainties.

We think the reviewer is asking whether the NO_x flux calculated by a) summing the NO and NO₂ data and then calculating the flux is the same as calculating the fluxes separately and then summing. The answer is yes, we find the two methods to be equivalent. Text has been added to the manuscript to confirm this point.

We also add some examples of daily profile and daily C_{DELTA} analysis in the supplement section 2 to show how averaged pictures represent daily variability.

2) As a small aside - it needs to be clear in the paper that the same time periods are being used for all the data components.

→ The reviewer's statement is correct. We will add a sentence to the revised paper stating this fact.

3) Finally, the paper would benefit from presenting a more explicitly correct description of mass balance equations relevant to turbulent exchange. My main suggestion would be to re-analyze the data using a Monte Carlo simulation approach and treat observations as probability distributions defined by mean value and the analytical uncertainties. The result will be probability distributions of net chemical reaction in the canopy.

→ Section 5 is mass balanced approach to interpret the difference in observed flux and gradient. While the analysis the reviewer suggests might be interesting, it would be a substantial new research project and we do not anticipate it would change the basic conclusions of the paper. We do not know how to interpret probability distributions of net chemical reaction in the canopy. We encourage the reviewer and other readers to think more about this question and what our community would learn from the answers to it.

Page by page comments and suggestions

Page: 12447 Do the reported detection limits also represent the minimum resolvable differences for individual 1-min sample intervals? Considering that gradients are so important to the analysis, the resolution is equally important as the detection limits.

→ The minimum resolvable differences are governed by standard error propagation. That is for a 1 minute difference of two measurements with identical precision, the precision of the difference is the square root of 2 larger than the precision of the individual measurements. We will add the precision for half hour averages to the text so that the reader can more easily see that the differences in the gradients are above the detection limit.

Page: 12449 The selection of criteria for filtering out low and high friction velocity needs to be discussed. It is not appropriate to just use the value from the literature. Show how the observed fluxes depend on u* for this site. The rationale for excluding low u* is based on observations that an emitted tracer (CO₂) has a lower flux in calm conditions than can be expected from soil and vegetation respiration so there must be some 'lost' flux that gets away by horizontal advection or storage that is not adequately captured by measuring the profile at a single point. Low fluxes of CO₂ in calm conditions are considered an artifact of the eddy flux method. However, it is not clear that low fluxes of a depositing species should be considered artifacts. Have you considered the storage term in addition to the eddy flux to quantify the total exchange? If storage is ignored you should present a calculation of what its magnitude

would be and demonstrate that it is small.

→ We added text to the revised manuscript to clarify our reasoning. We tested a window of u^* that had a range from 0.05 - 0.2 m/s at the lower end and found our conclusions insensitive to the choice. We agree with the reviewer that the sensitivity of emission and deposition fluxes to advection and weak turbulence is different. We emphasize that we don't a priori know the relative balance of those two terms to the net flux. And thus make what we believe are conservative choices for the u^* window.

Page: 12450 pg 12450 line 2 should read 'slightly smaller than the'

→ Changed.

It would be better to calculate the flux detection limits separately for each point or at least varying with time of day. Because the turbulence is not constant over the day the effective detection limits are not constant either.

→ We calculated the "detection limit" in conventional way for unidirectional fluxes with different time windows (NO- 21.3, 22.8, 24.6% and NO₂-18.7, 20.2, 20.8% for 9:00-14:00, 14:00-18:00, 9:00-18:00) and list the largest number as the detection limit. Since NO and NO₂ both show bi-directional features in their exchange this detection limit is likely an overestimate at all times.

Page: 12452 The diel cycle and profile aggregate plots need to state explicitly over what period they are aggregating. Is it the whole of BEARPEX?

→ A phrase has been added to represent the time period for averaging.

Simply showing the mean and standard error for the aggregated data is not adequate. Either present a more complete picture of what the data distribution looks like or provide some discussion to demonstrate that the mean is a fair representation of the data. Atmospheric measurements typically have highly skewed data distributions and the means biased by high values. Showing a median and upper/lower quartiles might be a better representation of the data.

→ There is negligible skew in the data sets--the mean and median are essentially identical and the data are fit by a Gaussian distribution about the mean. We added text to the manuscript making this point.

Are the measurement intervals long enough at each profile height to capture a reliable mean value. Particularly at the lowest heights large fluctuations in concentration responding to intermittent mixing by wind gusts may give high variance. Gradient measurements need to sample sufficiently long that temporal variations aren't interpreted as vertical variations.

→ We cycled rapidly between different gradient heights so that we have multiple samples at each height during a 30 minute interval. The reviewer's suggestion about large gusts is plausible but we do not find evidence for that effect in the data,

Some discussion comparing the variability of an individual measurement interval with the instrument variability would be useful here, to demonstrate that the gradient measurements can actually resolve these differences that are so close to the measurement resolution. What fraction of time from each level is kept (is there a flushing period that is discarded), and how do the concentration gradients relate to the measurement precision?

→ We added additional text describing the sampling and the measurement precision of the gradients for half hour windows as described in a response above.

Page: 12453 Need to show some individual profiles or at least profiles that are only aggregated over a short interval with similar conditions to demonstrate that the patterns shown by aggregation hold up when viewed more instantaneously. Need some discussion of whether the choice of aggregation interval affects the results at all.

→ As the meteorology is extremely regular at this site, there were only two days that have wind and temperature patterns that are distinctive rain events on July 2nd and July 11th. We will include profiles from individual days in the supplement section 1.

The periods selected for the profiles shown in Figure 6 do not seem to coincide with the inflection points in the diel pattern (Fig 5) and perhaps span some air-mass changes associated with the transition from upslope to downslope flows. The overall results based on mid-day observations aren't influenced by this choice, but it would be clearer to show mean profiles for periods that don't span any transitions.

→ As the transitions are not coincident at all heights we are unable to identify a single choice of averaging window that meets the reviewer's criteria. We tried to divide the day into enough small windows that the reader can see the patterns of change and choose to ignore times of day as they think appropriate. Instead, we included daily profile pattern in supplement section 1.

Page: 12454 It might be a fairer discussion to note that the results are suggestive that chemical transformation has a greater magnitude than the turbulent transport of NO, instead of referring to counter-gradient flux. Flux should not be presented simply as turbulent transport. It needs to be recognized explicitly as being the sum of separate processes,

turbulent mixing, chemical reactions, and surface exchange.

→ We are confused by the comment above as we think this point is made throughout the paper.

Line 20, In this analysis it is not clear how the NO:NO₂ ratio converts to an NO₂ production.

→ A change in the NO:NO₂ ratio with height corresponds to a transfer of odd-N from one species to the other if the total is conserved.

Furthermore, I worry that it could be misleading to consider only two layers in the analysis. The gradients of reacting species may be counter to one another (eg. O₃ is high above and decreases near the ground while NO would go the other way. Is the computed reaction the same for the multi-layer average as it is for the sum when considering each layer separately, following the approach presented by Parrish et al 1987 and used by Bakwin et al for a tropical forest, with consideration of the influence of light. Parrish, D D yr:1987 vol:92 iss:D2 pg:2165 -2171 Bakwin, Peter yr:1990 vol:95 iss:D10 pg:16755 -16764

→ We believe the two layer model is illustrative. As we are not sure the turbulent flux is constant through multiple layers we worry that expanding to a multilayer model would end up with more invented parameters than we can constrain with the observations.

Page: 12455 The similarity argument is being misapplied by extending it into the canopy layer. An important restriction on any of the flux-gradient approaches is that they be applied to constant flux layer outside the canopy. Nevertheless, this approximation is frequently used, and I recognize that the authors may prefer to base their analysis on this simple analysis rather than construct a fully coupled diffusion chemistry model (e.g. Gao et al, JGR 1993) that may have to rely on inadequately constrained parameterizations. It would be better to refer initially to the correct mass balances and then introduce simplifications and approximations. Because the canopy is included it is important to keep the emission/deposition terms in mind, and be sure to only apply similarity among species that have sources or sinks in the same canopy space. I am not doubting that the observations here are evidence that chemical reactions in the canopy are important. But I believe the quantitative results will be more convincing if the analysis stays closer to the theory and carefully considers the impact of violating the underlying assumptions.

→ As described in p.1256 line 22-24, we also did same analysis using above canopy numbers and found our conclusions insensitive to the choice lower level height. Further we checked the calculation against multiple tracers that are unreactive and found the flux/gradient relationships to hold independent of the choice of lower level at this site. We think this is mainly due to the open forest canopy. To reflect the reviewer#1's concern, we have added few sentences to clarify these points.

Rather than relate the observations to a hypothetical conserved tracer it might be preferable to relate NO/NO₂/NO_x to an actual species. I gather that you are deriving eddy diffusivity from heat flux and temperature gradients. You need to comment on the associated uncertainty in the K, and whether you have to be concerned about either of these terms approaching detection limits. For mid-day observations I expect H will be large but deltaT might be quite small and hard to measure accurately. Secondly, have you considered whether the results depend on which species is chosen to derive a K. Heat may not be the tracer with most similarity to NO_x. Consider the approach of computing a turbulent transport term directly by flux ratios $F_1/F_2 = dC_1/dC_2$, for different choices of species 2. Do you have gradient and flux data from CO₂, O₃, or H₂O that can be used here? Then evaluate how well the results based on different tracers agree.

→ We use inferred K from heat flux and temperature as $K = \text{Flux}/(\Delta C/\Delta Z)$. As described in the text, by using the LNF concept analysis of H₂O, CO₂ and relatively long-lived BVOCs, and we were able to achieve similar result which also indicates the K inferred from temperature and LNF analysis of H₂O, CO₂ and relatively long-lived BVOCs provides similar K. Also, additional details of a similar analysis applied to BVOC can be found in Park et al., 2014.

The difference between observed flux and predicted turbulent flux yields the net chemistry and deposition terms. Flux + storage = vertical transport +P+E-L-D (neglect storage if it is in fact small). P and L are integrated production and loss through the column and E and D are emission and deposition from/to surfaces (integrated through column if not restricted to soils) Note that this gives a result flux units, rather than a hypothetical mean canopy concentration, which plugs directly into the next section. Page: 12456 Simply computing the integrated Production or loss terms directly and not presenting the intermediate result of a concentration would be simpler. Because the gradients are not linear, thinking about the results as concentrations is not as satisfying as thinking about integrated production or loss.

→ We will include the expected process time (turbulent time scale) for easy conversion from concentration to rate. We intended to use concentration unit to compare C_{DELTA}. This keeps the focus on something we measure.

Line 16 It is not correct that there are no sources of H₂O in the canopy - there is evapo-transpiration.

→ Corrected. The small difference of C_{DELTA, H2O} is possibly due to the source/sink process difference with temperature and H₂O. However, the magnitude of C_{DELTA} is smaller than the estimated uncertainty, so we conclude that the sources/sink difference in H₂O and temperature are not-detectable and the flux-gradient

similarity holds for conserved tracer even within canopy at this site.

Line 21: Say something more about what these uncertainty bounds are. If it is just the standard deviation of all data it may not adequately represent the uncertainty on the result. A monte carlo approach that simulated the result based on distributions of observed concentrations considering the analytical uncertainties.

→ **The additional description of the data and its uncertainty described above should clarify this point in the revised draft, again the data is normally distributed.**

I would much rather see the net chemistry terms computed for individual observations and then averaged. This allows for a better treatment of uncertainty and avoids the risk that a function of the mean values is not equal to mean values of the function applied to individual observations. I agree that averaging noisy data can be useful to detect a signal of interest if the data are somewhat noisy, but care must be taken not to average across dis-similar conditions. In particular it would be important to demonstrate that the relationship between mean flux and mean gradient is the same as the relationship between an individual flux and its associated gradient.

→ **For this data set as the conditions of the measurements are nearly constant and the issue of dis-similar conditions is not important.**

Page: 12458 Can you comment on the validity of using average values for each layer when the gradients of reactant pairs may be in opposition and not linear?

→ **We believe the averages are representative of the chemistry and that the cross-correlation terms are small.**

Do you have the data required to get a discrete approximation of the integral by summing up individual layers?

→ **The reviewer's suggestion corresponds to what we did. We will correct the language to avoid the impression that we solved an integral exactly.**

Page: 12460 It would be helpful to have a better consideration of the uncertainties. It looks like most of the terms used in analysis up to this point could all be treated as distributions with a mean and variance and generate a distribution of results.

→ **Propagated error has been added in the context as well as mean and median.**

The statement starting on line 9 needs to be clarified. What goes up and what comes down. Overall what matters most would be the flux of NO_x and whether the higher nitrogen oxides not included in NO_x can be recycled and eventually contribute to photochemistry. What you say in this section should be consistent with what is in the conclusions.

→ **We revised the sentence to read: "We investigate multiple chemical and ecophysiological processes to explain the NO_x removal during vertical transport and conclude that the chemical formation of PNs and ANs and their vertical transport before they cycles back to NO_x are the primary mechanisms responsible—implying that the reactive nitrogen does escape the canopy and may be returned as NO_x by further chemistry downwind."**

Introducing the concept of a canopy reduction factor is not consistent with your final sentence that NO_x does escape the canopy. Traditionally the canopy reduction factor was based on a model of NO being converted to NO₂ that was subsequently deposited. Instead these results are suggesting that higher oxides are generated and there is no retention in the canopy. I think the conclusion paragraph should vary clearly emphasize that your data point to chemical transformation from NO_x to higher oxides rather than any sort of canopy uptake. Mentioning canopy reduction factors makes the conclusion a little ambiguous.

→ **We will rephrase this paragraph to emphasize the importance of chemical conversion of NO_x to NO_z. Here we are proposing to use the term "Canopy Reduction Factor" to include all terms that reduce the availability of NO_x for chemistry outside the canopy.**

Page: 12479 The flux plots need to present estimation of where the flux detection limits are in order to assess what fraction of the data points are actually showing measurable flux. In methods there is mention that fluxes with high and low u* values are rejected.

→ **We are not clear on how to define a flux detection limit for bidirectional fluxes better than we have in the text.**

There needs to be some discussion of how the data selection may affect the aggregate results when the number of points for each hour is not the same.

→ **The numbers of points for calculations do not vary significantly since we applied same filters for all scalars and the averaged patterns are plotted where F_{NO}, F_{NO2} F_{O3} are all exists.**