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Interactive comment on "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" *by* K.-E. Min et al.

Anonymous Referee #1

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This paper presents a slice of data from the BEARPEX campaign looking at the fluxes and gradients of NO and NO2 individually and as their sum (NOx). There are few if any studies with as comprehensive a suite of both NO and NO2 measurements of eddy flux and gradients. The paper concludes that chemical transformation to higher nitrogen oxides within the canopy space accounts for an apparent removal of NOx during transport. The topic is highly relevant to ACP and should be published, but I have some reservations about the manuscript in its current form. My overarching concerns are that uncertainties are not adequately treated and that the data analysis is applied

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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 analysing individual data points and averaging the results as was obtained by aggregating the data and analyzing the averages. 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.

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. With a little more work this paper can be a definitive contribution to the question of what happens to soil NO as it passes through a canopy, and the work will be a guide for similar experiments in different ecosystems.

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

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. 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? 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. 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 sufficientlylong that temporal variations aren't interpreted as vertical variations. 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? 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. 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. 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. Line 20, In this analysis it is not clear how the NO:NO2 ratio converts to an NO2 production. Furthermore, I worry that it could be misleading to consider only two layers in the analysis. The gradients of reacting species may by 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 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. Rather than relate the observations to a hypothetical conserved tracer it might be preferable to relate NO/NO2/NOx 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 NOx. Consider the approach of computing a turbulent transport term directly by flux ratios F1/F2 = dC1/dC2, 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. 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. Line 16 It is not correct that there are no sources of H2O in the canopy - there is evapo-transpiration. 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. 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. 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? Do you have the data required to get a discrete approximation of the integral by summing up individual layers? 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. 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 NOx and whether the higher nitrogen oxides not included in NOx can be recycled and eventually contribute to photochemistry. What you say in this section should be consistent with what is in the conclusions. Introducing the concept of a canopy reduction factor is not consistent with your final sentence that NOx 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 NOx to higher oxides rather than any sort of canopy uptake. Mentioning canopy reduction factors makes the conclusion a little ambiguous. 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. 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

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not the same.

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