Atmos. Chem. Phys. Discuss., 13, C4814–C4819, 2013
www.atmos-chem-phys-discuss.net/13/C4814/2013/

Atmospheric Chemistry and Physics Discussions

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 #4

Received and published: 15 July 2013

The authors present eddy covariance (EC) fluxes above the canopy and vertical concentration gradients (within-above canopy) of NO and NO2 at the Blodgett Forest Station. They find that the EC based upward NOx flux above the canopy is smaller than nearby measured NO soil emission and also smaller than the emission determined by flux-gradient similarity relationships. Based on this observation (and results of previous studies at the same site) they conclude that fast chemical reactions consuming NOx and forming (partly un-identified) organic nitrates can explain the discrepancy to a large part.

There are presently only few experimental studies available about the total NOx exchange and canopy processes of forests (or other ecosystems). Therefore such measurements and evaluations are generally valuable. However, in my view, the present manuscript includes some highly speculative parts with unproven/non-validated assumptions and suffers from serious shortcomings. My main concerns are detailed in the following.

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).

(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 non-continuous time series. This is especially a problem for spectral analysis as presented in Fig. 4.

(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

ACPD

13, C4814–C4819, 2013

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.

(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.

(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!

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.

ACPD
13, C4814–C4819, 2013

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).

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.

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!

(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.

(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

ACPD
13, C4814–C4819, 2013

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!

(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.

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.

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!?

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

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

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

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

ACPD
13, C4814–C4819, 2013

in the cospectrum.

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

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

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