Interactive comment on “Nitrous oxide net exchange in a beech dominated mixed forest in Switzerland measured with a quantum cascade laser spectrometer” by W. Eugster et al.

W. Eugster et al.

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We appreciate the comments from A. Knohl, the Editor (Y. Prairie), and an anonymous reviewer which will help us improving our manuscript. In this final response we address all issues raised by the reviewers and indicate how this will be incorporated in the final article.

The title of the paper should more adequately reflect the methodological nature of the study (Prairie)

We agree and suggest to change the title to “Methodological study of nitrous oxide eddy covariance measurements using quantum cascade laser spectrometry over a Swiss forest”
The criterion of significant correlation seems a logical and objective criterion to use to filter out flux estimate of poor resolution. However, it confounds two possibilities: that the correlation is near zero because the flux is too small, or that the flux is non-zero but the correlation is poor due to other sources of uncertainty. By replacing these rejected values by zero, the authors clearly believe that the poor correlation is because of low flux. It would have been interesting to show a figure with the flux distribution for the rejected flux measurements (Prairie).

This is an excellent clarification that also addresses one essential aspect raised by anonymous reviewer 1 (see below). You are correct: we need to change the wording accordingly to make clear that the essential source for error are not fluxes “below detection limit”. In fact, most fluxes removed by this criterion are outliers on the far end of the flux distribution.

A figure showing the flux distribution for rejected flux measurements (red) clearly shows the removal of almost all large (positive and negative) outliers (Fig. 1 below). Most important is that this approach is able to retain the correctly measured, but small fluxes around zero. The figure below will be included in the final text.

I have, however, serious doubts on the correctness of the correlation method to remove "bad" flux data. Firstly, the method should remove fluxes around 0 (contrary to what the authors state) since correlations are usually lower when fluxes are low. For example, if we would measure the fluxes above an inert surface we would have 0 correlation and 0 fluxes. So I would think that the correction method could well bias the fluxes by removing mostly 0 values. Since the average of the data is not 0 this will bias longer period flux estimates. Methods based on standard errors of the estimates would be more appropriate (Anonymous Referee #1)

We do not agree in all details, but will attempt to further clarify the following aspects, because we believe that the employed method is well suited for real-world data with systematic and random errors:
(1) Methods based on the standard error of the estimate implicitly assume normal distribution of data; this is however not necessarily the case for eddy covariance flux data. Moreover, any type of noise in the signal may have a normal distribution on its own, with a different mean and standard deviation than the distribution of the signal. Thus, the reviewer is certainly right IF the raw data are normally distributed, AND there is no noise process that has a different mean than the signal itself. We doubt that this is the best possible approach to the question under discussion.

(2) It is certainly correct that the method tends to remove fluxes around 0 and as the figure above shows, the mean of the removed flux is basically around zero. However, it is essential to note that the spread (standard deviation) of the removed fluxes is much larger than of the ones retained, and a largely dominating fraction of flux values close to zero are retained, as we postulate from theory (Eq. (1) in manuscript). This of course points to a potential problem with inflated variances of $w$ and/or $c$, which is a requirement to yield large covariances but insignificant correlation. Thus, we will keep this information in our manuscript, but accept the criticism by the reviewer that we should be clearer in the wording along the lines expressed by the Editor and commented above at the very beginning of our Final Remarks.

(3) The argument that for fluxes above an inert surface we would have 0 correlation and 0 fluxes may or may not be correct. So far we have never measured over an inert surface. By re-arranging Eq. (1) we see that

$$r \cdot \sqrt{w'^2} \cdot \sqrt{c'^2} = w'c'. $$

Thus, over an inert surface we expect the variances of $c$ to vanish, even as there is turbulence and thus $w'^2 \gg 0$. Unless there is noise in $c$, and here the implicit assumptions made by Reviewer 1 influence the viewpoint: if that noise is normally distributed and has a mean of 0, then he’s perfectly correct (and does not contradict our views). If not, then the more general case presented in our paper is appropriate where all considerations based on the implicit assumptions about error terms may not be correct.
In reality one often finds that depending on where noise comes from it need not be normally distributed and it can be correlated with noise in the component used in a covariance. This is especially the case if spikes or glitches or internal signal filters are used to process raw sensor signals of any of the instruments involved. In our revisions we will add text to explain this issue more clearly. In summary, there is no disagreement between the view of Reviewer 1 for a purely Gaussian random noise system, but our approach is more generally applicable for field research where non-Gaussian random noise processes may be relevant.

Every reference to yearly fluxes or offsets of CO2 fluxes by N2O fluxes MUST BE REMOVED from the paper (Anonymous Referee #1)

We’ll accept this criticism and will revise our manuscript accordingly. We agree that it is basically difficult to defend any scaling-up method without having comparable measurements for a similar year and a similar location that would allow to validate any such approach. We felt it beneficial for the reader to get an impression on how relevant N2O fluxes might be in the annual budget, but we have no problems to remove the corresponding statements.

I also disagree with their statements on the effects of fog on the emission of Nitrous oxides. I think that the theory and statements on that are pretty swampy. I would think that particular conditions related to the onset of fog could be responsible for that (Anonymous Referee #1).

We will revise this section with close reference to the three paper article references provided by A. Knohl. Most likely we will have to consider “plant mediation” in place of “emission”. The particular conditions related to the onset of fog are actually the availability of liquid water droplets wetting the canopy. It would have been interesting to learn from the reviewer of which other conditions he or she was thinking that go beyond our argumentation and interpretation in the manuscript.

While the H2O fluxes seem to match very well, the true test is not to plot the daily
curves of CO2 or H2O fluxes (as in Fig. 6) but rather simply have correlation plots of the fluxes estimated with the two different instruments, both for CO2 and H2O. If the correlation is poor (which I think it is for CO2 taken from the two instruments), then part of the rejected measurements might be more the result of imprecise measurements rather that low flux (Prairie).

In the meantime this issue has resolved. Unfortunately, it turned out that we happened to select an absorption line of $^{13}$CO2 instead of $^{12}$CO2. While we originally interpreted the scatter in a pairwise plot of CO2 concentrations to be related to the inaccuracy of how the absolute concentrations can be computed for the open-path Licor 7500, we now realize that we are comparing total (mainly $^{12}$CO2) with the minor isotopomere ($^{13}$CO2). In our revisions we will elaborate on this in the methodical section and take out all comparison and analyses of the CO2 data from the QCL instrument. For H2O we will add a pairwise plot for fluxes as A. Knohl suggested in his comments, point 2.

**Calibration scheme details (A. Knohl)**

The questions asked are relevant, and indicate that the text was not clear enough. The following aspects will be clarified and added in the final paper:

a) the calibration procedure consisted of measurements of nitrogen (background) and pressurized air with traceable concentrations of CO2 and N2O (reference). Background and reference were measured for 20 seconds each after flushing of the measurement cell.

b) the precision was determined every 30 minutes from the reference measurement, i.e. the calibration measurement was also used to determine precision. This is relevant because changes such as optical alignment, laser intensity and detector sensitivity are very likely to increase the noise level and thus reduce precision.

c) ambient air, nitrogen and reference gas were sampled at 6 L min$^{-1}$. All three had to pass the same filter to obtain similar pressure conditions in the cell during background,
calibration and measurement.

d) the calibration factor showed slight drifts that are probably due to an increasing pressure drop over the filter, which was changed three times during the measurement campaign. Due to filter clogging, the cell pressure varied between 53 and 85 mbar. The most pronounced variations in calibration factor were found for N2O. They were always smooth and less than 4

Comparing QCLAS with IRGA LI-7500 (A.Knohl)

We will add such a panel for H2O fluxes but remove the CO2 part due to the reasons mentioned above.

In results the authors argue that the observed increase in N2O fluxes before precipitation events might be caused by fog or increased atmospheric moisture. Data, however, showing that fog or atmospheric moisture is increasing are missing. Why not adding an extra panel on top of figure 9 showing atmospheric humidity vs. hours since first measured precipitation? (A. Knohl)

We produced a new version of Figure 9 to show how relative humidity evolves shortly before and after rain events (see Fig. 2 below; we will however keep the original figure in our manuscript for simplicity). The thick red line is the median curve of relative humidity that corresponds to the thick black curve of cumulative N2O fluxes. For each event a thin red line of the time trace of relative humidity has been added to the original graph. Basically, we originally started with relative humidity, but as this figure shows, there is little insight provided by relative humidity. Our measurements were carried out during a period with frequent fog, and thus it is not surprising that relative humidity starts to increase again shortly after the onset of precipitation, whereas before the onset of precipitation, the air gets slightly drier. In direct contact with A. Knohl we found an inconsistency in our wording on page 1182, line 7, which created confusion: only fog, not gaseous water vapor is a realistic candidate for the increase of N2O flux that starts 4.5 hours before a rain event. We’ll revise our text accordingly.
More profound literature search (A. Knohl)

We appreciate the references found by A. Knohl that will help us elucidate this issue in more detail. We will carefully address this. Although we did a literature search, we missed the three mentioned articles, and therefore this feedback is a valuable contribution to the improvement of our manuscript.

Interactive comment on Biogeosciences Discuss., 4, 1167, 2007.
Figure 1: Additional panel or figure to show which values were rejected (red) and which were retained (green) by the significance-of-correlation approach.
Figure 2: Figure 9 but with additional corresponding lines for the time traces of relative humidity in red.