

Interactive comment on “Measuring the biosphere-atmosphere exchange of total reactive nitrogen by eddy covariance” by C. Ammann et al.

Anonymous Referee #1

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This is a rather nice manuscript about a new measuring system for determining ecosystem-level fluxes of reactive N-species. The technique of N-conversion followed by NO-chemiluminescence is not new – it has been used in many previous studies; however, there are few studies using this method to determine fluxes. This is especially true for NH₃ (or amine species) as described here. Furthermore, as pointed out by the authors, this system can likely function as a long-term continuous flux measurement technique. This is critical to understanding the sporadic and (off-times) bi-directional nature of reactive-N fluxes. The tests both for concentration measurements and flux determination are thorough and well-described (as well as corrections for to the fluxes). I only have a few minor suggestions for the authors' consideration before publication.

Specific Comments: 1. Section 2.2.1, system description. I certainly understand that

C2965

most of the instrument details tests are provided in a second manuscript (Marx et al., 2012) and should not be repeated here. But I do feel that a few more details concerning some of conversion efficiencies is warranted since these are key to this instrument for providing both accurate flux and concentration data. Perhaps a table with the measured conversion efficiencies and some indication of the error bars, plus a brief comment on any tests for longer-term contamination or degradation of the converters (a previously observed phenomenon) would be sufficient. Also, during the calibrations when a standard gas was added at the inlet – was this calibration done using a standard diluted in dry air or was this calibration done via standard addition to ambient air that is aspirated into the inlet? It is usually necessary to use ambient air to dilute the calibration standard to maintain constant concentration of other species, such as water vapor, that can quench the NO chemiluminescence and alter the measured signals. Please clarify this point.

2. Section 3.3. I am a bit surprised by the observation that the Total-N fluxes tend to follow NO_x flux. Even though NO_x is certainly the highest observed concentration of the reactive N-species, it is often HNO₃ that dominates the flux. This occurs even though HNO₃ may only constitute 3-10% of the concentration. This suggests that your original non-heated inlet (in 2006) may also not be transmitting HNO₃ fluctuations as was observed for NH₃ later in the manuscript. HNO₃ and NH₃ tend to have the same adsorption issues when it comes to sampling lines. The work of Horii et al (2006) is mentioned in section 4.2.3 as a contrasting study (as they found HNO₃ to dominate the flux); however, it may be just due to the initial inlet used here.

3. Page 6873. Discussion about the zero offset. Typically the use of a pre-reaction chamber is to maintain conditions within the detector as close to that of ambient (primarily for such species as water vapor) in order to measure the offset properly. However, since the purpose here is to measure total nitrogen, small changes in the offset are likely small compared to the total measured signals and, thus, the use of zero air is likely to be more acceptable. This does raise a more subtle question concerning H₂O.

C2966

Does the presence of water vapor flux (rapid [H₂O] fluctuations) affect the total N-flux via rapid quenching of the NO chemiluminescence?

4. Section 4.3.1. Measuring a “flux detection limit” from looking at periods where fluxes are expected to be near zero is a bit problematic. One can really only estimate at what point the random instrument noise overwhelms the concentration fluctuations that are correlated with vertical wind motions. This was the course described in the Rummel et al. (2002) paper cited here and was originally described by Lenschow and Kristensen (1985), JOA Tech., 2, 68-81.

5. I would agree with the authors that this system has the capability of providing long-term continuous N-flux measurements to complement corresponding carbon and water exchange measurements. However, it might be instructive to also mention a few practical concerns, such as the power required (many flux sites are quite remote) or the feasibility to use with tall canopies.

Interactive comment on Biogeosciences Discuss., 9, 6857, 2012.