Final Author Response to Referee Comments

(Ammann et al.: Measuring the biosphere-atmosphere exchange of total reactive nitrogen by eddy covariance, Biogeosciences Discuss., 9, 6857–6898, 2012)

We thank the two referees for the careful reading of the Discussion Paper and their valuable comments. We follow their suggestions as far as possible and will improve the manuscript accordingly. In the following we give a detailed response to all individual comments. Original referee comments are printed in blue italic.

Christof Ammann on behalf of all coauthors.

Anonymous Referee #1

1. Section 2.2.1, system description. I certainly understand that 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.

Reply: We agree with the referee that (near-full) conversion efficiencies for all individual Nr compounds are crucial for the measurement system and in principle we also agree that an informative survey table would be desirable. However, as discussed in detail in the companion paper by Marx et al. (2012), the preparation of well defined concentrations of individual N_r compounds is not easy and often the conversion efficiency tests are limited by the uncertainty of the reference measurements or calibration gas mixture. This is especially true for the highly soluble gases like NH_3 and for the aerosol species (also considering the issue of time response between different converter versions discussed here). Therefore a simple table summarizing conversion efficiency values and error bars from Marx et al. (2012) would be misleading here without detailed explanations of the various calibration setups. We therefore decided to refer to the original paper, which is easily online accessible, rather than to repeat the lab conversion results here. In addition, Figs. 2b and 8a-10a in this manuscript give a good illustration about the effective conversion efficiency of the relevant compounds under field conditions.

Concerning longer-term contamination or degradation: as stated in Section 4.3.2, the present study did not focus on really long-term measurements. For that issue we refer to the results of the year-long study over an agricultural field in Germany. The corresponding field calibration results have been presented in Marx et al. (2012) and more detailed results of that study will be presented elsewhere (Brümmer et al., in preparation).

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.

Reply: Standard addition to ambient air was not a feasible option at our measurement site, because (as explained in Sections 3.1 and 4.3.1) the ambient air concentration usually showed quite fast variations. Therefore, cylinder standard gas diluted with dry synthetic air was used for automated checking of the temporal stability of the system in the field. An additional humidification of the synthetic air would have been possible but would also have been an additional source of uncertainty. The quenching interference of water vapor in the

NO detection had been quantified in a lab setup before the field experiment (see Reply to Comment 3 below).

2. Section 3.3. I am a bit surprised by the observation that the Total-N fluxes tend to follow NOx flux. Even though NOx 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.

Reply: We agree with the referee that the non-heated inlet most probably has the same strong damping effect on NH_3 and HNO_3. We will include this in the text. We also agree that the statement about the contrasting results by Horii et al. (2006) was not fully justified. It will be rephrased in a more appropriate way.

Horii et al. (2006) found a strongly dominant role of HNO_3 deposition over NO_2 deposition despite the lower HNO_3 ambient concentration due to the much higher (estimated) deposition velocity for HNO_3. Such a dominant role of HNO_3 deposition was not expected nor observed in the present study because NO_2 and NH_3 concentrations were about two orders of magnitude higher than the HNO_3 concentrations (see Fig. 2a) due to the closer anthropogenic sources in contrast to the more remote location of the Harvard forest site. A concentration difference of about two orders of magnitude cannot be (over-) compensated by the different deposition velocity (or surface resistance). In this context, it has to be noted that the deposition velocity over low vegetation like grass is relatively less affected by differences in the surface resistance than for forest because of the higher aerodynamic resistances. We will add these considerations in the manuscript.

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

Reply: We thank the referee for this comment. We originally thought that the water vapour interference is generally very small and thus we did not include it in the manuscript. However this is not fully adequate for all conditions. For the NO analyser used here, Marx (2004) determined a 0.19% NO sensitivity reduction per 1 mmol/mol water vapour increase. For a typical background N_r concentration of 20 ppb, this results in a cross-sensitivity of -0.038 nmol N (mmol H_2O)$^{-1}$. For the maximum daytime H_2O fluxes during the study period of about 5 mmol m^{-2} s^{-1}, one gets an apparent NO interference flux of -0.19 nmol m^{-2} s^{-1} or -2.7 ng-N m^{-2} s^{-1}. This is in the order of 5-10% of daytime background N_r deposition fluxes (Figs. 8-10) and thus cannot be generally neglected. We thus corrected all ΣN_r fluxes with the simultaneously measured H_2O flux. A corresponding description of the H_2O interference effect will be added in the methods section.

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.

Reply: We basically agree with the referee. As mentioned in the manuscript, the purely random instrument noise related flux detection limit would be similar to the value given by

Rummel et al. (2002). But we think that the term "flux detection limit" is not fully restricted to the instrumental white noise effect. As explained in the manuscript (last paragraph of 4.3.1) the purely instrument white noise related error may often be irrelevant compared to the site specific "red noise" related flux uncertainty (due to varying ambient concentration).

5. I would agree with the authors that this system has the capability of providing longterm 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.
Reply: The system in total needs about 700 W from mains power or a strong and stable generator. This is not primarily due to the converter but rather due to the NO analyser and vacuum pump. In this respect the power requirements are similar to modern fast closed-path CH_4 and N_2O analysers (quantum cascade laser or cavity ringdown instruments) used for eddy covariance GHG flux measurements. We will add a statement about this issue in the manuscript.
  Concerning the use with tall canopies, we see no major problems in comparison with low canopies. As mentioned in the manuscript (1) p6875,L24-25 the high-frequency damping problem will be more relaxed over forests; (2) p6878,L13-18 the maintenance requirements for the converter installed on the tower are very moderate; (3) p6862,L19-21 & Fig.1 the use of a long sampling tube between the converter (e.g. on the forest tower) and the analyser and pump (located usually in a shelter at the ground) is not problematic because of the low pressure in the tube due to the use of a critical orifice behind the converter.

Anonymous Referee #2

1. Error analysis: The authors do an excellent job of describing most details relevant to eddy covariance measurement, including attenuation, lag-times, and cospectral/ogive analysis. However, while the authors present a 'flux detection limit', they do not provide an estimate of the error surrounding each individual flux point. Such an analysis would be useful, particularly for comparing time series of flux measurements between the TRANC and individual nitrogen species.
Reply: Following the Referee suggestion we will add error bars to the individual data points of the TRANC EC flux in Figs. 8-10. They are quantified from the variability of sub-interval fluxes similar to the concept by Foken and Wichura (1996).

2. The authors describe a 'slight' dependence of high-frequency damping as a function of wind speed (Fig.7). However, the correlation for the Oensingen (lower height) does not look statistically significant considering both the error bars on the individual points and the likely error on the slope. Please use the error on the slope to determine whether this dependance is statistically different from 0.
Reply: It has to be noted that the vertical bars in Fig. 7 do not represent error bars but inter-quartile ranges (i.e. they illustrate the scatter of indiv. values in the wind speed bin). For reason of robustness, the linear regression was calculated using the median values. The indicated moderate slope of the regression line is actually statistically significant with a 95% confidence range of -0.015 ± 0.009 $(m/s)^{-1}$. We will add this information to the Fig. 7 caption.

3. I am confused by the discussion of an offset signal in the CL detector due to molecules other than NO reacting on longer timescales (p. 6873). Reactions occurring on longer timescales would contribute to the a background - but would not likely, I think, be as consistent throughout the experiment as described in the manuscript - such interferences would presumably vary throughout the field project. Please provide some literature references or experimental observations to support this hypothesis. The background of the

system seems more likely noise in the photomultiplier tube detectors in the CL system rather than long chemiluminescent reactions.

Reply: The referee is right; according to the instrument manual, the offset signal (usually detected as pre-chamber counts) is due to both dark counts of the photomultiplier and possible slower reactions of molecules other than NO. It is evident from zero air measurements and from the relatively low variability during the field experiment that the dark counts are the dominant source. We will rephrase the text accordingly.

4. p.6877, line 15/16: The authors suggest that problematic points may pass through the stationarity test 'accidentally': please clarify what is meant by this. were points manually tested or automatically?

Reply: The stationarity test was fully automated. However, we agree that the formulation was not very useful and misleading. We slightly adjusted the stationarity test to be more effective against outliers and will modify the text accordingly, also in the context of the newly displayed error bars (see Ref#2, Comment 1 above).

Technical notes:
p.6870, l.16, remove an 'and'
p.6874, l. 15, should read "with an unheated inlet"
Fig.2: y-axis font size should be larger

Reply: We will correct all three points.