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Atmospheric Measurement Techniques Discussions

Interactive comment on "TRANC – a novel fast-response converter to measure total reactive atmospheric nitrogen" *by* O. Marx et al.

Anonymous Referee #3

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The aim of this paper is to report the performance of a total gas-phase nitrogen converter. Only the converter performance is presented. Ambient data and demonstration of its utility in field experiments is largely split off into several other publications. While I'd rather see a single, more comprehensive publication, this is up to author's taste and editor's discretion.

I fully agree that simple to operate nitrogen analyzers intended for making routine nitrogen deposition measurements across regional to national networks are a critical research need. As part of a research network, un-speciated fluxes are adequate, and more feasible logistically than separate speciated fluxes, though I am skeptical of the approach of summing all N compounds that has been applied here. This manuscript makes too strong a claim for being first to quantify fluxes of a large group of nitrogen compounds. Total oxidized nitrogen fluxes have been measured at Harvard Forest for many years, but the instrumentation requires some custom modification that impedes it's widespread use. The research community would be well served by developing commercial-off-the-shelf analyzers with the required performance. This paper presents a step in that direction.

I am concerned that lumping both oxidized and reduced nitrogen species together is going to generate data that are hard to interpret. Firstly, not all the species in this group (termed Nr) are equally plant available, The uptake pathways and consequences of oxidized nitrogen (mostly absorbed as NO3-) and reduced nitrogen (mostly absorbed as NH4+) are different and I think it would be more useful to track them separately. I would like to see a more thorough introduction explaining why it is valuable to lump all the nitrogen compounds together rather than keep the oxidized and reduced compounds separate. Has the community identified a need to measure the sum of all nitrogen compounds together? Are there insurmoutable technical challenges to keeping them separate? Since it has been demonstrated that gold catalyst alone will suffice for doing NOy flux, it would at least be simple as a next step to do NOy and Nr, and hope that the difference (reduced N) is large enough to determine by difference. Some results and discussion demonstrating how observations of this Nr contributes to new understanding would be helpful, but is to be the topic of another paper

A second critical missing component is a convincing demonstration that the converter does not have negative interferences (see below).

I would agree to disagree about the usefulness of total Nr measurements vs separate oxidized and reduced N measurement, but the issue of possible negative artifacts needs to be dealt with before final publication.

Some specific comments on the text are given below.

Page: 7626 Line 12 that states nitrogen flux measurements are mostly limited to short campaigns should note the exception of multi-year measurements of NOy eddy flux at Harvard Forest referenced in Munger et al 1998,1996, and Horii et al., 2006. Though this work is noted later, it ought to be mentioned and not leave the reader with the impression that the topic is a completely blank slate. Munger, J. W., et al. (1996), Journal of Geophysical Research-Atmospheres, 101(D7), 12639-12657. Munger, J. W., et al. (1998), Journal of Geophysical Research-Atmospheres, 103(D7), 8355-8368. Horii, C. V., et al. (2006), Agricultural and Forest Meteorology, 136(3-4), 159-174

Page: 7627 line 7, In noting previous work using laser spectrometers, cite also first NO2 fluxes by laser spectrometer reported by Horri et al 2004 Horii, C. V., et al. (2004), Journal of Geophysical Research-Atmospheres, 109(D8)

lines 22-25 In noting the Harvard Forest NOy fluxes, note that the measurement duration exceeds 5 years, additional years are included in Horii et al 2006. Horri et al 2004, 2006, also report NO2 eddy flux by TDLAS as well as note the serious sampling issue with HNO3 even with a carefully designed inlet intended to avoid impeding HNO3 fluctuations, which strongly supports the need for avoiding all inlet surfaces in order to make valid flux measurements including HNO3.

Page: 7630 Is 870C really needed to dissociate NH4NO3? In aerosol mass spectrometer using thermal desorption, 420C is adequate for NH4NO3 volatilization. Likely refractory aerosol containing NaNO3 or Ca(NO3)2 if they were present would be undersampled, but otherwise it would seem wise to use the lowest temperatures possible to limit unwanted reactions. Is there any evidence that typical Au or Mo converters do not volatilize and convert the NO3- in NH4NO3 aersosol? It is often assumed that they do.

Line 11 The use of Pt in the TRANC gives me serious concern. Kliner et al 1997 report up to 50% loss of NO on Pt catalyst. Have you checked for losses? To check for negative artifacts, a test adding the same amount of NO upstream and downstream of the converter needs to be done. Kliner, D. A. V. et al. (1997), J.Geophys. Res., 102(D9), 10, 759–10, 776

Since CO has potential for impurities why use it instead of H2, which as noted by Kliner et al has equivalent or better properties as reducing gas and was free of impurities.

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In making the assumption that HNO3 is probably converted also, it would be especially appropriate to cite the report by Kliner et al that HNO3 is more readily converted than NO2.

Page: 7641 In comparing the time constants for the TRANC system to previously reported work it is should be noted that Munger et al report exponential decay time constants not half-value periods, which are analogous to the time constants reported for the TRANC system. Note also that Figure 2 in Munger et al compares the response of NO2 and HNO3 and finds very little difference, which provides evidence that the catalyst does not impede transmission of HNO3 fluctuations. Furthermore, note that the reported flow rate for NOy flux measurement at Harvard Forest was considerably less than the flow in the TRANC analyzer, suggesting that in both cases the response time is governed by the residence time in the detector cell and sample inlet line, so in all cases the response time could be increased by optimizing flow rates and cell volumes.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 7623, 2011.