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Response to reviewer's comments

TRANC – a novel fast-response converter to measure total reactive atmospheric nitrogen

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We greatly appreciate the excellent comments and suggestions made by the three reviewers. Please find below a point-by-point response to the requested topics and issues.

Comments from Reviewer #1:

General remarks:

'*The development of techniques to augment tools for characterizing atmospheric compounds has a value in itself. A few thing are not touched, however. They include potential interferences due to the high temperature converter. Even if in clean air conditions such compounds may contribute minor amounts, their behavior within the converter should be characterized: HCN, CH3CN, and N2O.*'
>>HCN and CH_3CN are reduced organic N_r compounds. While their full or partial conversion in 300°C gold converters (see Kliner et al., 1997) represents an interference problem for NO_y measurements, their expected full conversion in the TRANC (870°C) is welcome as part of total reactive nitrogen (including reduced compounds). Concerning potential interference by N_2O, we didn't find any indication of a significant conversion of N_2O in the TRANC (see the detailed response to Referee #2). We added the reference to Kliner et al. (1997) on these issues and the implications for the total N_r conversion in the text (Section 4).

'What also needs more attention is the air inlet of the converter system. This part will be critical for aerosol which purposely is to be cracked. Is there an influence of (changing) humidity on the conversion ? Especially the nitrate containing aerosols would show a delicate behavior.'
>>The converter inlet is actively heated so that all inner surfaces in contact with the sample air have temperatures above 100°C (see Fig. 2). We assume that in such conditions the effect of humidity is not very important (see also Chapter 4, second paragraph). We will additionally emphasize this issue in Chapter 2.1.

Specific points:

p2/l30
'It seems that the authors use the designation Nr for reactive nitrogen containing compounds but also for the sum of them.'
>>We intended to differentiate between a general use of the term reactive nitrogen (denoted as 'N_r') and the sum of all nitrogen-containing trace species (denoted as 'total N_r'). However, we understand the problem raised by the referee. Therefore in the revised manuscript, we generally use the symbol $\sum N_r$ to denote the total sum of N_r compounds as measured by the TRANC-CLD.

4/2
'Brümmer et al., 2011 2011 a and/or b ? appears more than once'
>>This issue had already been solved with the publication of the online document in the interactive discussion. It is now consistently cited as either Brümmer et al., 2012a or 2012b. The year has been changed to 2012 as the 'in press' paper is now officially published and the other is to be submitted soon.

4/10
'Besides the necessity ...: rephrase this sentence' (starting Page 7627, Line 11)
>>Sentence has been rephrased to: 'Further problems in measuring N_r compounds are the lack of capable techniques for fast-response detection, issues regarding inlet design, sampling losses and air column chemical reactions for highly reactive and soluble N_r species (Horii et al. 2004; 2006). Hence, the establishment of large-scale dry deposition monitoring networks of N_r remains nearly impracticable.'

5/24 (Page 7629, Line 4)
'the interactions ...: it may be useful to more spell out these interactions, especially in respect to the sampling of the air to be measured.'
>>We restructured this sentence to clarify that the interactions are mainly due to gas phase reactions and gas-aerosol interactions. We also added two references (Meixner, 1994; Wolff et al., 2010) that describe these processes.

12/22
'It is interesting to note that the sum of the individually measured nitrogen containing compounds in the comparison shown in Figure 7 match better the TRANC-result than one would expect according to Figure 6. What would an error propagation analysis tell when measuring the assumed individual compounds and adding them up for comparing to the sum.'
>>The scatter plot in Figure 6 is only for aerosol compounds, which play a minor role at the field measurement site represented in Figure 7, and thus would cause only minor absolute deviation of generally <0.5 ppb. For illustration of the (random-like) errors associated with the field intercomparison data, we include and discuss an additional Figure with a scatterplot and regression analysis between the TRANC-CLD results and the sum of the individual N_r compounds (see also response to Referee#2). We have also added another potential explanation, i.e. the missing of organic N_r compounds, for the minor systematic deviation (ca. 7%) in the field observations.

Table 1:
'Why not adding TRANC-Chemiluminescence to the list ?'
>>Line containing information about TRANC-CLD added.

Figure 4:
'It is difficult to infer stability of the calibration over time from this figure.'
>>For a better demonstration of the system's long-term stability, we've added a second panel to Fig.4 showing the data included in the linear regression analysis as time series.

Figure 5:
'It were helpful to mention the calibration gas mixing ratios (not concentrations) in the caption. Otherwise the conversion efficiencies are not recognized.'
>> The used calibration gas mixing ratios are plotted as columns and an additional listing of the values in the figure caption would be fully redundant and of no use in our opinion.

Figure 6:
'Is there an explanation why ammonium nitrate measurement points are above the 1:1 line and ammonium sulfate below ? The explanation for the deviation given in the text is rather weak. The authors should keep in mind, that the usefulness of their converter were given only if the conversion rates of all compounds they subsume under Nr were 100 %.'
>> We agree with the referee that the most striking feature of Fig. 6, i.e. the large differences between NH_4NO_3 and the other aerosol types, is not treated sufficiently in the text. Considering possible causes for differences between the measurements of the TDMPS and the TRANC-CLD, and differences in the results for different aerosol species, we found a plausible reason for (at least part of) the differences between NH_4NO_3 and the other two aerosol species. NH_4NO_3 is semi-volatile under ambient conditions, forming a thermodynamic equilibrium between the particulate NH_4NO_3 and gaseous NH_3 and HNO_3 (Stelson et al., 1979, Mozurkewich, 1993), while $NaNO_3$ and $(NH_4)_2SO_4$ are not. For normal chamber air conditions (relative humidity around 50% and air temperature around 20°C), a significant part of the dry aerosol most likely evaporated to the gas phase (cf. Seinfeld and Pandis, 2006). Consequently, the TDMPS measured 'a reduced' particle number, while the TRANC-CLD system would measure both, particulate and gaseous phase, leading to an apparent overestimation of the TRANC-CLD system. We will address this issue in the text and introduce a modified Fig. 6 which is more appropriate to present the results and related uncertainties.

'Reference to the publications
- *Sigsby, J. E., Jr., F. M. Black, T. A. Bellar, and D. L. Klosterman, Chemiluminescent Method for analysis of nitrogen containing compounds in mobile source emissions (NO, NO2, and NH3), Environ. Sci. Technol.,7, 51-54,1973.*
- *Winer, A. M., J. W. Peters, J. P. Smith, and J. N. Pitts, Jr., Response of commercial chemiluminescent NO-NO2 analyzers to other nitrogen-containing compounds, Environ. Sci. Technol., 8, 1118-1121, 1974.*

would be appropriate, as they deal with high temperature converters combined with NO-chemiluminescence analyzers.'
>>We've added a reference to these 2 papers in Section 1.2 (Page 7627, Line 20).

'Remains the question, what is the added value of Nr in respect to eddy covariance (EC) measurements. Nr is an operational definition for the sum of a mixture of nitrogen containing compounds. So what is won, when knowing the deposition (or loss to the atmosphere) of nitrogen when not knowing which compound contributes. For a long term measurement the total nitrogen flux may be a useful information. For short term measurements as EC, the lifetimes of all comprising compounds would have to be taken into account. Especially, when the conversion factors of the TRANC are open for discussion. So again, which of the nitrogen

containing compound(s) of the composite would be relevant to or be utilized to which extent by the ecosystem is still open.
>>We agree with the referee that one useful application of the TRANC-CLD system is the long-term monitoring of the total reactive nitrogen exchange of ecosystems (in connection to e.g. GHG budget studies). The system runs continuously with low maintenance, thus it is an ideal tool for quantifying N_r exchange over seasons and years and helps establish a sound calculation of N_r budgets, which had been problematic in the past due to measurement issues of single compounds and high operational and analytical costs. It is clear that the same information for all (or a relevant group of) individual N_r compounds would be preferable over just the total N_r exchange. However, since usually resources (instrumentation and maintenance) for reactive nitrogen measurements are limited, information on total N_r may often be more useful than just one specific compound.
For short-term studies, total N_r measurement can provide important constraints and validation data in combination with additional selective converters or detectors.
Although these two main applications of the TRANC-CLD system and also the analytical shortcoming of a missing differentiation of single N_r compounds had already been stressed in Sections 1.1, 2.1, and 4, we slightly modify the formulation to clarify this issue (see last paragraph in Section 4).

New References:

Horii, C. V., Munger, J. W., Wofsy, S. C., Zahniser, M., Nelson, D., McManus, J. B.: Atmospheric reactive nitrogen concentration and flux budgets at a Northwestern US forest, Agric. For. Meteorol., 136, 159-174, 2006.

Kliner, D. A. V., Daube, B. C., Burley, J. D., Wofsy, S. C.: Laboratory investigations of the catalytic reduction technique for measurement of atmospheric NO_y. J. Geophys. Res., 102, D9, 10759–10776, 1997.

Meixner, F. X.: Surface exchange of odd nitrogen oxides. Nova Acta Leopoldina, 70(288), 299-348, 1994.

Mozurkewich, M.: The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size, Atmospheric Environment. Part A. General Topics, 27, 261-270, 1993.

Sigsby, J. E., Black, F. M., Bellar, T. A., and Klosterman, D. L., Chemiluminescent method for analysis of nitrogen containing compounds in mobile source emissions (NO, NO_2, and NH_3), Environ. Sci. Technol., 7, 51-54, 1973.

Stelson, A. W., Friedlander, S. K., and Seinfeld, J. H.: Note on the equilibrium relationship between ammonia and nitric-acid and particulate ammonium-nitrate, Atmospheric Environment, 13, 369-371, 1979.

Winer, A. M., Peters, J. W., Smith, J. P., and Pitts, J. N.: Response of commercial chemiluminescent NO-NO_2 analyzers to other nitrogen-containing compounds, Environ. Sci. Technol., 8, 1118-1121, 1974.

Wolff V., Trebs I., Foken T., and Meixner F. X.: Exchange of reactive nitrogen compounds: concentrations and fluxes of total ammonium and total nitrate above a spruce canopy. Biogeosciences, 7, 1729-1744, 2010.

Comments from Reviewer #2:

General remarks:

'The paper describes the development and characteristics of a novel fast-response converter to measure total reactive atmospheric nitrogen. Contrary to measurements of total reactive odd nitrogen (NOy) this also includes reduced species like NH3. The paper is well written and deserves publication in AMT. My only criticism is, that the description of the instrument performance is often rather qualitatively. It would be nice if the authors could give some more quantitative information:

Specific points:

The converter is described in great detail, but dimensions (length of the individual sections, inner volume of the whole converter, flow through the converter and residence time inside the converter) would be quite helpful.'
>>Requested information has been added in Section 2.1.

During the NO calibrations a low positive NO signal slightly different from 0 was observed. Please be more quantitative by quoting the mean offset and its standard deviation. How does the offset change with time? Also associated to the NO calibrations: Does it really take approx. 15 min to reach a clearly stable signal? Why is this?
>>Mean offset (±standard deviation) for pure air calibration was 0.055 (±0.028) and has been added on Page 7634, Line 18. Offset (0.173 ± 0.091) and slope (0.051 ± 0.003) for the linear regression have been added to Figure 4 (right panel). Calibration data is now plotted as time series in Fig.4 (left panel). The reason for only using data of the 10-min period from 15 to 25 minutes after the initial valve switch to calculate NO concentrations was the slow response of the calibration gas system and not because of the response time of the TRANC-CLD system (see description in Section 3.3 and Fig. 9). This assures a well conditioned calibration gas tube up to the inlet of the TRANC and thus a stable instrument response. Note that the length of the calibration gas tube is largely dependent on the individual system setup and may easily be several tens of meters (cf. Fig. 3).

In Figure 4 please provide a liner regression analysis including standard deviations for the slope and the offset. Again a quantitative measure for the offset is not given.
>>Linear regression equation is now given in Fig. 4B. Also added are calibration data plotted as time series for a better visualization of the system's long-term stability (left panel, see comments above).

Although in the cited field experiment HNO3 was only of limited importance, this might be different in other environments. Therefore, I think it is necessary to determine the conversion efficiency for HNO3 in the lab.
Unfortunately, we did not have the opportunity to perform high-quality conversion tests for HNO_3 due to the lack of specific analysers. However, we refer to other published results about the performance of similar gold converters (NO_y converters, e.g. Munger et al. 1996) and specifically to the reports of Kliner et al. (1997) who point out that HNO_3 is more readily converted than NO_2 (see also respective comment of Referee#3).

In addition, you state that N2O will not be converted. Has this been tested? Due to its high mixing ratio even a small conversion of N2O might be significant.

>>We did not explicitly test the conversion of N_2O in the TRANC. However, since N_2O is generally present in the ambient air (with > 300 ppb) but not in the calibration air, the minimum observed ambient measurements by the TRANC-CLD give an upper constraint of a potential interference. Over a period of several months, there have been a considerable number of measurements < 2 ppb (more than 100 half-hourly means, especially in the cold season). We therefore conclude that no significant conversion of N_2O occurs in the TRANC.

The description of the in-field intercomparison is again rather qualitative. It is only stated in the final section of the paper that the TRANC tends to measure slightly higher values compared to the sum of the individual measurements. Here again a quantitative regression analysis based on the data presented in Figure 7 would be helpful.
>>We follow the suggestion of the referee and add a Figure with a scatter plot for the intercompared data and a corresponding linear regression analysis. This should give a more quantitative representation of the field intercomparison results.

Comments from Reviewer #3:

General remarks:

'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.'
>>We acknowledge the important previous work at Harvard Forest on cumulative NO_y fluxes and added more credit and references to this work as detailed in the responses to the specific comments below.

'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'
>>As mentioned in the manuscript (a.o. Section 4) we agree with the referee that lumping of N_r species has considerable disadvantages in the (mechanistic) interpretation of the measurements. It is obvious, that any additional information (e.g. for individual N_r species or the partitioning between oxidized and reduced Nr compounds) is superior to lumped total N_r measurements alone.
However, since precise CLDs are expensive and usually resources (financial and manpower) are limited, often a choice has to be made. In case only one CLD (channel) is available we consider the information on the exchange of total N_r more useful for ecosystem studies than just of NO_y or of a single compound. Ecosystem protection regulations (e.g. UNECE CLRTAP) often specify critical loads for total (reactive) nitrogen.
On the other hand, if additional instrumental capacity is available, the total N_r measurements can provide important constraints and validation data complementary to selective converters or detectors. See also the response to referee #1 on this issue.

'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.'

>>We assume that the mentioned negative artefacts concern the potential loss of NO on the Platinum-gauze mentioned below. In the revised version, we include test measurements which show that no significant loss of NO occurs on the Pt-gauze (see details in the specific response below and Section 3.1.1).

Specific points:

'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'
>>References added.

Page: 7627 line 7
'In noting previous work using laser spectrometers, cite also first NO2 fluxes by laser spectrometer reported by 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. Horii 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.'
>>References added.

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.'
>>We agree that lowest possible temperatures should be used that provide the intended conversions. However it has to be noted that the high temperature of 870°C was chosen by good reason in order to assure the complete conversion (oxidation) of NH_3.

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'
>>We thank the Referee for pointing to this issue. Actually we regularly checked for potential loss of NO through the converter by alternately feeding NO calibration gas upstream and downstream of the converter. We found no reduction of NO by the TRANC and thus no effect of the used Pt catalyst. We added this information at the end of the first paragraph in Section 3.1.1.

'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.'
>>We are aware of the mentioned problem of CO concerning impurities. On the other hand, H_2 has the disadvantage that it is oxidized to H_2O which may cause interference in the CLD analyser as for example reported in Perez et al. (2007).

Page: 7640
'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.'
>>We thank the referee for this suggestion and added the study of Kliner et al. (1997) in the text.

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.'
We have corrected the term 'half-value-period' to 'e-folding time' which is identical to the 'exponential decay time constant'. We agree that generally the response time in these setups is largely influenced by both the residence time in the detector cell and flow rate. This has been mentioned on Page 7638, L.27. We also added the information about the lower flow rate in Munger et al. (1996) in Section 4.

Reference:

Pérez, I. M., Wooldridge, P. J., Cohen, R. C.: Laboratory evaluation of a novel thermal dissociation chemiluminescence method for in situ detection of nitrous acid. Atmos. Environ. 41, 3993–4001, 2007.