

Author's Response to Referee #1

In this response, the referee comments (in black) are listed together with our replies (in blue) and the changes to the original manuscript (in red).

This paper reports the development of an instrument to measure NO₂, total NO_y and total particulate nitrate based on Cavity Ring-Down spectroscopy for measuring NO₂ and thermal dissociation for NO_y. The accurate measurement of NO_x down to low (ppt) levels is crucial for understanding the chemistry of remote atmosphere and combining such an instrument with thermal dissociation to measure total reactive nitrogen compounds and particulate nitrate further adds to the potential uses of such an instrument. Whilst a few examples of this type of approach exist in the literature, CRDS is a relatively new method and so work like this is important.

In general the paper details a comprehensive laboratory study of the instrument, including the thermal decomposition of different NO_y species and the performance of the denuder for the particulate measurements. It is well written, easy to follow and within scope of the journal. I recommend publication subject to the following, largely minor amendments and additions.

We thank the referee for the positive review of our paper and the constructive comments, which we address in the following responses.

A detailed description of the CRDS NO₂ / NO_x instrument is given in a previous paper (Thieser et al 2016), however I feel this new paper would benefit from some more details on the performance of the instrument to NO₂ and NO. There is no mention of how these species are calibrated, or what the precision / accuracy are. Whilst this data may be able to be found elsewhere, I believe the authors should include it here as well. It would greatly assist readers wishing to get a full understanding of the performance of the instrument. I would suggest at least adding what calibration gases were used for NO and NO₂, what is the accuracy and precision of these measurements at various time resolutions and what is the magnitude of any interferences.

We added the following paragraph to Sect. 2.2 as a short overview of the instrument's performance in detecting NO₂ and NO.

For NO₂, the performance of the instrument was first described by Thieser et al. (2016), who reports a measurement uncertainty of 6 % + (20 pptv * RH/100) which is dominated by uncertainty in the effective cross section of NO₂ and the wavelength stability of the laser diode. The NO_x detection limit of 40 pptv (2σ, 1 minute average) for the present instrument (laboratory conditions) was derived from an Allan variance analysis and is worse than that reported by Thieser et al. (2016) (6 pptv at 40 s) due to degradation of the mirror reflectivity. Corrections applied to take into account humidity and pressure changes are discussed in Sect. 2.1. The total uncertainty in NO_y will depend on the uncertainty in the conversion to NO_x of both gaseous and particulate nitrate and thus depends on the individual components of NO_y in the air sampled. For purely gaseous NO_y, the major problem is likely to be related to loss of sticky molecules at the inlet and we choose to quote a "worst case" uncertainty of 15%.

We have amended the LOD we quote to that obtained on a stationary platform (the one mentioned in the last version was derived from the AQABA dataset obtained on a ship):

In this context we note that the deployment on a ship resulted in a degradation in performance (LOD was ≈ 100 pptv) owing to the ship's motions, especially in heavy seas, which resulted in drifts in the instrument zero.

On page 8 lines 17-20 it is stated that complete conversion of HNO_3 to NO_2 occurs at temperatures above 800°C , but then that the amount of NO_2 detected of 13 ppb is 85% of that expected based on the permeation and dilution flows. These two things do not seem to be consistent with each other – could the authors please clarify? Also, no mention is made of any potential losses of HNO_3 to the surface of the instrument or the inlet, something that is often a problem with this type of instrument?

The uncertainties of the measurements have to be taken into account. We have modified our text and now write:

A custom-made permeation source was used to provide a constant, known flow of HNO_3 (with $\sim 8\%$ NO_x impurity) to the TD-CRDS inlet. The permeation source consisted of a length ($\approx 1\text{m}$) of PFA tubing immersed in 66% HNO_3 solution held at 50°C through which 100 sccm of dry, zero-air was passed. The concentration of HNO_3 and thus its permeation rate, $(1.62 \pm 0.2) \times 10^{-4}$ sccm, was derived by measuring the optical extinction of HNO_3 at 185 nm using the absorption cross section of Dulitz et al. (2018). The uncertainty is related to uncertainty in the absorption cross-section and the reproducibility of the output. The HNO_3 thermogram (Fig. 2 and Fig. S2c)) has a plateau at temperatures above $\approx 800^\circ\text{C}$. In the plateau region of Fig. 2, the HNO_3 mixing ratio measured is 13.0 ± 0.8 ppb, which (within combined uncertainties) is in agreement with the expected value (15.2 ± 1.98 ppb) calculated from the permeation rate and uncertainty in the dilution factor. We cannot rule out some loss of HNO_3 in the tubing connecting the permeation source to the TD-CRD, through previous studies have shown that irreversible losses are $\sim$ of 5% or less under dry conditions (Neuman et al., 1999). We note that inlet loss of HNO_3 is minimized under ambient sampling conditions as only a short section (~ 20 cm) quartz tubing at ambient temperature is upstream of the heated section in which HNO_3 is converted to NO_2 . Our observations are thus in accord with previous studies that found complete conversion of HNO_3 to NO_2 in similar set-ups (Day et al., 2002; Di Carlo et al., 2013; Wild et al., 2014; Womack et al., 2017).

Could the authors comment on if there would be an effect of HONO on the NO_y channel?

We have performed additional experiments with other trace gases, including HONO. Our results indicate efficient conversion of HONO to NO_x in our heated inlet and are described in a new section 3.1.5.

In section 3.3.1 could the authors make some comment as to how much particles greater than 414 nm in diameter are transmitted? I would have thought that, especially in remote marine environments, particulate nitrate have a significant fraction on larger particles and thus provide an interference to the instrument.

We have addressed this comment by adding text in Sect. 3.3.1:

The PLC does a better job in predicting a reduction in transmission for the largest particles which we measured and indicates a transmission of 74% at $1\ \mu\text{m}$ and 45 % at $2\ \mu\text{m}$. In certain environments, nitrate associated with coarse mode particles thus represents a potential bias for TD-CRDS measurements of NO_y .

In section 3.3.2 could the authors comment on how the efficiency of the denuder changes with age and how often it may need to be regenerate or replaced.

This will depend on the conditions of its deployment (e.g. highly polluted or remote) and we cannot suggest a regeneration schedule. Also, the behavior of our denuder is not necessarily identical to that of other designs.

In section 4.1 the authors state that they do not present an analysis of the NO_z data as it will be presented in a future publication. I think they should at least comment on the NO_z data observed. This paper is about the development of an instrument to measure NO_z and to not comment on the measurements made even a little seems very strange.

Unlike NO_x, there were no measurements during AQABA with which to directly compare our NO_z data set. The separate publication will be non-technical and will deal with the atmospheric chemistry of NO_z which is not in the scope of AMT. We see little value in reproducing information from the planned publication here. We now write:

Here we compare the NO_x and pNit measurements with other measurements of these parameters made during the campaign.

Likewise section 4.2 would also benefit from an expanded discussion of the NO_z data. For instance why is the diurnal cycle observed as it is, especially the nighttime peak values.

We expanded the discussion and now write:

The diel profiles of NO_z/NO_y are strongly influenced by fresh emissions of NO_x. As the measurement location is strongly influenced by traffic, there is a decrease in NO_x (and increase in NO_z/NO_y) at nighttime. Nighttime increases in NO_z (13th-14th, 15th-16th, 18th-19th and 19th-20th of January 2020) may also be partially caused by formation of N₂O₅ as previously observed (Schuster et al, 2009) and which would have been favoured by the low nighttime temperatures (< 10 °C) in winter.

Finally I wonder if the authors could comment on now the particulate nitrate measurement could be improved. There are some suggestions given in section 3 but I think there should be something in the conclusions about this. Currently I read the paper like there was not much hope that the technique could be used for accurate particulate nitrate measurements but I am sure this is not the case, thus the authors should say so.

The following text has been added to the conclusions:

Under humid conditions the denuder suffered from direct breakthrough of NO and the re-release of previously stored iPN and NO₂ in the form of NO, indicating a potential bias of pNit measurements using this technique and potentially limiting its deployment to low-NO_x and low-NO_z environments. When using comparable denuders, we recommend regular checks with humidified zero air to characterize potential breakthrough. Our experiments demonstrated that the release of NO_x from the denuder exposed humid zero-air for several hours can decrease to values below 1 ppbv, which, in a first approximation could be treated as an offset. Cycling between multiple denuders would help in reducing the size of any bias.

Page 13 line 6: 'humidified significant' does not make sense.

Typo has been removed

humidified ~~significant~~

References

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