Response to Reviewers

Manuscript Number: egusphere-2022-145

Manuscript Title: Development of a broadband cavity-enhanced absorption spectrometer for simultaneous measurements of ambient NO₃, NO₂, and H₂O

This document contains the complete text from the reviewer (black) and the responses to each comment (blue) as well as the corresponding changes in the revised manuscript (red). All the line numbers refer to the original manuscript.

Response to Reviewer #2 Comments:

General Comments:

This paper details the development of a new BBCEAS system for simultaneous measurements of the trace gases NO₃, NO₂, and H₂O. Unlike previously developed absorption-based sensors for NO₃, this study emphasizes the utility of retrieving the water vapor signal, which has strong absorption features in the detected spectral region around 662 nm, instead of correcting for water vapor as an interference in the NO₃ signal. The instrument demonstrates superior precision and comparable accuracy as compared to existing BBCEAS NO₃ measurements. Overall, this paper presents a thorough characterization and evaluation of the instrument performance and its field operation. It is well within the scope of AMT, and I recommend publication subject to the minor revisions detailed below.

We would like to thank the reviewer for the positive review and the useful comments. Our point-by-point responses follow with updated manuscript and supplementary materials.

Specific Comments:

1. I agree with RC1 that the description of measuring the H₂O absorption spectrum in the original text is unclear. I believe the authors have sufficiently addressed this concern in their response, as well as any concerns relating to temperature control of the instrument.

   We agree with the reviewer about the insufficient descriptions for the H₂O absorption spectrum measurement and the temperature control of the instrument in the original manuscript. We have extended the description in the manuscript as written below. Please refer to our response in AC1 (Reviewer #1 General comment for Line 187-195).

   Line 110: “… lines (NE-2, Ocean Optics Inc., USA). The entire optical layout was housed in a temperature-controlled optic box to maintain constant performances regardless of environmental changes.”

   Line 190-192: “For that, H₂O was produced by flowing injected via constant flow of ZA through a deionized water bubbler at room temperature of 22.7 °C and pressure of 991.5 hPa with 12.3 % relative humidity as averages, while activated carbon denuder (6 mesh, Ecotech Pty Ltd., Australia) as well as Drierite filter (8 mesh, Thermo Fisher Scientific, USA) were installed on upstream of the bubbler to remove possible contaminants in ZA cylinder.”

   Line 329: “… due to the sea ice breaking activities. During the mission, the averages (±1σ) of temperature and pressure of the sample in the cavity were 22.02 (±0.90) °C and 997.6 (±25.9) hPa. And the changes in the absorption cross-sections due to these variations were small to be detected by our instrument.”
2. L207 states a “Fourth-order polynomial was applied to account for the optical drift and/or unaccounted extinctions such as absorption by ambient ozone.” Was there any basis for selecting this functional form? The retrieval demonstrates that the polynomial fit is a quiet a large component of the overall signal. Please elaborate or clarify why this is the case.

To our best knowledge, there are insufficient discussions on how it should be selected. In our case, an empirical decision was made to attain better fitting performances from laboratory and field measurements rather than just following the previous broadband cavity-enhanced absorption spectroscopy (BBCEAS) works that used fourth-order polynomial (Thalman and Volkamer, 2010; Thalman et al., 2015; Min et al., 2016; Washenfelder et al., 2016; Jordan et al., 2019; Barbero et al., 2020). More specifically, we decided the order of polynomial based on changes in fit coefficient uncertainty, root mean square (RMS) and chi-square of residuals.

For example, Figure S1 shows the residual RMSs, residual chi-squares, and fit coefficient errors of each species (normalized ones for simple comparison) as a function of polynomial orders for the data corresponding to the spectrum in Figure 4 in the main manuscript. Overall, the fitting with fourth-order polynomial shows better performance than the others. This exercise was repeated for different measurement environments.

We have added the sentence in the manuscript and Figure S1 in the SI:

Line 207-208: “Fourth-order polynomial was applied to account for the optical drift and/or unaccounted extinctions such as absorption by ambient ozone. Fit order was selected based on the resulted fitting statistics (i.e. fit coefficient uncertainties, root mean square and chi-square of residuals, Figure S1), which needs to be verified for different measurement applications.”

Figure S1: Statistics of spectral fitting for ambient data with the order of the polynomial. Data was acquired on August 26th, 2021 (UTC) from shipborne observation, which matches with data in Figure 4. Normalized fit coefficient uncertainty which ranged from 0 to 1 was used for convenience.
3. How reproducible are the NO\textsubscript{3} transmission results to the field environment? It seems this has been clarified in the author’s response to RC1, but I’m curious if this would have to be characterized in each new environment.

Based on the experiences we have with this newly built system, the transmission efficiencies of NO\textsubscript{3} (\textit{T}_{NO\textsubscript{3}}) for all parts from the coaxial overflow inlet to the detection region hardly changed with varying aerosol loading within the experimental range (2480–12308 μg, described in Sect. 3.3.2). However, \textit{T}_{NO\textsubscript{3}} is sensitive to the residence time along the airway (Liebmann et al., 2017). Thus, we presumed that the \textit{T}_{NO\textsubscript{3}} verified in Sect.3.3.2 can be used unless changes in residence time exist due to the modifications in length and configuration of the coaxial inlet part as well as the flow rate of the sample.

However, individual mission has its own limitation in instrumental deployment, thus the inlet characteristics such as length, shape, and material can be changed. For this reason, \textit{T}_{NO\textsubscript{3}} for the individual setup should be quantified for every campaign. We think that on-site verification of \textit{T}_{NO\textsubscript{3}} is ideal, and regular base checks throughout a mission is recommended.

In the case of Arctic mission, however, we were not able to quantify \textit{T}_{NO\textsubscript{3}} during the mission due to the logistical issue (consumable supplies were not allowed due to COVID-19). Therefore, \textit{T}_{NO\textsubscript{3}} of the weatherproof-designed inlet with elongated PFA tubing before the cavity was evaluated after the campaign in the laboratory.

To address this concern, the text in the main manuscript has been edited as:

Line 319-321: “However, due to the physical limitation of the instrument placement in the seatainer, the length of subsampled PFA tubes was elongated (length: < 1 m, residence time: < 1.5 s) and the total transmission efficiency of NO\textsubscript{3} for this deployment was decreased by 65.1 % (±2.14 %, 1σ), quantified by post-campaign experiments through the same method as described in Sect. 3.3.”

4. The description of the NO\textsubscript{3} dilutions in the linearity test are somewhat unclear. Where is the drift in the NO\textsubscript{3} concentration evidenced in Figure 7? Or have the data in Fig 7a,b already been corrected for the linear drift? Please be explicit as to what the red and black dots indicate in these figures. It is not stated in the text or in the figure caption.

Data in Figure 7 (a and b) have already been corrected for the drift in the NO\textsubscript{3} source. For more clarity, we added Figure S2 which shows the data without the correction. NO\textsubscript{3} concentration under the constant dilution condition (black) was interpolated (gray dotted line in Figure S2 (a)) and used as the baseline for the drift of NO\textsubscript{3} standard. This baseline was subtracted from the data under both constant (black) and different (red) dilution conditions.

We have added the phrases in the manuscript and Figure S2 in the SI:

Line 261-265: “As described in section 3.3.2, a slow and steady increase in NO\textsubscript{3} was observed, varying from 746 to 1045 pptv under the constant dilution ratio of 1:150 from beginning to end of throughout the experiment (Figure S2). For tracking this drift in NO\textsubscript{3} standard, we alternated various dilution conditions with the base one (dilution ratio set as 1:150, shown in black markers in Figure 7 (a, b)) and applied the linear interpolation of retrieved NO\textsubscript{3} concentrations in those conditions (gray dotted line in Figure S2 (a)). This baseline which depicts the changes in NO\textsubscript{3} source drift was subtracted from the data for both constant (black) and different (red) dilution conditions.”
Line 793-796: “Figure 7: NO$_3$ (a, b), NO$_2$ (c, d), and H$_2$O (e, f) mixing ratios with elapsed times and other independent abundance evaluators evaluation parameters in standard addition experiments. For NO$_2$, correction of the steady drift in NO$_3$ source bath was applied by linear interpolation of data with frequent injections of constant dilution condition (black). Error bars in (b, d, and f) represent 1σ variabilities for 2 seconds integration data (vertical) and uncertainty of evaluators (horizontal). For NO$_3$, data with constant (black) and varying (red) dilution conditions were corrected for the steady drift in NO$_3$ source by linear interpolation (Figure S2). In (b, d, and f) axes of ellipse represent 1σ variability for 2 seconds integration data (vertical) and uncertainty of each variable (horizontal) while dashed lines show linear correlations.”
5. L321: The wording is unclear. Was the total transmission efficiency reduced by 65% of the lab-based value? Or reduced to a total transmission efficiency of 65%?

The total transmission efficiency was reduced to 65.1%. To be clear, we have edited the corresponding words as we have replied in the 3rd specific comment.

Technical Corrections:

1. It would be helpful to see all the detection limits in Table 1 for the same integration time if possible (for ease of comparison).

We have checked the references in Table 1 to match the integration time for the detection limit by collecting all available information. In general, no explicit information were reported with another integration time, but a few papers (Langridge et al., 2008; Kennedy et al., 2011; Wang et al., 2017) provide Allan deviation plots which can be used to approximate their detection limits for the same integration time. However, due to the errors in reading from printed graphs, we included the approximated detection limits only in Table S1 and SI. In regard to Table 1, we have corrected for the mistakes we made in describing the performance of Venables et al. (2006) and Varma et al. (2009); the integration time is 57 rather than 60 seconds in Venables et al. (2006) and the detection limit in Varma et al. (2009) is 2 rather than 1 pptv.

We have added the words in the manuscript and Table S1 in the SI:
Line 306: “Table 1 summarized the cavity characteristics and performances of the existing BBCEAS for NO₃ measurement. Inferred detection limits with the same integration time are available in Table S1.”
<table>
<thead>
<tr>
<th>Reference</th>
<th>Reflectivity (max. performance)</th>
<th>Detection limit (time resolution)</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball et al. (2004)</td>
<td>99.9965 % @ 670 nm</td>
<td>2.5 pptv (1σ, 516 seconds)</td>
<td>N/A</td>
</tr>
<tr>
<td>Venables et al. (2006)</td>
<td>99.775 % @ 665 nm</td>
<td>4 pptv (N/A, 57 seconds)</td>
<td>- 14 %</td>
</tr>
<tr>
<td>Langridge et al. (2008)</td>
<td>99.9913 % @ 660 nm</td>
<td>0.25 pptv (1σ, 10 seconds)</td>
<td>0.35 pptv (1σ, 5 seconds) 0.1 pptv (1σ, 60 seconds) N/A</td>
</tr>
<tr>
<td>Varma et al. (2009)</td>
<td>99.98 % @ 662 nm</td>
<td>2 pptv (1σ, 5 seconds)</td>
<td>- 16 %</td>
</tr>
<tr>
<td>Kennedy et al. (2011)</td>
<td>N/A</td>
<td>1.1 pptv (1σ, 1 second)</td>
<td>0.35 pptv (1σ, 5 seconds) 0.1 pptv (1σ, 60 seconds) 11 %</td>
</tr>
<tr>
<td>Wu et al. (2014)</td>
<td>99.991 % @ [638, 672 nm]</td>
<td>7.9 pptv (N/A, 60 seconds)</td>
<td>12 %</td>
</tr>
<tr>
<td>Wang et al. (2017)</td>
<td>99.9936 % @ 662 nm</td>
<td>2.4 pptv (1σ, 1 second)</td>
<td>0.6 pptv (1σ, 5 seconds) 0.3 pptv (1σ, 60 seconds) 19 %</td>
</tr>
<tr>
<td>Suhail et al. (2019)</td>
<td>99.95 % @ 660 nm</td>
<td>36 pptv (N/A, 600 seconds)</td>
<td>- N/A</td>
</tr>
<tr>
<td>Wang and Lu (2019)</td>
<td>99.985 % @ 662 nm</td>
<td>3.0 pptv (2σ, 30 seconds)</td>
<td>- 11–15 %</td>
</tr>
<tr>
<td>Fouqueau et al. (2020)</td>
<td>99.974 % @ 662 nm</td>
<td>6 pptv (N/A, 10 seconds)</td>
<td>- 9 %</td>
</tr>
<tr>
<td>This work</td>
<td>99.9995 % @ 662 nm</td>
<td>1.41 pptv (1σ, 1 second)</td>
<td>0.60 pptv (1σ, 5 seconds) - 10.8 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.15 pptv (1σ, 60 seconds)</td>
</tr>
</tbody>
</table>

*: Estimated detection limits from Allan deviation plot readings
Reference


