Response to Referee # *2*

All of the line numbers refer to Manuscript ID: amt-2020-520.

We thank the referee's valuable comments and sugestions, we response the comments points to points, revised the manuscript carefully, and polished the language throughout the manuscript. As detailed below, the referee's comments are shown as italicized font, our response is in orange, new or modified text is in blue.

Summary: The authors present a new thermal dissociation cavity enhanced absorption spectrometer (TD-CEAS) for measurement of NO_2, peroxy nitrates (PNs), and alkyl nitrates (ANs). They demonstrate, through lab tests and box model simulations, that interferences can be corrected for, and that the instrument outputs accurate measurements when compared to a chemiluminescence detector. Finally, results from a measurement campaign in Chengdu, China are presented, demonstrating its effectiveness in ambient conditions.

In general, this manuscript successfully demonstrates the performance of this new instrument, carefully considering the difficulties in converting PNs and ANs to NO_2 in a thermal dissociation oven. There are some significant grammatical/English errors throughout the manuscript, which in some cases make the details difficult to understand but these can be fixed. I would recommend publication, after the authors address some comments below, as well as editing the English.

Thanks for the referee's positive and constructive comments. In addition to the detailed response to the referee' s comments, we have polished the language of the full text.

General comments:

1. *The authors sometimes refer to the ANs channel, and sometimes to ONs channel, which is confusing. This should be made clear throughout the manuscript that these are different, but related to each other.*

   The name of the 380 °C channel is uniformly named as ANs channel.

2. *Section 3.4 demonstrates that the 180 degree oven is not sufficiently hot enough to prevent recombination of PA and NO_2, with efficiencies ranging from 0.5 to 0.9 at 180 degrees. Are the authors correcting for this incomplete thermal dissociation in the rest of the paper? If so, this should be stated clearly. If not, this seems like a major inaccuracy of the measurement and should be addressed. Figure 9 makes it look like it isn't being made, since the intercept at x = 0 doesn't match what the legend says the input PAN concentration is.*

   In this secton, we showed that the thermal dissociation efficiency can be affected by the wall loss of PA and the level of PAN source in the 180 degree channel. This effect of incomplete pyrolysis of PAN has been well considered in the look-up table, and applied in the field campaign. The results showed in Figure 9 and 10 were not corrected, since the box simulation results shown in Fig.9 and Fig.10 were to reproduce the difference of measured NO_2 between two channels.

The text in Sect. 3.4 is revised as follows: "…In addition, the interference of incomplete dissociation for PAN in the PNs channel at 180 ℃ is considered in the look-up table for correction, which is detailed in Sect. 4.1. "

3. *The authors should more clearly demonstrate how they convert the measured α(λ) to [NO_2]. Perhaps another equation would be helpful here in section 3.3, demonstrating that it is a linear fit of all the possible gas-phase absorbers in that wavelength region.*

   There is a equation in the manuscript shown as Eq.1, so the text is revised as follow: "The measured absorption coefficient (α) is processed by the DOASIS (Differential Optical Absorption Spectroscopy Intelligent System) according to Eq.1. "

4. *As the authors state on line 533, sudden changes in the ambient NO_2 while this instrument is measuring from the PNs and ANs would pose a significant problem. Probably this instrument is only useful when a simultaneous measurement of NO_2 is available. Most field campaigns do have NO_2 measurements, so this likely isn't a major issue, but the authors should address it anyway.*

   We agree with the comment. In generally, adding another NO_2-CEAS in parallel in our system for NO_2 mesurement would greatly helpful for the detection of ANs and PNs.

   The Sect. 5 is revised as follow: "However, when the ambient NO_2 in the sampled air masses changes drastically, there will be great errors for the measurement of ANs and PNs, as the NO_2 mixing ratio between adjacent measurement phases in a cycle will be definitely different. Adding another NO_2-CEAS in parallel in the instrument for continuous NO_2 measurement will avoid this limitation. "

5. *Many of the references have titles listed in all capital letters, which should be changed.*

   Corrected accordingly.

Specific comments:

6. *Line 32: "One is peroxy acyl nitrates (PANs)…". The other one is never defined. Is it the peroxy nitrates without an acyl group, as mentioned in line 34?*

   Yes, the text has been modified as follows: "The other is some peroxy nitrates without acyl groups, which are only abundant in cold regions (Roberts, 1990;

Roberts et al., 1998b; Thieser et al., 2016; Wooldridge et al., 2010)."

7. *Line 33: Define PAN here, to differentiate from the more general PANs.*

   The definition of PAN has added in the text as fellows: "…, among which PPN (peroxypropionyl nitrate) and PAN (peroxyacetyl nitrate) dominate PNs with percentages of 75-90% due to their relatively high thermal stability."

8. *Line 46: "with a small branch ratio (1% - 30%)": Which reaction (R3a or R3b) is defined as the one with the 1 – 30% branching ratio, and which is the 70 – 99% reaction?*

   The reaction (R3a) is the one with the 1-30% branching ratio to form ANs. The text has been revised as fellows: "During the daytime, there is a branching reaction between RO_2 and NO to form ANs (R3a) with a small branch ratio (1-30%)…"

9. *Line 75: "the importance of PNs and ANs in regulating ozone formation has not been well studied [in China]": The absence of citations here implies it has not been studied at all, which is not true. Examples include: Liu 2010, Zhang 2014, and Liu 2018. Some citations should be included here.*

   Thanks for the suggestion, the citations have been included in the text as fellows: "Although many studies have examined the effect of PNs and ANs on regulating ozone formation (Chen et al., 2018; Ling et al., 2016; Liu et al., 2018; Liu et al., 2012; Liu et al., 2010; Zeng et al., 2019; Zhang et al., 2014), but the issue has not been well studied."

10. *Line 92: Fig S1 only shows the wavelength range 430 – 460 nm, so this line should be changed to match.*

    Revised accordingly.

11. *Line 151: "… for the ANs and PNs channels are controlled at 180 degrees and 380 degrees, respectively". These numbers appear to be backwards, as the ANs channel was at 380, not 180 degrees.*

    Yes, corrected as accordingly: "…, the heated temperatures for the ANs and PNs channels are controlled at 380 °C and 180 °C, respectively."

12. *Line 154: Presumably the solenoid valves are made of stainless steel? Do the authors expect any NO_2 losses on this steel?*

    Yes, the solenoid values are made of stainless steel. However, there are cooling lines after the quarz tube in heated channels, the temperature of the air flow has returned to ambient temperature, so the wall loss of NO_2 is expected to be negligible as previous tests have demonstrated (Fuchs et al., 2009; Osthoff et al., 2006).

13. *Line 175: Define the MCM, and include a citation.*

    The definition of the MCM and the citation have been added in the text: "…, and the reaction rate of these reactions is mainly taken from the Master Chemical Mechanism, MCM v3.3 (website: http://mcm.leeds.ac.uk/MCM) (Jenkin et al., 1997; Saunders et al., 2003). "

14. *Line 229: "The corresponding fitting residual is in the range of 10 x 10^-9, suggesting the system can guarantee the accuracy…". What is the meaning of this number and why does it imply the system's accuracy? Wouldn't it be better to compare the residuals between the two different fits to demonstrate they are similar in their magnitude?*

    This statement was confusing. An accuracy fitting means that the residual is much smaller than the absorption of absorbers and without special structures of the absorbers. Here we revised the statement as follows: " The corresponding fitting residual, which is the difference between the measured and fitting results, is in the range of 10×10^{-9} at 435-455 nm."

15. *Line 247: Move the "CONC" label to after "One is the differential concentration method" on line 245.*

    Corrected accordingly.

16. *Line 245 – 255: In general, this paragraph is more confusing than it needs to be. You can simply state that there are two methods, one which calculates [NO_2] in each channel from equation (1) using N_2 as I_0, then subtracts [NO_2]_ambient to yield [ANs] and [PNs]. The other method uses I_ambient as I_0 to first derive a corrected $\alpha(\lambda)$, and then uses this to calculate [PNs] and [ANs]. I do not think that equations 3 – 8 are necessary.*

    Thank you for the suggestion, we think the description of this paragraph is detailed, which maybe more friendly for readers who are not in this field to understand it. In order to state more clearly, the statement is revised as follows: " There are two methods to determine the mixing ratio of ONs and PNs. One is the differential concentration method ('CONC'), as shown in Eqs. 3-6, the I_0 is fixed during data analysis by using the N_2 spectrum: I_{TD380} and I_{TD180} are the spectra obtained when the CEAS detects ANs channel and PNs channel, respectively; I_{N_2} is the N_2 spectrum obtained when the cavity is filled with N_2 (>0.99999); α_{TD380} and α_{TD180} are absorption coefficients when setting I_{N_2} as I_0, and setting I_{TD380} or I_{TD180} as I, respectively; and after deleting the abnormal points caused by measurement phase switching, [ONs] is obtained by subtracting $[NO_2]_{TD380}$ from the average of $[NO_2]_{REF}$, and [PNs] is obtained by subtracting $[NO_2]_{TD180}$ from the average of $[NO_2]_{REF}$. The other method is the differential absorption method ('SPEC'), by using the dynamic background spectrum method for spectral fitting (Eqs.7-8): I_{REF} is the spectrum obtained at the reference channel; ONs can be retrieved based on I_{TD380} and I_{REF}; PNs can be retrieved by I_{TD180} and I_{REF}."

17. *Line 254 and elsewhere: The "SPEC" method is often misspelled as "SEPC".*
    Corrected accordingly.

18. *Line 271 – 274: This is helpful information about why two different oven setpoints will yield PNs and ANs separately. It should be moved to earlier in the manuscript, perhaps in the introduction.*
    The line 271-274 are moved to the introduction section.

19. *Lines 282: "platform" should be replaced with "plateau".*
    Corrected accordingly.

20. *Line 345: These interferences of a few percent, while not large, are still non-negligible. Are the measurements being corrected for these interferences? If so, that should be stated clearly.*
    As shown in the manuscript, the interferences for ANs channel and PNs channel are within 3% in a typical case on an ozone pollution day, which is smaller than the uncertainty of NO_2 measuremnts. Therefore, the interference is ignored in the measurement correction.
    The text is revised as follow: " The interferences are within 3% in the typical case, which is smaller than the uncertainty of the NO_2 measuremnts. Therefore, the interference is ignored in the measurement correction."

21. *Line 366: "as described above" should be "as described below"*
    Corrected accordingly.

22. *Line 367: To stay consistent with previous sentence, replace "RO_2" with "PA"*
    Corrected accordingly.

23. *Lines 426 – 441 and equations 9 – 12: This is another example of a paragraph that is much more confusing than it needs to be. It seems that you could just say that to accurately measure ANs, you must first measure PNs in the 180 degree channel, apply a corrective factor based on the first look-up table, then subtract this from*

the raw ANs channel, then apply a second corrective factor based on the second look-up table. The way the authors have written it, with many new parameters such as [PNs_C] is just more confusing.

Thank you for the suggestion. In order to explain the correction more clearly, the text are revised totally as shown in Sect. 4.1 according to the following equations. "…We derived the PNs corrected by C1 and [NO_2_180] as mentioned above. To determine the corrected concentrations of ANs, as Eqs. 10-11 shows, we need to apply another correction factor (C2) to determine the contribution of PNs to ONs, in which this is subtracted from the raw ONs measurement ([NO_2_380]), and finally the third correction factor (C3) is applied to obtain corrected ANs measurements. …"

$$[\text{PNs\_real}] = [\text{NO}_2\text{\_180}] \times C1 \tag{9}$$

$$[\text{NO}_2\text{\_380}] = \frac{[\text{PNs\_real}]}{C2} + \frac{[\text{ANs\_real}]}{C3} \tag{10}$$

$$[\text{ANs\_real}] = \left([\text{NO}_2\text{\_380}] - \frac{[\text{PNs\_real}]}{C2}\right) \times C3 \tag{11}$$

24. *Line 472: "… the interference in the heated channels, which should be larger than 8%". Where does this number come from?*

    The number comes from the uncertainty of NO_2 measurement by CEAS as mentioned above.

    The text is revised as follows: "The uncertainty of [ANs] and [PNs] mainly comes from spectral fitting to derive the concentration of NO_2 and the interference correction in heated channels, which should be larger than 9%."

25. *Line 484 – 487: This is repeating how the corrections are made, and was already stated in the previous section, so it doesn't need to be repeated here. Doing so implies that the technique is different here.*

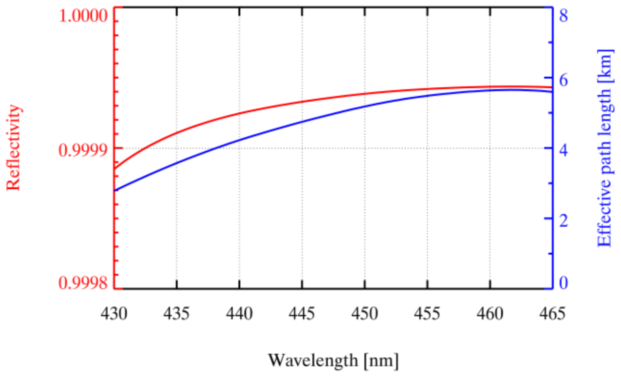
    The text is revised accordingly as fellows: "We determined the raw data of PNs and ONs during the observation period, and then the raw data were corrected as mentioned above. "

26. *Line 535 – 538: These lines are introducing new information to the analysis, and should be included in the results and discussion section instead of the conclusions section.*

    Yes, those new information are included in Sect. 4.3: "However, when the ambient NO_2 changed drastically at night during the campaign, the background NO_2 level (REF channel) between adjacent measurement phases in a cycle was great, resulting in the unfeasible measurements (Fig. S10). The simultaneous measurements show that the N_2O_5 mixing ratio during nighttime is low and zero during the daytime. Therefore, the interferences of the N_2O_5 were negligible for the ONs measurements during the daytime during the CHOOSE campaign. Nevertheless, the observed ANs may be subject to the inferference from $ClNO_2$. ”

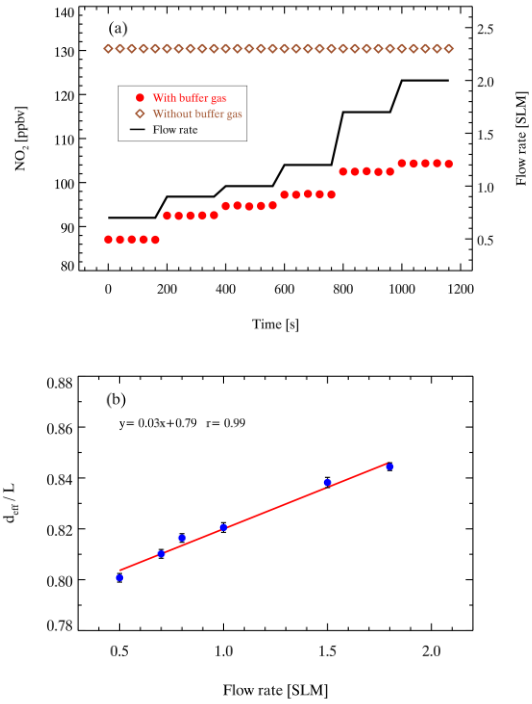
27. *Figure 2: Zoom in on the left-hand axis which shows reflectivity. It is difficult to see the full range of R.*

    Thank you for pointing out the issue. The Figure 2 is revised as fellows.



28. *Figure 3: Why do the authors expect the d_eff / L vs flow rate plot to be linear? A linear fit implies that at the intercept, where flow rate = 0, then d_eff / L will be 0.79, when in fact, d_eff / L should approach 0 as the flow rate decreases to 0. On the other end, as the flow rate gets larger, the d_eff / L will get larger, but will never get to 1 or higher, as a linear fit would imply. It seems that an exponential fit (d_eff / L = A – Be^(C*flow_rate)) would be more appropriate.*

    Thank you for the suggestion. The experimental data show that there is likely to be a linear relationship between d_eff/L and flow rate when the latter is in the range of 0.5-1.8 L/min, which is the possible range of the sampling flow for TD-CEAS. However, as you said, an exponential fit maybe be more appropriate if more experimental data, including very low and high flow rate, are available.



29. *Figure 7: The caption states that the orange columns correspond to* HNO_3*, but the legend indicates* $CH_3O_2NO_2$*. Which is correct?*

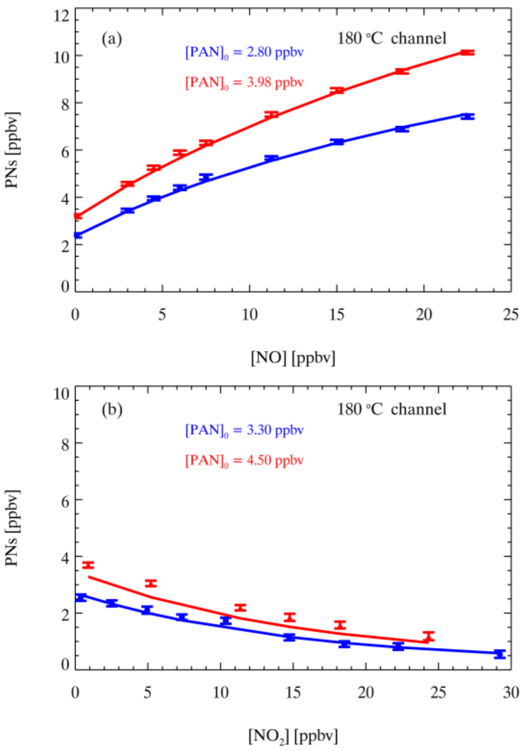
Thank you for pointing out the mistake. The orange columns correspond to $CH_3O_2NO_2$, and the name has been revised in Figure 7.

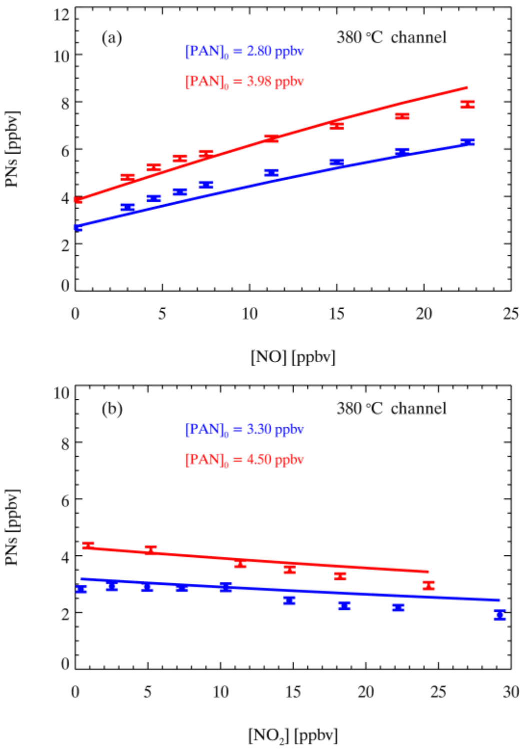
30. *Figure S5: How was this simulated? Was it checked experimentally? How do the authors reconcile this non-uniform temperature profile with their statement on line 152 that "it is assumed that the temperature of the heating part is uniform"?*

We measured the temperature profile of the cooling line after the heated tube (when the distance is greater than 35 cm) by insertion of the thermocouple when the flowing rate is the same value during the sampling, and the temperature profile of the heated tube is simulated according to previous reports (Sobanski et al., 2016; Thieser et al., 2016; Wild et al., 2014). The statement on line 152 that "it is assumed that "temperature of the heating part is ninform" is used to show the limit of the residence time for the air flow. In order to avoid confusing readers, the statement is deleted.

31. *Figure 9: The y-axis label is confusing. Doesn't using the SPEC method mean that the resulting* $[NO_2]$ *is simply [PN], without needing to subtract* $[NO_2]$*_ref?*

The y-axis label renames as 'PNs [ppbv]'. Here 'PNs [ppbv]' is determined by PNs channel and reference channel by the 'SPEC' method.





References.

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