We thank the reviewer for her/his time and effort reviewing this manuscript. All reviewer comments are reproduced below in **_bold, italicized font_**. Our responses are shown in regular font. Changes to the text are indicated as <u>underlined</u> text for insertions or are ~~crossed out~~ for deletions. Line numbers given below are for the revised version with all markups shown. We numbered the reviewer comments for easier cross-referencing.

Anonymous Referee #1

Received and published: 21 May 2018

Taha et al., report an approach to quantifying peroxynitric acid and peroxyacyl nitrates (PNs and PANs) by combining the techniques of differential thermal dissociation (TD), peroxy radical chemical amplification (PERCA) and cavity ring down spectrum for NO2 detection (CRDS), named TD-PERCA-CRDS. The instrument has single channel (on-off mode), duel channel (background NO2, background + amplified NO2) and four channel detection modes (differential temperature measurement). The chemical amplification module is optimized by injecting 0.6 ppm NO and 1.6% C2H6, the chain length (CL) is range from 20 to 70. They found that the measurement was suffered with the ambient O3 interferences by thermal dissociating O3 to O above 150 oC and the following reaction with ethane; the differential temperature TD-PERCA-CRDS at 60110 oC was also unfeasible in ambient due to the unknown interferences in ambient air.

Compared with TD-CRDS /LIF/CAPS, this technique still can't be well performed in field measurement, while the adding of PERCA provide a way to improve the detecting capacity of PNs and PANs to several pptv level. Overall the manuscript is well written and would be of interest and contribute to the community, I recommend this paper to be published on AMT subject to these comments below.

We thank the reviewer for these kind comments.

Major comments:

1. This instrument can calibrate the CL for several PNs or PPN produced in the lab at certain temperature and RH, but the CL is highly varied for different kinds of peroxynitric acid and peroxyacyl nitrates in ambient conditions, which also prevent the application of field measurement.

We agree that the variability of the chain lengths is a challenge and acknowledge that field measurements will require further work before they can become a reality (lines 492): "... the TD-PERCA-CRDS method has several drawbacks, some of which still need to be overcome to make ambient measurements a reality."

However, these are unsurmountable. Variable chain lengths also occur in regular PERCA instruments, and this has not prevented measurement of OH and ΣRO_2 with those instruments. Since the main chain carriers are OH and HO_2, and the chain lengths are large, the variability is not because of the nature of the radical precursor, but rather functions of temperature, humidity, and reagent gas concentrations. As we stated on line 507, frequent calibrations will be a necessity for this reason.

We have not amended the manuscript in response to this comment.

2. Is it possible to carry out the simultaneous measurement of CIMS with the four channel detection measurement in ambient condition to look insight of the unknown species? CIMS measurement might provide some useful information about the unknown interference.

This is an interesting suggestion. With CIMS operated with iodide reagent ion, it is certainly possible to quantify HNO_4, PAN, PPN, etc., and much could be learned from a side-by-side comparison. It could, for example, give insight into the magnitude and time-of-day dependence of the interference.

We have added to the following on line 532:

"Furthermore, such measurements should be complemented by parallel measurements of PNA, PAN and PPN by CIMS."

Specific comments:

1. Line 105, if the majority of the experiments conducted by single-channel TDPERCA-CRDS, the schematic figure of the single channel is worth to be shown in Figure 1.

This schematic is shown in the Electronic Supplementary Material of (Taha et al., 2018), which is subject to copyright. We have therefore chosen not to reproduce it here, but altered to the text on line 105 as follows:

"The majority of the experiments described in this manuscript were conducted using a single-channel TD-PERCA inlet that is described and depicted as Figure S1 of the Electronic Supplementary Material o~~has been described elsewhere~~ (Taha et al., 2018)."

2. Line 45 and line 457: "10s to a few 100s" change to "tens to a few hundreds of".

We have changed the manuscript as requested by the reviewer.

3. Line 228, it is not necessary to set the single sentence to a paragraph.

This has been corrected.

4. The format of tables (1-6) does not conform to the academic norm.

We believe the reviewer is referring to the following instructions (taken from the Manuscript preparation guidelines for authors) on the AMT web site:

"Horizontal lines should normally only appear above and below the table, and as a separator between the head and the main body of the table. Vertical lines must be avoided."

We have amended the table borders as per the above instructions.

5. Section 3.5.2, suggest the authors unify all the units to be pptv.

We have changed the manuscript as suggested by the reviewer.

6. Line 893 the legend in Figure 7. (A): "Legend Sample time series of PNA observed by TD-PERCA-CRDS in the reference, NO2 channel (shown in green) and PERCA channel (grey)." is not consist with the description in line 274, please correct it.

We apologize - the colors were reversed in Figure 7A. NO_2 is now shown in green, and the heated channel in ash (aka grey) colour, consistent with the main text (lines 275-280) and the caption of Figure 7A.

7. Is figure 8(A) only show part of the data presented in figure 7(A), as we can see the maximum NO2 in figure 7(A) was about 20 ppbv while in figure 8(A) the maximum was only 16 ppbv. The authors should clarify it.

Figure 8A was set to <0.6 ppbv on the x-axis and <16 ppbv on the y axis, as this was the linear dynamic range. We updated the figure to show the entire concentration range and also moved the result of the linear fits (slope, intercept and r^2) to the figure caption for clarity.

8. Figure 10 shows the CL dependence on the radical concentration (PAN, PPN and PNA), the PNA seems decreasing with the increasing of PNA concentration, and in line 320-335, no text gave the description or explanation about PNA dependence, I suggest adding some words to describe the CL dependence on the PNA concentration.

We agree with the reviewer that the PNA data in Figure 10 at first glance look as if they decrease with concentration. However, looks are deceiving in this case since this trend falls within the scatter of the individual measurements, and Figure 8A clearly shows the absence of a concentration dependence. The main chain carriers are identical (HO_2 and OH) for PAN and PNA, such that one would expect the dynamic range for PNA to be the same as that for PAN or PPN, so PNA does not need to be discussed separately.

We modified a sentence on line 324 to make this clearer:

"It is well known in the PERCA community that the chain lengths decrease at high radical concentrations due to radical-radical reactions. Figures 8A and 8B demonstrate that the response of TD-PERCA-CRDS is linear for both PNA and PAN/PPN at low, atmospherically relevant mixing ratios (i.e., below ~600 pptv). The linear dynamic range is similar for PNA and PAN and PPN since the radical chain carriers are the same for both."

9. I suggest the authors summarizing the existed TD techniques that applied in the field measurement of peroxynitric acid or peroxyacyl nitrates, which offers convenience to the readers and contributes to the community.

We have added a Table summarizing TD techniques on line 783 as requested by the reviewer.

Table 2. Selected thermal dissociation methods for quantification of daytime NO_y species.

Species quantified	NO_2 detection method	Group	Reference
NO_2, ΣPAN, ΣAN, HNO_3	LIF	Berkeley	(Day et al., 2002)
ΣPN	LIF	Berkeley	(Murphy et al., 2004)
HONO	CL	Berkeley	(Perez et al., 2007)
NO_2, ΣPAN, ΣAN	CRDS	Calgary	(Paul et al., 2009)
Aerosol nitrates	LIF	Berkeley	(Rollins et al., 2010)
$ClNO_2$	CRDS	Calgary	(Thaler et al., 2011)
NO_2, ΣPAN, ΣAN, HNO_3	LIF	L'Aquila	(Di Carlo et al., 2013)
NO, NO_2, HONO, NO_y, ammonium nitrate	CRDS	NOAA	(Wild et al., 2014; Womack et al., 2017)
NO_2, ΣPAN, ΣAN	CRDS	Max-Planck-Institut	(Thieser et al., 2016)
NO_2, ΣPAN, ΣAN	CAPS	Osaka	(Sadanaga et al., 2016)
NO_2, RNO_2	CRDS	Hefei	(Chen et al., 2017b)
ΣPN, ΣPAN	PERCA-CRDS	Calgary	this work