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 underlined 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 #2

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This paper describes laboratory characterization of a new method for quantifying peroxynitric acid (PNA) and peroxyacyl nitrates. Overall the article is well written and describes important results and I recommend publication after the mostly minor issues below are addressed.

We also thank reviewer #2 for this assessment.

Line 79: "The measurement of peroxy radicals by PERCA is prone to interferences", but the text proceeds to discuss that the amplification must be determined by calibrations and that it varies with relative humidities. These are not interferences! Later in the text an actual interference by ozone for TD-PERCA_CRDS is well described .... But variation of calibration factor with RH is not an interference.

The reviewer is correct, of course. We modified the text on line 79 as follows:

"The measurement of peroxy radicals by PERCA is prone to matrix effects and interferences. For instance, a key operational parameter of any PERCA instrument is the radical chain length or amplification factor (CL), ..."

Same for 89: replace "interference" with "disadvantage" or "property"?

The thermal decomposition of PAN produces radicals and interferes in the measurement of ROx radicals by PERCA, so we believe that the word "interference" is used correctly in this context.

We modified the text on line 87 to improve its clarity:

"... apply heat. When quantification of ambient RO_x radicals is the goal, this is avoided to prevent TD of ΣPN or ΣPAN (which are more abundant than free RO_x radicals). TD of ΣPN or ΣPAN produces radicals that ~~as these molecules would~~ interfere with the measurement of free RO_x radicals (Mihele and Hastie, 2000). On the other hand, if measurement of ΣPN or ΣPAN is desired (such as in this paper), this interference is turned into a measurement principle. "

Ling 143 – "Teflon" – what kind – PFA? PTFE?

It is FEP. We inserted "fluorinated ethylene propylene (FEP)" prior to Teflon on line 145.

Section 2.3.2 – clarify that the concentration of PNA is determined by the NO2 mixing ratio, correct? Ie, NO2 is the limiting reagent and HO2 is in excess.

The mixing ratio of HO_2NO_2 delivered by this source was quantified by TD-CRDS (i.e., the difference in $[NO_2]$ between the heated and room temperature channel.

We added the following sentence on line 194:

"The amount of PNA delivered from this source was quantified by TD-CRDS."

Line 190-191 – O2 is not readily photolyzed to form O3 by 254 nm – replace with "...generated by photolysis of O2 by 185 nm radiation from a low-pressure mercury lamp"?

We used a 254 nm lamp as stated in the text - both the 254 and 185 nm version will photo-dissociate O2. The 185 nm one generates way too much O_3 for our particular application, however.

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

Box model simulations (in SI) The SI discusses formation of C2H5ONO and C2H5O2NO2, but what about the temperature dependence of C2H5ONO2? That is, ethyl nitrate, formed by C2H5O2 + NO.

The reviewer is referring to section S1.4, where we discuss molecules whose formation is not included in the MCM. Formation of ethyl nitrate is included in the MCM and did not need to be discussed in this section.

For $C_2H_5O_2 + NO \rightarrow C_2H_5ONO_2$, the MCM rate expression is $2.25\times10^{-14}\times e^{(380/T)}$, i.e., the reaction has a negative activation energy and slows down at higher temperatures. The branching ratio (relative to $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$) is 0.9%, which implies that this reaction is an important radical sink especially at higher chain lengths (in the simulations, anyhow).

However, a general problem with using the MCM to simulate TD-PERCA chamber kinetics is that rate constant expressions in the MCM are for atmospheric temperature regimes, i.e., < 300 K. We acknowledged this limitation in section S1.0 "An additional limitation~~s~~ is that the MCM has only been validated at ambient temperature and below, and the rate constants are more uncertain at elevated temperatures."

We agree with the reviewer that the temperature dependence of ethyl nitrate formation may perhaps be worth another look at. However, given that this would be speculation only, we have chosen not to wade into this discussion and have not altered the manuscript in response to this comment.

Section 3.2 and figure 5. This is overall very good demonstration of the technique. It is a bit confusing that, apparently, both the inlet heater and PERCA chamber can be heated separately. This should be more explicitly pointed out in the earlier experimental sections.

The reviewer is correct that we can apply heat to two separate inlet sections.

We added the following on line 117:

"The remaining two channels were equipped with heated quartz tubes to monitor NO_2 + ΣPAN and NO_2 + ΣPAN + total alkyl nitrates (ΣAN) (Paul et al., 2009)."

and modified the text in section 3.2 (lines 234-241) as follows:

"A time series demonstrating amplification of PAN and PPN in the TD-PERCA-CRDS ~~operated with its inlet at 250 °~~C is shown in Figure 5. In this experiment, PAN and PPN were delivered via the preparatory-scale GC (Figure 2), and the single-channel setup (section 2.1.1) was used.

PAN and PPN eluted from the GC column after 3 min and 6 min, respectively. The compounds eluted as plateaus because of the relatively long (~30 s) injection time. In Figure 5A, PAN and PPN are observed only by the heated (NO_2+ ΣPAN) TD-CRDS channel. This channel was operated with its quartz inlet at 250 °C ~~where they~~ to quantitatively (see Figure 5 of (Paul et al., 2009)) decompose PAN and PPN to NO_2 ~~at~~. In this example, mixing ratios of 2.00±0.09 ppbv and 1.86±0.12 ppbv were observed, respectively (errors are 1 σ of 1 s data)."

Ling 281: the text in the parenthesis, though likely true, makes the sentence awkward to read

We agree and have removed the text in the parenthesis.

Section 3.5: interestingly the amplification factor for PNA (yielding HO2) is less than that for PAN (which forms CH3CO3). The following sections address details of the chain length with T, RH, but is there is a conclusion for why the PNA vs. PAN results are so different?

Yes, the amplification factor itself is temperature dependent. An entire section of text (section 3.5.3) is devoted to this. Specifically, line 350-353 state that "It is obvious from Figure 11 that the amplification factor is strongly dependent on temperature: Even though PNA fully dissociates at temperatures > ~90 °C in our inlets (Figure 4), the amplified signal increases by ~60% in the region from 90 °C to 135 °C (Figure 11, insert), corresponding to amplification factors of ~15 and ~22, respectively. This increase is qualitatively consistent (if extrapolated) with the higher amplification factor observed with PAN or PPN at 250 °C."

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

Line 309: ": : :operated under optimal conditions and : : :" – this assumes that the optimal conditions do not change under varying circumstances. Might it be possible that the optimum NO or ethane concentrations are different at different temperatures or RH values?

It's possible, though we don't believe that the optimum concentrations would change by much. However, since we didn't re-optimize at every RH and temperature, the reviewer has a point that we cannot claim that that TD-CRDS was operated optimally throughout. What we tried to say was that NO and ethane concentrations were constant in these experiments; these mixing ratios are stated in the caption of Figure 9.

We have modified the text on line 312 as follows:

"... the RH dependence was investigated systematically at constant NO and ethane concentrations ~~with TD-PERCA-CRDS operated under optimal conditions and with PAN and PPN at 250 °C inlet temperature~~. The results are summarized in Figure 9."

Section 3.7.2: The observed interferences are very interesting, and are likely relevant not only to TD-PERCA-CRDS but also to non-amplified thermal dissociation methods, e.g. TD-LIF.

This is conceivable, but unlikely. The ethane-PERCA will amplify any molecule that generates trace levels OH, HO_2, RO_2, RO, or O when heated; in un-amplified TD, concentrations of these radicals are likely too small to have much impact. The only exception is, perhaps, O_3, which generates O, that can react with NO_2 to NO and O_2. Ron Cohen's group is aware of this: In Atmos. Chem. Phys., 14, 12441-12454, 10.5194/acp-14-12441-2014, 2014, Appendix A, Lee et al. discuss the impacts of O3 pyrolysis in their system.

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

Section 3.8, discussion of detection limit. Some of the terms here are confusing.

1. Do the authors actually mean precision when they have written LOD? LOD needs to be defined – is it for signal to noise ratio of 2? Or 3? The LOD is quoted as 87 ppt (1 sigma, 1 sec), but this seems much more like a description of the precision, not the LOD (ie, 1 sigma for precision, signal to noise ratio for LOD).

We agree with the reviewer that this section requires a few clarification.

Detection limit is defined by the International Union of Pure and Applied Chemistry (IUPAC) (https://goldbook.iupac.org/html/L/L03540.html) as follows: "The limit of detection, expressed as the concentration, c_L, or the quantity, q_L, is derived from the smallest measure, x_L, that can be detected with reasonable certainty for a given analytical procedure. The value of x_L is given by the equation

$x_L = \bar{x}_{bi} + k\, s_{bi}$

where $\bar{x}_{bi}$ is the mean of the blank measures, s_{bi} is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired."

In CRDS, $\bar{x}_{bi}$ equals zero, since we subtract the "zero" level from the signal (i.e., $1/\tau_0$ from $1/\tau$). The confidence level for the LOD calculation was stated on lines 25, 445, 446, and 448 as (1 s, 1 σ); from this, it is straightforward to calculate the LOD by multiplying with the k value of one's choice. However, the reviewer is correct that we should have been more careful here since k = 2 or k = 3 are more commonly chosen. In response to the reviewer's comments, we have the changed the definitions on these lines to (1 s, 2 σ) and adjusted all values accordingly.

2. The authors have taken the "LOD" for the CRDS of 87 ppt (1 sigma, 1 s) and divided by the CL of 69 to come up with the LOD for PANs of 1.3 ppt. Realistically, measuring PANs involves measuring NO2 twice in amplification mode and in reference mode (either sequentially in a single channel instrument, or simultaneously with in a multi-channel instrument), so there should probably be another factor of sqrt(2).

Our apologies as we should have stated how the calculation was made. The statistics we stated are based on time series after subtraction of the reference channel, making multiplication by another factor of √2 unnecessary. We inserted the following on line 448:

"... LOD for ΣPAN* (calculated on the basis of observed precision after subtraction of the reference channel signal, multiplying by √2, and dividing this precision by the CL) was ..."

We also noted that the precision can vary slightly between days and detection channels and added the following on line 444:

"The precision of the NO_2 measurement (and hence the LOD) varied slightly between detection channels and from day to day. Typically, w~~W~~hen sampling zero air, the LOD for NO_2 was ~100 pptv~~47 pptv~~ (1 s, 21 σ~~1 σ~~)."

Also, the authors point out that the precision of the CRDS NO2 measurement is affected by the presence of NO and ethane reagent gases. For measurement in ambient air, or laboratory air, what is the precision of measuring NO2?

We have only determined the precision under laboratory conditions and stated on line 445 that "In the presence of NO and ethane reagent gases, the LOD ~~increases to~~was larger, typically ~174 pptv~~87 pptv~~ (1 s, 2 σ~~1 σ~~)."

In ambient air, NO_2 and O_3 concentrations vary naturally; the extent of these fluctuations depend on the measurement location. We use parallel detection channels to keep track of (most of) such changes, but we agree that this could still be a source of additional noise. In addition, there may be noise associated with locating the instrument at a field site, where power, temperature, etc. can fluctuate. We have added the following statement on line 452:

"Under field conditions, where NO, NO_2 and O_3 concentration vary, the LOD is expected to be higher, though this was not evaluated in this work."

The LOD (and precision) for an actual PNs measurement in ambient air would be affected by the precision of the CRDS NO2 measurement at the actual measurement conditions. For example, if O3 is 25 ppb, some portion of the O3 will react with the NO to give up to 25 ppb NO2 – is the precision the same at 0 ppb and 25 ppb? This has likely been addressed in earlier NO2 CRDS papers but should be mentioned for the reader's sake.

Please see our response to the preceding comment.

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Paul, D., Furgeson, A., and Osthoff, H. D.: Measurement of total alkyl and peroxy nitrates by thermal decomposition cavity ring-down spectroscopy, Rev. Sci. Instrum., 80, 114101, 10.1063/1.3258204 2009.
Taha, Y. M., Saowapon, M. T., and Osthoff, H. D.: Detection of triacetone triperoxide by thermal decomposition peroxy radical chemical amplification coupled to cavity ring-down spectroscopy, Anal. Bioanal. Chem., 10.1007/s00216-018-1072-0, 2018.