

**Anonymous Referee #2**

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**General comments:**

This paper describes a new denuding technique that could enable HO<sub>2</sub> and RO<sub>2</sub> radicals to be selectively measured using PERCA. As the authors suggest, the application of such a technique would enhance field PERCA radical measurements considerably. Currently, however, it is not clear from the information provided in the manuscript how applicable this technique will be to field measurements, and so, the following concerns should be addressed before publication is considered:

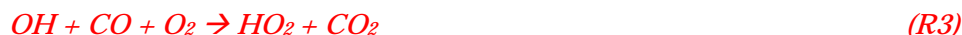
More information on the application of this denuding technique to field measurement is given as follows.

**Specific comments:**

**Pg 3294, line 9, R1:** the method used to make HO<sub>2</sub> radicals will generate equal quantities of OH also. In the presence of 150 pptv of radicals, is there a significant signal contribution from OH? If there is, the removal efficiencies of OH and HO<sub>2</sub> need to be distinguished in these experiments.

CO was added to photolysis gases to convert OH to HO<sub>2</sub> during the removal efficiency measurement for HO<sub>2</sub>. We added some more experimental description as following. Page 3294 line 8 we have added the following sentence:

*By addition of CO, generated OH is converted to HO<sub>2</sub>*



**Pg 3299, Line 18:** The removal efficiency of HO<sub>2</sub> ( $\alpha$ ) has been shown to vary as a function of initial radical concentration and, as shown in Fig. 4, decreases steeply over the typical ambient HO<sub>2</sub> concentration range – at these lower removal efficiencies can you confidently say that HO<sub>2</sub> is selectively removed relative to RO<sub>2</sub> (at the lower concentrations  $\alpha \ll \beta$ )?

As Referee#2 indicated, the removal efficiency of HO<sub>2</sub> ( $\alpha$ ) decreases steeply over the typical ambient HO<sub>2</sub> concentration range.

In this experiment, removal efficiency was set to approximately 90% for HO<sub>2</sub> radicals at around the HO<sub>2</sub> concentration of 150 ppt for easy comparison. However, some improvement is necessary for the observation under ambient HO<sub>2</sub> concentrations as Referee#2 has indicated. For example, if this HO<sub>2</sub> loss reaction occurs through bimolecular reaction on the surface, relatively high removal efficiency for HO<sub>2</sub> even under ambient concentration range can be obtained by increasing the residence time or controlling the surface temperature. Some optimization is necessary for the

ambient measurement with high precision.

As discussed below, LOD for each HO<sub>2</sub> and RO<sub>2</sub> measurement was calculated to be 4 ppt in dry condition considering the removal efficiency for HO<sub>2</sub> and RO<sub>2</sub> under this experimental condition. This performance is applicable for the observation in high peroxy radicals concentration, e.g. in summer season.

Page 3300 line 1 we have added the following sentence:

*In this experiment, the geometry of the removal cell was designed to achieve a removal efficiency of approximately 90% for HO<sub>2</sub> radicals at HO<sub>2</sub> concentrations of ~150ppt, allowing for an easy comparison. However, some improvement is necessary for observations under ambient HO<sub>2</sub> concentrations because the removal efficiency for HO<sub>2</sub> decreases steeply over the typical ambient HO<sub>2</sub> concentration range. If the HO<sub>2</sub> loss reaction occurs through bimolecular reaction on the surface, relatively high removal efficiency for HO<sub>2</sub> even under the ambient concentration range can be obtained by increasing the residence time or controlling the surface temperature. Some optimization is necessary for ambient measurements to be made with high precision.*

*As discussed above, the LOD for HO<sub>2</sub> and RO<sub>2</sub> measurements was calculated to be 4 ppt in dry conditions considering the removal efficiencies for HO<sub>2</sub> and RO<sub>2</sub> under experimental conditions. This performance could be applicable to observations at high peroxy radicals concentration, e.g. in summer and low organic complexity environments e.g. marine boundary layer.*

Does the removal efficiency of RO<sub>2</sub> ( $\beta$ ) also depend upon the initial [RO<sub>2</sub>]? If this is the case, an additional figure showing the removal efficiency ( $\beta$ ) vs RO<sub>2</sub> is needed –

No. The constant removal efficiency of CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub> was obtained at a concentration of ~150ppt. Page 3299 line 25 we have added the following sentence:

*On the other hand, constant removal efficiency for CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub> was obtained at a concentration of ~150ppt.*

would this be dependent upon the specific RO<sub>2</sub> radicals present?

No. Some test shows that removal efficiency for HO<sub>2</sub> does not depend on the presence of RO<sub>2</sub> radicals.

C<sub>2</sub>H<sub>6</sub> was added to photolysis gas instead of CO generating HO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> radicals by the same concentrations. The LIF signal obtained through this experiment was consistent with calculated LIF signal using separately pre-measured removal efficiency for HO<sub>2</sub> and RO<sub>2</sub>. Page 3300 line 1 we have added the following sentence:

*Some test shows that removal efficiency for HO<sub>2</sub> does not depend on the presence of RO<sub>2</sub> radicals. C<sub>2</sub>H<sub>6</sub> was added to photolysis gas instead of CO generating HO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> radicals by the same concentrations. The LIF signal obtained through this experiment was consistent with calculated LIF*

signal using separately pre-measured removal efficiency for HO<sub>2</sub> and RO<sub>2</sub>.

**Page 3300, eqns 8 & 9:** It isn't clear how ambient [HO<sub>2</sub>] and [RO<sub>2</sub>] are determined using equations 8 & 9 alone as there seems to be too many unknowns (α[HO<sub>2</sub>], β[RO<sub>2</sub>], [HO<sub>2</sub>], [RO<sub>2</sub>]). It should be demonstrated explicitly how ambient [HO<sub>2</sub>] and [RO<sub>2</sub>] can be determined.

As mentioned above, the constant removal efficiency of CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub> can be obtained at a concentration of ~150ppt. According to this result, Eq6, 7, 8 and 9 can be revised as follows:

$$S_{\text{HO}_2}[\text{HO}_2] + S_{\text{RO}_2}[\text{RO}_2] = \frac{I_{\text{blank}}}{C_{\text{humid}}}, \quad (6)$$

$$(1 - \alpha_{[\text{HO}_2]})S_{\text{HO}_2}[\text{HO}_2] + (1 - \beta)S_{\text{RO}_2}[\text{RO}_2] = \frac{I_{\text{removal}}}{C_{\text{humid}}}, \quad (7)$$

Then we can get each concentration of HO<sub>2</sub> and RO<sub>2</sub> as follows:

$$[\text{HO}_2] = \frac{(1 - \beta)I_{\text{blank}} - I_{\text{removal}}}{(\alpha_{[\text{HO}_2]} - \beta)S_{\text{HO}_2}C_{\text{humid}}}, \quad (8)$$

$$[\text{RO}_2] = \frac{(1 - \alpha_{[\text{HO}_2]})I_{\text{blank}} - I_{\text{removal}}}{(\beta - \alpha_{[\text{HO}_2]})S_{\text{RO}_2}C_{\text{humid}}}. \quad (9)$$

A full propagation of errors should also be shown for these analyses and the uncertainty associated with a typical ambient radical concentration measurement should be stated.

As mentioned above, some optimization of this instrument is necessary for ambient measurement.

Under this experiment condition, LOD for each HO<sub>2</sub> and RO<sub>2</sub> measurement was calculated to be 4 ppt in dry condition considering the removal efficiency for HO<sub>2</sub> and RO<sub>2</sub>.

Page 3300 line 1 we have added the following sentence:

*As discussed above, the LOD for each HO<sub>2</sub> and RO<sub>2</sub> measurement was calculated to be 4 ppt in dry conditions considering the removal efficiencies for HO<sub>2</sub> and RO<sub>2</sub> under experimental conditions. This performance could be applicable for observations at relatively high peroxy radical concentrations, e.g. in summer and low organic complexity environments e.g. marine boundary layer and low organic complexity environments e.g. marine boundary layer.*

**Minor comments:**

Pg 3293, line 2: Provide an appropriate reference for the PERCA technique

As Referee#1 suggested, a reference of the original PERCA work of Cantrell and Stedman was added to revised manuscript. Page 3293 line 1 we have added the following sentence:

*originated by Cantrell and Stedman [Cantrell and Stedman., 1982]*

Pg 3293, lines 2 – 5: Description of the PERCA technique should be re-phrased for clarity

As Referee#1 suggested, description of PERCA was re-phrased as revised manuscript.

Page 3293 line 2 we have added the following sentence:

*peroxy radicals are converted to high concentrations of NO<sub>2</sub> via a chain reaction by the addition of high concentrations of NO and CO in a reaction tube*

Pg 3293, line 6: suggest change 'method' for 'technique' – also provide examples of NO<sub>2</sub> detection techniques

As Referee#1 suggested, 'method' was changed to technique. Also, we added NO<sub>2</sub> detection technique ever used for PERCA. Page 3293 line 5 we have added the following sentence:

*The NO<sub>2</sub> product is then quantified by the appropriate measurement technique, e.g. luminol chemiluminescence [Alex et al., 2009], laser-induced fluorescence [Sadanaga et al., 2004] and cavity-ring-down [Liu et al., 2009] technique.*

Pg 3293, lines 6 – 8: suggest reorganisation of sentence 'In order to obtain absolute concentrations, the chain length of the amplification and the response of the NO<sub>2</sub> detector has to be determined in calibration experiments.'

Pg 3294, line 2: remove 'as described'

Pg 3295, line 18: change 'up' to 'down'

Suggested sentence and correction were adopted.

Pg 3296, line 16, eqn. 1: I would expect the laser energy to be outside the square-root? Please amend and update LOD estimate accordingly.

No. Laser energy is inside square root when the photon detection event follows the Poisson distribution and background signal is governed by laser scattered light.

Pg 3296, line 19: suggest SBG = background 'signal' rather than 'sensitivity'?

Suggested sentence was adopted.

Pg 3296, line 26: where was O<sub>3</sub> measured? Please highlight in Fig. 1.

O<sub>3</sub> concentration was measured at the exit of peroxy radical generator by changing the inlet tube.

The point was described in revised Fig. 1

Also, page 3296 line 26 we have added the following sentence:

*O<sub>3</sub> concentration was measured by an ozone monitor (Dylec, Model 1100) at the exit of peroxy radical generator by changing the inlet tube.*

Pg 3298, line 10: where was the H<sub>2</sub>O added to test  $\alpha$  and  $\beta$  as a function of humidity? After the radical generation point?

As described in Pg 3294 line 21 and Fig.1, humidified air was added to flow at the exit of the radical generator.

For easy understanding, page 3294 line 25 we have added the following sentence:

*In order to investigate the water dependence of the peroxy radical removal efficiency, varying quantities of dry air and humidified air (the air is humidified by passing it through a water bubbler) were mixed allowing air of varying relative humidity to be added to the flow at the exit of the radical generator as shown in Fig.1.*

Pg 3299, line 21: replace 'when getting to low radical concentration' with 'over ambient HO<sub>2</sub> concentration range'

Suggested sentence and correction were adopted.

Pg 3300, line 6, eqn 7: replace ' $\beta$ [CH<sub>3</sub>O]' with ' $\beta$ [RO<sub>2</sub>]'

As mentioned above, removal efficiency for RO<sub>2</sub> ( $\beta$ ) was not function of its concentration. So,  $\beta$ [CH<sub>3</sub>O] can be changed to  $\beta$ . All of  $\beta$ [RO<sub>2</sub>] was revised to  $\beta$ .

Pg 3301, section 4 – Conclusions: This section should be revisited once the specific comments above have been addressed – particularly this work needs to be able to conclude that this denuding technique will be applicable for field measurements otherwise the paper becomes redundant.

Considering for discussions as above, we revised the conclusion as follows:

*An improvement to the well-established PERCA technique allowing the selective measurement of HO<sub>2</sub> and RO<sub>2</sub> radical concentrations has been described in this paper. Advantage is taken of different heterogeneous removal efficiencies for HO<sub>2</sub> and RO<sub>2</sub> radicals prior to the inlet of the PERCA reaction cell. Three different materials have been tested to investigate the variation of the removal efficiency as a function of relative humidity. From these results, glass has been found to be best suited as the material for the removal cell as it shows very low dependence on relative humidity, the difference of removal efficiency seems to be linked to the surface structure. The removal cell filled with glass showed about 90 % removal efficiency of HO<sub>2</sub> over the entire relative humidity range, compared to only 15 % removal efficiency of CH<sub>3</sub>O<sub>2</sub>. The investigation of the dependence of the removal efficiency on the concentration at a given relative humidity has been tested for HO<sub>2</sub>*

radicals on glass and PFA as filling material. Both materials show a pronounced dependence on the concentration, i.e. the removal efficiency decreases steeply at low initial radical concentrations, probably due to the removal mechanism. On the other hand, the constant removal efficiency for  $\text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  was obtained at a concentration of  $\sim 150\text{ppt}$ . Again, glass seems to be the more suited material, as it does not show any dependence on the relative humidity. However, this characteristic needs to be carefully investigated and improved to get high removal efficiency for  $\text{HO}_2$  over ambient  $\text{HO}_2$  concentration range before applying this technique to atmospheric measurements. LOD for each  $\text{HO}_2$  and  $\text{RO}_2$  measurement was calculated to be 4 ppt in dry condition considering the removal efficiency for  $\text{HO}_2$  and  $\text{RO}_2$  under experimental condition. This performance could be applicable for the observation in high peroxy radicals concentration, e.g. in summer and low organic complexity environments e.g. marine boundary layer.

The results presented in this work are promising and indicate the possibility of selective measurement of peroxy radicals. It has been shown that the concentrations of  $\text{HO}_2$  and  $\text{RO}_2$  can be independently corrected by separate sensitivities of  $S_{\text{HO}_2}$  and  $S_{\text{RO}_2}$ . Clearly, there is more work needed in order to generalise these observations to other types of  $\text{RO}_2$ , but we think that this technique has the potential of increasing the precision of atmospheric peroxy radical measurements in the future.

Figure 2(a): why is the BG mode LIF signal higher through the blank cell compared to the BG mode signal in the removal cell for  $\text{HO}_2$ ?

The signal of BG mode in the removal cell for both  $\text{HO}_2$  and  $\text{RO}_2$  is lower than that in the blank cell. We think it might be caused by the removal of  $\text{O}_3$  in the removal cell, but it was not confirmed.