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Response to Interactive comment on "Peroxy radical detection for airborne atmospheric measurements using cavity enhanced absorption spectroscopy of NO_2" from Anonymous Referee 2

Received and published: 4. December 2013

M. Horstjann et al.

We'd like to thank both reviewers for their contribution to help us improve this publication. Addressing their comments, both the introduction and results chapters have been partly rewritten, and new measurement results have been introduced. Below are our answers to the specific comments (in bold); text cited from the revised publication is in italics.

Review of "Peroxy radical detection for airborne atmospheric measurements using cavity enhanced absorption spectroscopy of NO_2" by Horstjann et al.
This paper describes a technique to measure the sum of peroxy radicals using chemical amplification with NO and CO, and detection of the NO_2 product with cavity ring-down spectroscopy. The method builds on other chemical amplifier approaches in which various NO_2 detection schemes have been used, although most have used luminol chemiluminescence. As the authors point out, luminol chemiluminescence detection, while fairly sensitive, has drawbacks. The new detection scheme is described in quite a bit of detail, which is appropriate since that is the main difference from previous instruments. The approach described thus adds a new variant for peroxy radical detection. The paper is fairly well written with appropriate level of detail. Most of the figures are appropriate and relevant. I believe the paper should be published after the authors consider some suggestions for changes.
General comments.
When an analytical technique is presented in a scientific paper, I believe it is important to describe in detail the uncertainties in the measured quantity. This includes propagation of errors, which involves estimates of random and systematic uncertainties, and a clear description of the confidence intervals of the stated uncertainties. Within the paper, there are several uncertainties given, but rarely is it stated whether these correspond to $1\sigma, 95\%$ confidence interval or other interval, and whether they correspond to total uncertainties or just random variations of observed signals. Because of the lack of propagation of errors analysis being presented, some uncertainties are not addressed. An example is the absorption cross section of NO_2, but there are other uncertainties that should be stated and included in the presentation of uncertainties.
We have added a more detailed description about the NO_2 absorption cross section and added a reference measurement showing its verification. Information about the uncertainties has been added to all instances noted by this reviewer.
—

The presentation would be more exciting if the detection limit/measurement uncertainty/time response for NO_2 was significantly better than other approaches. If I understand the factors presented, the performance appears comparable to other methods. The main advantage appears to be the lack of humidity dependence as compared to luminol chemiluminescence.
This comment was addressed below in more detail. Regarding the comparable sensitivity of luminol chemiluminescence and CRDS detection, the following statement has been added to the introduction:
The use of an optical method to detect NO_2 *presents some clear advantages. Optical detection of* NO_2 *is chemically specific, does not require a constant addition of* NO_2 *to assure detector signal linearity, and is not affected by* NO *which is added to the sampled air. These benefits provide greater freedom in selecting measurement conditions maximizing conversion and amplification parameters (e.g. increasing* NO *mixing ratios in the reactor for improving the chemical conversion without deteriorating detection sensitivity). Furthermore, the decrease of the sensitivity of the luminol detection at lower pressures limits its use for measurements in the upper layers of the troposphere.*
Regarding the question about improving the set-up (second to last comment), we're presently working on reducing the laser noise which at present dominates the ring-down time variations.
—

The instrument appears to be a two channel instrument (with two chemical reactors and two NO_2 detectors), but this is not clearly stated. The advantages of a two channel approach are also not discussed, even briefly, as presented in other papers in the literature (including the Bremen group).
We are grateful the reviewer mentioned this as it is indeed mentioned nowhere but only implicitly stated in the results chapter. We have amended the introduction:
For the determination of the peroxy radical concentrations, the PeRCA technique usually operates alternatingly between a so called "amplification mode" (CO *is added, so the chain reaction takes place) and a "background mode" (where* CO *is replaced with* N_2*, suppressing the chain reaction).*
Also, in the chapter "Experimental", the following sentence has been added:
The availability of two parallel sampling lines increase the instrument's reliability and allows continuous monitoring of the NO_2 *background and its short-term variations.*
—

The plots of instrument signal should also then present two signals, one for each channel. It is very surprising that two chemical reactors cannot be built with the same chain length, although if they are stable and known, signals can be

corrected. Perhaps more laboratory work should have been done in this area.
An $eCL_{\mathrm{HO_2}}$ calibration for both reactors is now shown in the graph.
According to our experience there are always differences in the eCL of the individual reactors which we attribute - as stated in the text - to unavoidable mechanical differences during their construction and coatings. However, as the eCL values are calibrated separately and assuming that those of the individual reactors have a good reproducibility (which was now confirmed as stated in the results chapter), differences in the absolute values play no critical role.

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The production of $\mathbf{NO_2}$ by ambient ozone is not mentioned.
The $\mathrm{NO_2}$ production by ozone is briefly mentioned in the introduction:
The background concentration $[\mathrm{NO_2}]_{ambient}$ *is enhanced both by species reacting with* NO *(e.g. ozone) or by being (thermally) decomposed in the inlet (e.g. PAN).*

—

This is one of the difficulties of this chemical amplifier approach – that the radical signal is measured on top of a fairly large background due to ozone. This also means that detection limits measured with no $\mathbf{NO_2}$ present are not that meaningful. The noise on a $50\,\mathrm{ppbv}$ signal are more indicative of that which determines the peroxy radical detection limit. I suggest some more experiments to complement the measurement uncertainty discussion on page 4.
We have amended both the $\mathrm{NO_2}$ detection limit and Allan statistics to represent the mentioned background conditions. The values are comparable to those of synthetic air background measurements.

—

No ambient data are presented. I think the case for the value of the method would be much stronger if some sample data were shown. The design goals (aircraft speed, altitude, radical levels, polluted or clean atmospheres, etc.) of the instrument should also be briefly presented. While it is stated that it will be deployed on HALO (which should be defined), will the instrument be able to make measurements above the detection limit for the full altitude range of the aircraft (surface to about 50 kft) at least for some photochemical conditions? I expect that levels above about 25 kft, even in summer, will be at or near the instrument detection limit. This is fine – it should just be stated. Suggest using some modeled levels to help with this analysis.
There are only scarce measurements of peroxy radicals in upper layers of the troposphere. According to those we expect values from 5 to $60\,\mathrm{pptv}$ depending on the history of the air mass. The detection limit of PeRCEAS in its present form is on the lower range of the mixing ratios expected.
A text paragraph and a graph were added to clarify the instrument operation during flights with HALO.

—

Specific comments. Abstract, page 1. The detection limit of $\mathbf{NO_2}$ is presented as a mixing ratio and an absolute concentration. I don't see the reason for the later, and suggest it be eliminated.
The concentration information was shifted to the chapter "$\mathrm{NO_2}$ detection limit". The intent for adding this value is to enable comparability with instruments measuring at different pressure levels.

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Introduction, page 1, second column, last paragraph. The acronym CIMS should stand for Chemical Ionization Mass Spectrometry.
Done.

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Page 2, first column, first paragraph. Here, it states that the 3σ detection limit for peroxy radicals using luminol chemiluminescence is $3\,\mathrm{pptv}$, the same as the 1σ detection limit for the present method. This leads the reader to wonder why use the new approach. There is a sentence describing the drawbacks of luminol, but I suggest a bit more discussion of why the new approach is so much better.
The following statement has been added to the introduction:
The use of an optical method to detect $\mathrm{NO_2}$ *presents some clear advantages. Optical detection of* $\mathrm{NO_2}$ *is chemically specific, does not require a constant addition of* $\mathrm{NO_2}$ *to assure detector signal linearity, and is not affected by* NO *which is added to the sampled air. These benefits provide greater freedom in selecting measurement conditions maximizing conversion and amplification parameters (e.g. increasing* NO *mixing ratios in the reactor for improving the chemical conversion without deteriorating detection sensitivity). Furthermore, the decrease of the sensitivity of the luminol detection at lower pressures limits its use for measurements in the upper layers of the troposphere.*

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Several references are given for reports of ground-based and airborne measurements using a luminol based chemical amplifier. They are very Euro-centric, and most are from the Bremen group. I suggest including a few references to other groups, including non-European groups.

Done.

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Suggest changing "…Institute of Environmental Physics, and it employs…" to "…Institute of Environmental Physics, which employs…"

Done.

—

Page 2, first column, reaction 4. While many RO radicals react with O_2 to produce HO_2 and carbonyl compounds (not just aldehydes), there are RO radicals that either react to produce RO_2, do not react with O_2 at all, or primarily undergo isomerization or decomposition. The point is that the chemical amplifier chemistry does not measure 100% of RO_2. For most situations, the measured concentration is close to the true one, but this limitation should be briefly mentioned. This is also relevant in equation (1).

The following statements were added to the introduction:

Note that the efficiency for RO_2 *conversion is affected by additional terminating reactions depending on their chemical complexity.*

Chain length calibrations of HO_2 *and* CH_3O_2 *are appropriate for airborne measurements where these two peroxy radicals are expected to dominate.*

—

Page 2, second column, reaction 5. This is not a chemical reaction, so should probably be equation (1). Regardless, the contribution due to the reaction of NO with O_3 should also be included. Also, the meaning of $[NO_2]_{\text{other}}$ should be discussed.

All equations and reactions are now properly denoted. The ozone contribution to the NO_2 background was already included, and an additional sentence introducting $[NO_2]_{\text{other}}$ has been added.

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Page 2, second column, reaction 6. This should be labeled as an equation.

All equations and reactions are now properly denoted.

—

Page 2, second column, near end of last paragraph. The term "absorption coefficient" is used without specific definition. It appears to be the equivalent of (1-I/Io) x l, which is the absorptance times the path length or equivalently, the radiation absorbed per unit length. Continuing on to the equations and discussion at the top of page 3, no mention is made of the role of mirror reflectivity in the measurement of τ and thus α. Perhaps this is obvious with definition of α, but I suggest a bit of additional discussion on this topic.

Yes, the absorption coefficient is the one used in the Bouguer-Beer-Lambert law:
$I = I_0 \times e^{-\alpha \times l}$, so that $\alpha \sim (1 - \frac{I}{I_0}) \times l^{-1}$.

The mirror reflectivity is incorporated into the measurement of τ_0, as it is in principle a loss mechanism. The phrase "which also incorporates the mirror reflectivity" has been added at the description of the τ_0 measurement.

—

Page 3, Experimental, first paragraph. The air bypass is mentioned, but its purpose is not clear. This sentence should be changed to make it clearer.

The bypass is actually only needed for the inlet pressure stabilization, as mentioned in the text. This is also depicted in Fig. 1.

—

Page 3, Inlet. Why is the pressure controlled chamber so large? Given that it is one of the main limiting factors in the switch from one reactor to the other, I would think it should be much smaller. Consideration of the flow path by minimizing dead zones could also make the switch faster.

It is of course desirable to have the pre-reactor chamber as small as possible; however a certain air reservoir is needed for a functioning pressure stabilization, as are large diameter tubing to remove the surplus air ($\geq 8\,\mathrm{sLpm}$ for ambient standard pressure).

—

Page 3, second column, last paragraph. Here several uncertainties are given without defining what they mean (see general comment above).

This part of the manuscript has been modified. The data have been revised and a comparison of more statistical relevance has been included in the text.

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Page 4, first paragraph. It is stated that the chain lengths of the two reactors agree within their uncertainties. While there is not universal agreement what this means, I would say that it is just barely the case. I suggest pointing out that whatever the chain lengths are, they can be used to process the data.

This is true, and a series of additional measurements has confirmed the difference between the effective chain lengths of both reactors. The statement has therefore been deleted.

—

Page 4, first column, last paragraph. I suggest changing the word “schematised” to “shown schematically” or “shown in a schematic diagram”. While schematized is a perfectly valid word, in my experience it is rarely used.
Done.

—

Page 4, second column, end of first paragraph. Suggest changing “exposition” to “exposure”.
Done.

—

Page 4, second column, end of second paragraph. The statement that includes “…if the change is slow…” might be changed depending on the author’s response to my earlier comment about twochannel chemical amplifiers.
We have changed the sentence to represent the $60\,\mathrm{s}$ of one background mode measurement.

—

Page 4, second column, last paragraph. Not being a laser expert, I have trouble thinking in GHz when discussing wavelength scanning. Would it make sense to give the scan range in nm as well (I think 10 GHz is about 0.0056 nm)?
Done. The values are correct.

—

What does “certain resonator transmission threshold” mean? I’m guessing it has to do with selecting the wavelength at the maximum $\mathrm{NO_2}$ cross section, but there could be other explanations. Suggest making this a bit clearer.
The threshold is a ”generic” detector voltage (resonator transmission) which is used to determine when the laser should be switched off. The value depends on some parameters, e.g. laser intensity, resonator absorption and detector characteristics. If the resonator transmission decreases (for example if very high ozone levels are encountered) the operator may have to decrease the threshold to allow for continuing measurements.
The text has twice been amended to:
Usually a laser is used for resonator excitation, and if an operator-set resonator transmission intensity is reached, the laser is switched off rapidly.

—

The sentence with the phrase “draws the current” needs to be reworded.
Done. It now reads:
[...] fed to a FET circuit in parallel to the laser diode which then bypasses the laser diode, effectively switching off the laser.

—

It is mentioned that the data are acquired at 1 M-sample per second. If the ringdown times shown in the figures of about 20 μs are typical, would there be benefit to sampling faster. Perhaps a brief statement describing why this rate was chosen.
There is no special requirement to the sample rate, other than that it must be high enough to capture sufficient data points for fitting later on. It is very convenient to have samples at a $1\,\mu\mathrm{s}$ - rate for calculations later on, and since this is more than sufficient for ring-down times $\geq 10\,\mu\mathrm{s}$, this sample rate was chosen.

—

Page 5. $\mathrm{NO_2}$ detection limit. See general comment above. Perhaps add description of uncertainties when measuring 50 ppbv signals.
The $\mathrm{NO_2}$ detection limits and Allan variances are now calculated from $53/107\mathrm{ppbv}$ measurements (see chapter 3.1).

—

Page 5, second column, equation 4. Suggest pointing out that 2 radicals are formed per $\mathrm{H_2O}$ photolysed, and 2 ozone molecules are formed per $\mathrm{O_2}$ photolysed.
The following sentences have been added to the description:
Addition of $0.1\,\%$*vol* CO *assures the complete conversion to* $\mathrm{HO_2}$ *by reacting with both the hydroxyl radical and oxygen. Addition of* $1.6\,\%$*-vol* $\mathrm{CH_4}$ *instead produces a* $50\%/50\%$ *mixture of* $\mathrm{HO_2}$ *and* $\mathrm{CH_3O_2}$.

—

Page 5, second column, first paragraph. Suggest justifying using Hofzumahaus et al. 1997 $\mathrm{O_2}$ cross section, since it has been pointed out that the effective $\mathrm{O_2}$ cross section depends on the specific photolysis cell configuration.
This is certainly true, and the effective cross section is measured regularly for our calibration set-up in order to monitor any potential change in the lamp. The text has been changed to:
[...] is the absorption cross section of $\mathrm{O_2}$*, which has been determined specifically for the radical source employed here according to Hofzumahaus, 1997; the denoted error represents the* $\pm 1\sigma$ *standard deviation (Kartal, 2009).*

—

Page 5, second column, second paragraph. The statement that says measurement of small ozone concentrations is highly inaccurate, is not necessarily true. It depends on the analytical method and the definition of small. Suggest adding a bit more discussion. Also suggest finding someone with a state of the art reverse chemiluminescence ozone instrument.

The paragraph describing the ozone measurement has been revised and the misleading statement deleted.

Also, the there is an implicit assumption that the detector signal is proportional the ozone produced. Has this been demonstrated?

Yes, the appropriate reference of Reichert et al., 2003, has been added to the text.

—

Page 5, paragraph 4. Here is a propagation of errors analysis for the calibrator. This is good, but should include a definition of "errors".

All errors have now been clarified to be 1σ standard deviation errors. Thanks to the reviewer, the H_2O cross section error has been corrected, as it was provided as a 2σ error in the cited publication. The derived error for the HO_2 concentration is not affected.

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Page 5, paragraph 5. Is "magnet valves" the same as "solenoid valves"? If so, I suggest the latter.

Done.

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Page 6, paragraph 3. Suggest changing "probably" to "likely".

The sentence has been changed to include also other possible losses and now reads:

Possible reasons for the effective chain length decrease include higher radical surface losses due to more turbulent flow conditions, a lower radical conversion efficiency due to smaller reactor retention times, and the pressure dependence of contributing reactions (e.g. reaction R2)

—

Page 6, Summary and Conclusions. Suggest changing "…measurements is reported." to "…measurements are reported."

Done.

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Page 6, first column, last paragraph. Suggest changing "…field…" to "…ground-based…".

Done.

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Page 6, second column, first paragraph. This is related to my earlier comment to specifically match the instrument capability to the design goals, which are in part based on expected concentrations in different atmospheric regions. The statement about "the upper layers of the atmosphere" is too vague to be that useful. Suggest changing "end-2014" to "end of 20414".

This was addressed before in our answer to the comment about our design goals. The last two sentences now read:

As shown the PeRCEAS airborne instrument provides a means to accurately measure mixing ratios of peroxy radicals in the pptv *range in altitudes of up to* 13 km. *It is currently certified for aircraft operation, and will take part in the OMO mission onboard the HALO aircraft, whose start is scheduled for end of 2014.*

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Figures. Suggest combining Figures 1 and 3.

Done.

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No I consider the photos (Figure 2, 4 and 7) nice, but they could be left out.

Since these photos permit a better perception about the instrument in reality, we'd rather leave them in.

—

Figure 4. Suggest changing "aircraft fuselage level" to "aircraft wall".

The expression was changed to "aircraft fuselage", as it is the appropriate technical term.

—

Figure 5. Suggest adding a scale or conversion factor for GHz to nm.

We added the wavelength difference of 7.8 pm to the figure caption.

—

Figure 6 (and discussion in the text). Suggest adding in caption and/or in text a discussion of why the Vcavity is better for this application.

The following text was added to the chapter "$\mathrm{NO_2}$ detector" (and – slightly modified – also to the figure caption):
The continued use of the V-cavity allows the optical feedback to still provide high resonator transmission and bypasses the need for an optical isolator between laser and resonator.

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Figure 9. I really like the addition of the Allan variance analysis and figure.
As mentioned before the Allan variance graph has been updated to reflect the measurements at the $\mathrm{NO_2}$ backgrounds of 53 and $107\,\mathrm{ppbv}$.

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Figure 11. Suggest adding vertical lines separating the measurements of the various $\mathbf{HO_2}$ concentrations and giving those concentrations.
Done.

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Figure 12. The loss of 16 seconds of data in an aircraft campaign is unfortunate. I suggest modifications to the instrument to improve this. Perhaps a short statement saying this in text and/or in caption. Also suggest describing plans for improving the performance of the $\mathbf{NO_2}$ detectors.
This data loss is indeed unfortunate. Optimal measurement conditions are however the result of a compromise between different parameters affecting the overall instrument performance.
As stated in the text these 15 second data losses are caused by a pressure pulse which partly depends on the residence time of the reactor, the tubing connecting the whole system and the detector itself. As the connecting tubing is kept at a minimum, only the residence time in the reactor and detector might be modified by decreasing the corresponding sizes or increasing the air flow through the system.
Increasing the air flow would definitely decrease the residence time in the detector without significant changes in the S/N ratio. However, the corresponding decrease in the residence time in the reactor would be associated with a reduction in the chain length and a consequent loss in sensitivity. The CL loss can however be partly compensated by a potential decrease in the radical losses in the pre-reactor chamber, hereby increasing the eCL. In that respect, the pre-reactor chamber must possess a certain gas volume to allow for pressure stabilisation, which has an influence in the signal noise.
More convenient is therefore the size optimisation of the detector while keeping the V-resonator that provides high transmission. At the moment we're working on reducing the laser noise which at present dominates the ring-down time variations. The following statement has been added in chapter 3.1:
The present $\mathrm{NO_2}$ detection limit is adequate for the peroxy radical measurement task, but is limited by the characteristics of the laser source used. Different types of broadband diode lasers without extended cavities are at the moment investigated as possible improvements. Initial laboratory characterisations using a similar V-resonator show promising results in the form of decreased ring-down time variations.

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Figure 13. Here and in the text only $\mathbf{HO_2}$ calibration is discussed. You should perform and discuss calibration of $\mathbf{RO_2}$ as well. It is a simple matter to add various reactants to the water photolysis calibrator (CO, $\mathbf{CH_4}$, etc..). Just make sure that you don't add so much reactant as to influence the chemical amplifier chemistry.
Done. The results for the $\mathrm{CH_3O_2}$ chain length at $300\,\mathrm{hPa}$ has been added to the results chapter, as well as to the abstract.

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