Answers to Reviews of “The ICAD (Iterative Cavity Enhanced DOAS) Method” AMTD2019

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1. Introduction and general comments

We like to thank the referees for their constructive and helpful comments, which helped us to improve the manuscript. We followed most of the reviewers' suggestions and made the according changes to the manuscript. Below we answer the reviewers’ comments in detail and explain the changes made to the manuscript. We are convinced that the manuscript is now adequate for publication in AMT.
In the following we reproduced the reviewers' comments (in black) together with our responses (in red).

2. Replies to comments from Referee 1:

The authors have submitted a very interesting paper describing their work on the development and implementation of the ICAD method for CE-DOAS. This presents in my opinion novel and important work in the field of cavity enhanced spectroscopy which allows cavity enhanced measurements to be made without being limited by the stability of the light source and should be published in Atmospheric Measurement Techniques. I have no issues with the structure and content of the paper and there are only some minor typographical errors which need to be corrected. These are listed below.

Page 5, line 9, please change ‘lenght’ to length
Page 5, line 9, please change ‘optial’ to optical
Page 6, line 29, please change ‘me’ to be
Page 8, line 2, please change ‘aerol’ to aerosol
Page 8, line 8, please change ‘calucate’ to calculate
Page 10, line 12, please change ‘strop’ to stop
Page 11, line 4, please change ‘instrreducing’ to reducing
Page 11, line 5, please delete ‘andument’
Page 11, line 30, please change ‘too’ to ‘to’
Page 11, line 30, please change ‘good’ to ‘well’
Page 12, line 14, please change ‘to built a cavity set up’ to ‘a cavity setup to be built’
Page 14, line 19, please change ‘NO2’ to ‘NO 2 ’
Page 21, line 18, please change ‘march’ to March
Page 23, line 25, please change ‘cm3’ to cm
Reply:

Thank you for pointing out these typos and suggestions for rephrasing. We did another round of copy editing and included the suggested corrections.

3. Replies to comments from Referee 2:

This paper is the third in row with the publications of Platt et al., 2009 and Meinen et al, 2010. It describes the experimental setup of an improved broadband (BB) Cavity-Enhanced (CE) DOAS instrument which uses the well-known DOAS evaluation principle for the retrieval of trace gas concentrations from absorption spectra.
While in 'conventional' DOAS spectroscopy the optical path length between light source and detector is constant and precisely known this is not the case if an optical cavity is used to create the long absorption path. In this paper the authors thoroughly discuss the aspect of the shortening of the photon lifetime in the CEAS cavity due to the presence of absorbing trace species which leads to non-linear changes of the 'average optical path length' as a function of the trace gas concentration. 'Traditional' broad-band CEAS evaluation schemes (see papers of Fiedler et al.) inherently account for these path changes by measuring the absolute total light intensity. Hence these instruments require long-term stable light sources with very small intensity variations and mechanically rigid optical setups in order to assure equal light intensities at the detector during the measurements of the cavity transmission without and with absorbers.
In this paper the authors present a new spectral retrieval approach to overcome the above mentioned technically challenging restrictions. An iterative algorithm (ICAD CE-DOAS) was developed which, on the one hand, models the optical path length reduction as a function of the calculated actual optical density (OD) in the cavity. On the other hand the iterative method introduces the important DOAS advantage of being independent on the absolute light intensity into the 'CEAS world', however, at the expense of a significantly more complex data analysis.
The paper is certainly appropriate for publication in AMT after the comments below are appropriately answered.

Page 2, lines 18-30: I disagree with the statement 'the so far presented instruments can only be operated in a laboratory or at least in laboratory similar condition'. CEAS instruments already have been operated under harsh field measurement conditions so this statement needs rephrasing.
Reply:
We agree that the sentence might have been a bit too general. However, we do not know of any simple CEAS Instruments which could be operated under harsh conditions e.g. like in a bicycle trailer.
We re-phrased the sentence :
"Therefore, the so far presented instruments are typically limited to applications in a laboratory or larger mobile platforms (e.g. ships and medium sized air planes, see Zheng2018) where controlled environmental conditions are present. Applications in harsh environments are in principle possible, but require a high technical effort to achieve the required stability. "

Page 3, lines 7-10: Mentioning of 'a predecessor CE-DOAS instrument ...' should be removed from the text because it does not provide any useful information to the topic of the manuscript.
Reply:
We think that this information is useful as it shows further successful applications and validation measurements which are not presented in this paper.
We rephrased the sentence:
"A CE-DOAS instrument with an earlier version of the analysis scheme described in this publication was already successfully applied in several measurement campaigns"

Page 4, lines 26-29: I understand that the authors like to express how 'tolerant' their instrument is to intensity fluctuations but since the strong temperature dependency of the LED output power and spectrum is very well known in the community, nearly all LED driven CEAS instruments use temperature stabilization, usually by accurate and cheap Peltier cooling. Hence I think this is not a generally valid argument.

Reply:

It is true that LED temperature stabilization by Peltier cooling is routinely applied in CEAS instruments. However, from our experience Peltier cooling with sufficient temperature stabilisation adds an unnecessary level of complexity to the instrument, requires additional power and reduces the instrument's reliability in long-term operation. Also, while Peltier cooling helps to maintain stable light intensities over *periods of several hours, this is not generally possible for continuous long-term measurements. We saw examples where the LED light intensity suddenly decreased by more than 10% either due to degradation or in very harsh environments due to vibrations of the mechanical setup. Also, the optical fibre which typically feeds the light into the spectrometer easily changes their transmission by more than 10% if the bending radius changes slightly during transport or vibrations.*

We changed the paragraph to:

"Intensity drifts of this magnitude are typical for such optical setups, e.g. due to intensity drifts of used light sources like LEDs or changes in the transmission of fibres when their bending radius slightly changes during transport or vibrations. While there are technical solutions for these problems, they add extra complexity, weight, potential sources of hardware failure and often have to be adapted to the environmental conditions (e.g. parameters of the temperature controllers)."

Sects. 2.1 and 2.2, Eqs. 2, 3, and 4 need some clarification to avoid confusion. The molecular absorption cross sections used in Eqs. 2 and 3 are the total absorption cross section, i.e., sum of differential part σ'(λ) plus broadband part, called $\sigma_0(\lambda)$ in Sect. 2.2.
In contrast Sect. 2.2, Eq. 4 the DOAS approach just considers the differential part of the total cross section. Consequently the differential optical density should be denoted D' model (λ).

***Reply*:**

we agree with the reviewer and clarify the notation

1. *In Sect 2.2 $\sigma_0(\lambda)$ is a typo and changed to $\sigma_b(\lambda)$*
2. *For clarity we added equation (4)*
   $\sigma_i(\lambda) = \sigma'_i(\lambda) + \sigma_{i,b}(\lambda)$
3. *D model (λ) actually models the total optical density. The broadband part is modelled by the Polynomial Pk(λ)*

Furthermore we adapted the notation in section 3 to avoid confusion.

Page 8, lines 1 ff: The authors state that for cases when no particle filters in the inlet are acceptable due to trace gas losses on the surface the aerosol extinction term ε aerosol (m,λ) (Eq. 8) must be estimated 'by a suitable parametrization'.
However in Fig. 4 (first equation in the box) the broadband aerosol extinction ε b (see Eq.5) or ε aerosol (m,λ) (see Eq. 8), respectively, is omitted. The authors justify this by simply stating (page 9,
lines 1-3) that the present paper only regards the aerosol FREE case and that 'in the presence of aerosols the removal of broadband absorption, as part of the DOAS analysis, needs to be performed with care not to interfere with the aerosol absorption.'
- Please explain what is meant by 'suitable parametrization'.
- Could it be that in the case of strong aerosol extinction the iterative technique does not necessarily lead to a bijective solution?
I think this aspect must be discussed in greater detail in this paper in order to help interested future

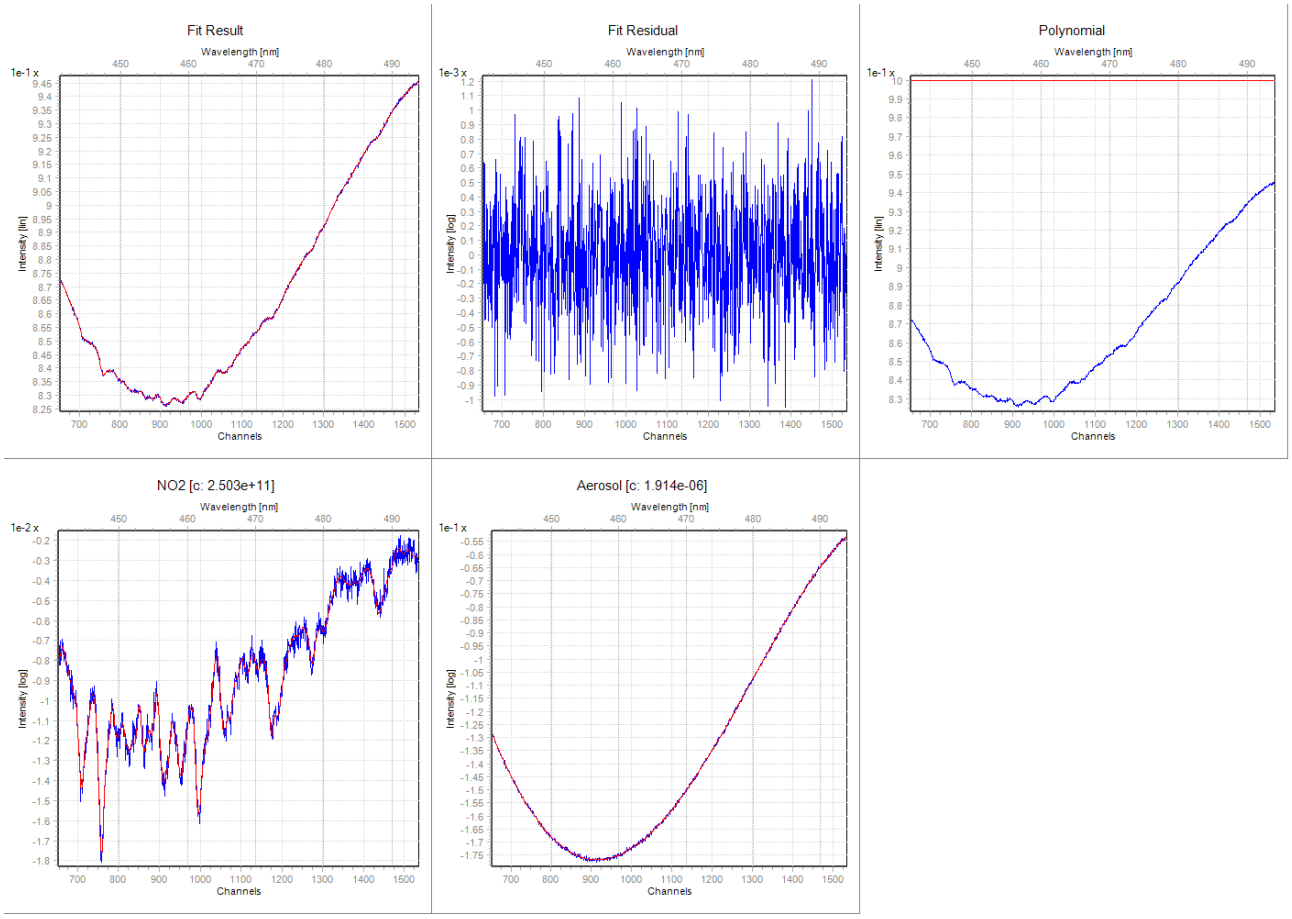
users of the ICAD technique to understand its potential limitations.

Reply:

We thank the reviewer for this useful comment. Our intention was not to confuse the reader with the iterative algorithm including aerosol absorption, since it is not the main part of the manuscript (in fact it could be the topic of another publication). But we agree that more general information should be given for the sake of clarity.

- *We added the sentence*
  "Typically an Angstrom exponent approach $\varepsilon_{aerosol}(\boldsymbol{m},\lambda) = m_1 \cdot \lambda^{-m_2}$ *could be used."*
- *We also included a Supplement Sect. S1 which gives a basic discussion of an ICAD approach which includes aerosol absorption.*

Below we present a sample ICAD Evaluation for a simulated spectrum with aerosol extinction. Simulations are based on section 1.3 with 10ppbv NO_2 *plus aerosol extinction with a typical Angstrom exponent of 1.7 and a peak aerosol optical density of 20% and Gaussian noise (*$\sigma = 10^{-4}$*). Fit settings are based on config 1 (Table 1). A broader fit range (441nm to 494nm) has to be chosen in order to include both wings of the aerosol fit reference (the shape of the aerosol extinction arises due to the mirror reflectivity), the DOAS Polynomial is set to first order and the High Pass Binomial filter is removed. The ICAD evaluation correctly retrieves (9.97±0.03)ppbv* NO_2 *which shows that the reduction of the light path by aerosol absorption is correctly accounted for by the correction factor K(λ). This demonstrate that ICAD can in principle also be used in the presence of aerosol extinction. Further studies with aerosol application are beyond the scope of this manuscript.*



Page 8, lines 7: What is meant by 'if all absorbers have sufficiently wavelength dependent absorption structures'? I assume this only refers to the differential part of the trace gas absorption spectra. How does this help to overcome the broadband aerosol absorption?

Reply:

It is not limited to typical differential absorption. E.g. the aerosol extinction, typically modelled with an Angstrom exponent , has a relatively broadband wavelength dependency compared to trace gasses. However, due to the strong wavelength dependency of the path length $L_{eff}(\lambda)$, the effective reference spectrum $\vartheta_{aerosol}(\lambda) = L_{eff}(\lambda) \cdot \varepsilon_{aerosol}(\mathbf{m},\lambda)$ is sufficiently wavelength dependent (see fit above). Therefore, it can be distinguished from other broadband variations, like instrumental intensity drifts e.g. of the LED, which do not take place in the cavity and therefore are not modulated with the optical path length in the cavity. Of course fitting the Aerosol extinction requires a broad fit range. For an optimal trace gas fit we therefore suggest a two stage fit which first retrieves the aerosol extinction and in a second step with smaller fit range and high pass filter retrieves the trace gas concentration as described now in supplement S1.

Page 9, Fig.5: This figure shows the iterative procedure to calculate the concentration from theoretical CEAS spectra for an extremely high NO 2 concentration.
In principle the figure is well suited for this topic, however due to the exclusion of the fundamental shot noise the archived minimal peak-to-peak noise levels of the residual (Fig. 5d) of 10 -9 to 10 -6 might give the reader false expectations what can be achievable with ICAD. It should be made clear that in reality the min. expectable noise levels are fundamentally limited by the photon shot noise.

Reply:

This is true. We extended the figure caption to avoid confusion by:
"In a real measurement the achievable noise levels are limited by the fundamental photon shot noise and instrumental error sources (see Sect. 4.3) "

Page 12, Sect. 3.1.2: In Fig. 6 it is shown that the retrieval of trace gas concentrations by the BB-CEAS method linearly depends on the change of radiation intensity between zero-air and ambient air measurements. The simulations were done up to 90% intensity differences.
However the dramatic results (of 90% intensity change !) shown here should be put into perspective to realistically achievable intensity fluctuations of presently used temperature stabilized light sources and CEAS cavities, which I assume to be less than a percent.
Compare the following discussion of the requirements of equals light intensities during the calibration of the path length in the air filled cavity on page 15, line 17 where a relative intensity drift of 5x10 -4 over some minutes was denoted.

Reply:

This remark is similar to the reviewer's comment to page 4 of the manuscript (see above). We already answered this question in our response to the above reviewer's point.

Page 15, Section 4.3.1: It is the measurement PRECISION, not accuracy !

Reply:

Thank you. We corrected this incorrect use of terminology

Figures:

Fig. 2: Shows the light path length as function of wavelength.
There are three extinction processes contributing to the path length which should be explained to the reader for clearness.
Firstly, on the second ordinate the absolute contribution of mirror transmission losses should be indicated.
Secondly, the absolute contribution of Rayleigh scattering in synthetic air over the spectral interval

should be quantified.
Thirdly, the loss due to absorption of the water dimer should be shown in relation to both other losses.
Reply:
The extinction processes are explained in section 2.2, which we think is sufficient. We did not include the loss processes in the figure as we think that it would clutter the plot. Instead we added Fig. SF1 to the supplement which shows the contributions of the different processes for the ICAD in config 1.

Fig. 5 should be moved between Sect. 3.1 and 3.1.1
Reply:
We will try to fix this in the two final two column manuscript

Fig. 8: The text should read: 'The bottom graph shows the time series OF THE 1-σ ERROR OF THE NO 2 CONCENTRATION for different integration times'
Reply:
We disagree with this point, as the graph shown is actually the time series of zero measurements with different integration/averaging times. The 1-σ ERROR would be the standard deviation of these time series.

Typos, word replications, etc.:
p4 line 22 / p7 line 12 / p5, line 4 / p7, line 12 / p8 / in Figure 4: 'Rayleigh extinction'
p8, line 8 / p9, caption to Fig.5 / p11, line 3 / p20, line 1
Reply:
We did another round of copy editing and included the suggested corrections.

4. Replies to comments from Referee 3

Horbanski et al present a new processing technique for cavity-enhanced DOAS, termed iterative CE-DOAS (ICAD), which accounts for the change in the optical path length due to absorption in the cavity. This significantly reduces the required light source and instrument stability and thus enables a more compact, lower power CE-DOAS instrument to be built. The authors evaluate the performance of the technique with numerical simulations as well as intercomparisons with chemiluminescence detectors. They also show the advantage of the compact instrument by doing some vehicle-based measurements. Overall, the paper provides a good summary and characterization of the technique and is appropriate for publication in AMT.

Specific comments:

1. Have you run two of these instruments side-by-side? If so, it would be nice to have some of these data in this paper.
Reply:
During the long term measurements with config 2 we ran a second NO_2 ICAD side-by-side. The correlation plot between both ICADs called A and B was added to the supplement (SF4).

2. Suggested reference for cavity-enhanced equations: Zheng et al. Review of Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) for Gas Sensing SensorsÂˇ a2018,Âˇ a18(11), 3646; doi:10.3390/s18113646
Reply:

The reference was added to section 2.1

3. How often does the path length calibration using He and dry air need to be performed? Was this included for all of the measurements presented? If so, then the text on P23, L15 "without compressed gas cylinders" needs to be revised.

Reply:
Path length calibration using He and dry air, does not have to be performed routinely for our ICAD instruments as calibration only change if mirrors are contaminated (which is avoided by the aerosol filter). If we don't see a significant drop in intensity for zero air measurements (which happen if mirrors contaminate) we found that there is no need for a recalibration. Typically a calibration lasts for several month to years. In the rare cases when the intensity changed significantly we do a calibration run in our lab before taking the instrument to a field measurement.

4. In Figure 5, what causes the increasing error and residuals with increasing concentration? It seems like if you are fitting with the same cross section as used for the simulation, everything should be self consistent. Is it because the saturation occurs on lines that are narrower than the instrument resolution?
Reply
We used the exact (geometric) light propagation in the resonator to simulate our measurements (e.g. see Fiedler 2005). The basic ICAD and BBCEAS equations are only an approximation to the fundamental light propagation in an optical resonator. E.g see Platt 2009 or Fiedler 2005. Therefore these increasing residual structure show the limitations of the approximations done in the data evaluation. However for all practical applications these residual structures are still more than one order of magnitude lower than the fundamental photon shot noise and instrumental error sources which can be achieved.

5. For the ICAD measurements with calibration gas, how do you know that the 2.6 ppb offset is due to the zero air? Also, can you compare the observed discrepancy without path length correction to the prediction from Fig 3/6?
Reply:
We changed it to "The small offset of (2.6$\pm$0.1\,ppbv) is ***most likely*** *due to an impurity in the zero air gas cylinder from the \chem{NO_2} calibration source"*
It is we observed that synthetic air bottles often have a small NO_2 impurity. The ICAD uses for the zero air its own zero air filter and therefore is able to detect an impurity in the synthetic zero air of the calibration source.
However, the CLD in the calibration setup only measures the "missing" NO which was titrated to NO_2 and therefore cannot detect an NO_2 impurity in the zero air gas. Therefore the ICAD sees an offset.

6. On p18, L20 a 4s trend is subtracted from each data point. I don't understand what is happening here. The time resolution of the CLD is 44s, so where does the 4s trend come from?
Reply:
There was a typo: Actually a 4 min trend was used.
We also rephrased the sentences to make the filtering procedure clearer:

“ In order to analyse the CLD noise, the general trend (interpolated 4 min trend) is subtracted from each data point before computing the standard deviation of the 10 min intervals. Intervals with a deviation of more than 3.5ppbv are classified as non-physical and sorted out. This filtered CLD/BLC NO 2 measurements are used for comparison with the ICAD time series.”

7. What causes the offset in the ICAD vs APNA 370 measurements? If there is residual NO2 in the zero air, this should still be measured by both systems.

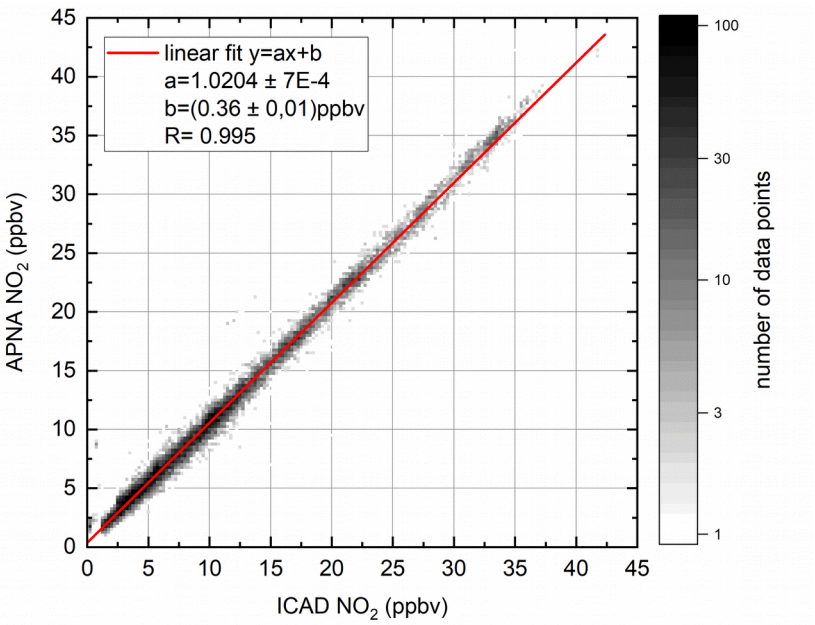
Reply:

By looking at the measurements of zero air we see that the zero point offset of the ANPA is only (0.07+/-0.18)ppb and for the ICAD (-0.05+/-0.03)ppb. Therefore we think that the offset in the fit might indicate a very small non-linearity in the correlation between both instruments. This might come form some interferences of the APNA 370 to other gases in the ambient air.

8. It also looks like there is a deviation between the ICAD and APNA 370 at 30-40 ppb. How does the linear fit change if you do not include the permeation source points? Any idea what would cause this?

Reply:

If the permeation source is removed the slope of the linear fit APNA 370 vs ICAD slighlty changes to (1.02+/-7E-4) but the offset stays quite the same (0.36+/-0.01)ppb (see figure below).
The deviation between the ICAD and APNA 370 at 30-40ppb is most likely caused by interferences of the APNA 370 to some gases in the sample air. We assume this, as we do not see such a deviation in the side by side inter-comparison of two ICAD instruments or by the comparison to the permeation source.



Technical corrections: There were several typos throughout, please run one more round of copy editing. I’ve noted some below but may have missed a few.

Reply:

Thank you for pointing out these typos. We did another round of copy editing

P1, L4: The phrase "opposite to classical Long Path DOAS measurements" is confusing. Perhaps saying "in contrast to classical Long Path DOAS measurements where the light path is fixed"

Reply:

We changed the sentence according to the referee's suggestion.

P2, L28-29: I'm not sure that ships or medium size airplanes would be considered "laboratory similar conditions". Perhaps it would be better to say "medium to large fixed or mobile platforms (e.g., ships and medium size airplanes)." Perhaps also add the Zheng et al ref here
Reply:
The sentence was rephrased. See reply to referee 2

Eq 5: Should the σ i be σ 0i ?
Reply: *There was a typo and an inconsistency in the notation of sect 2.1 an 2.2. We corrected this. See also reply to referee 2*

P6, L8: Should the reference to Fig 9 be to Fig 3?
Reply: *Both figures show the effect of path length reduction. Therefore we kept the reference to figure 9 but extended it by a reference to Fig 3*

P11, L2-3: I think that some text was inserted in the middle of a word.
Reply: *The copy errors were corrected*

P11, L29: "too" should be "to" and "good" should be "well"
Reply: *Typos were corrected*

P17, L6: Not sure what the "(a)" refers to
Reply*: "(a)" was removed*

P18, L9: Change "recorded" to "record"
Reply: *Typo was corrected*

P18, L20: Missing "." after "deviation"
Reply: *This paragraph was rewritten. See reply to referee 2*

Figure 2: Add curves showing Rayleigh scatting and O4.
Reply*: See reply to referee 2*

Figure 14: Please add a scale bar and maybe increase the figure size. The details of the measurement route and text on the map are both hard to see.
Reply: *A scale bar was added*