Answer to comments by Referee #2

Retrieval interval mapping, a tool to visualize the spectral retrieval range in differential optical absorption spectroscopy

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Anonymous Referee #2:

The paper describes a visualization tool for sensitivities in DOAS retrievals on the wavelength region that is evaluated. On the basis of synthetic spectra the authors evaluate BrO fit scenarios that are meant to resemble conditions of passive solar stray light DOAS conditions characteristic of zenith sky DOAS measurements of stratospheric BrO, and BrO measurements in volcanic plumes. The paper is well suited for publication in Atmospheric Measurement Techniques eventually, and interesting, though there are some major concerns that should be addressed prior to publication.

Answer:

The authors would like to thank the referee for his/her comments and suggestions. In the following, his major comments are addressed. It is important to keep in mind that the authors aimed at presenting a novel tool together with an example of application using synthetic spectra. This study only acts as a starting point, enabling the reader to optimize the evaluation of his/her data set by his/her own choice of priorities. The presented synthetic examples are only best possible cases and a direct application to field measurements must be done with care.

One of the major comments raised is that the Ring effect is not included in the synthetic spectra. However, for a realistic modelling of volcanic plumes, a radiative transfer tool to correctly model the ring effect in a 3 dimensional atmosphere is missing so far. Furthermore, retrieval wavelength ranges yielding highly erroneous SCDs without considering the Ring effect will not yield true SCDs when the effect is included. In order to yield a set of retrieval parameters for certain measurement geometries, a comparison between synthetic and measured spectra would be essential. This however would exceed the scope of this manuscript.

The authors will gladly assist in further studies (e.g., combining the theoretical approach with measured spectra) by providing existing algorithms and support. A supplement is added to the manuscript which includes all necessary files and description to perform Test 1 for both measurement scenarios.

In the following, the authors address all comments individually, with references of page and line corresponding to original AMTD publication.

Major comments:

Comment:

1) The paper discusses two passive DOAS applications, and mentions – for good reason as the reviewer agrees – about the need to consider 'insufficient corrections for the Ring effect' (abstract) and 'the wavelength dependency of the Ring effect' (p4198, l26), and 'dependency of the retrieved values on . . . the Ring-effect' (p4201, l15) in sensitivity studies to determine an optimal DOAS fit window.

It comes as a surprise that given this extensive introduction, the authors then decide to neglect 'most importantly the Ring-effect' (p4203, l5) without further justification. No further treatment of the Ring effect is done.

However, out of the blue the 'insufficient correction for the Ring-effect' appears again (p4218, l27) in what is supposedly the discussion of results section (Section 5.2 'Sensitivity to interfering absorbers'). Given the above, it appears somewhat ironical that one of the final statements (p4220, l24) concludes that 'realistic simulations of. . . the Ring-effect' is needed 'in order to advise for a specific retrieval wavelength range'. Without treatment of the Ring-effect, the practical use from this paper 'poses [more than?] certain limits' on the 'application. . . to measured spectra' (p4203, l11). A 'prime focus. . . to present the new method' (p4203, l12) seems to be in contrast to the ambition to 'demonstrate [a technique] . . . for stratospheric BrO measurements and for BrO measurements in volcanic plumes' (abstract). Since the author's choice is to discuss passive DOAS applications, an explicit treatment of the Ring-effect should be included in the revised version of this manuscript.

Answer:

The authors thank the referee for this comment. We agree that the Ring effect should be considered, which is apparent from the multiple mentioning of the problem. Its negligence is not an accident. This publication focuses on the presentation of the visualization tool and the presented tests and scenarios as examples. For the measurement scenario zenith-DOAS, the I0-effect plays a major role, whereas it is not so important for the measurement scenario of volcanic plumes. Up to date, the tools are missing to calculate the Ring effect in a 3 dimensional atmosphere in order to simulate the effect for volcanic plumes. A simplified approach by calculation of Raman scattering from the constructed synthetic spectra would not sufficiently consider the radiative transfer in volcanic plumes, especially when high SCDs of trace gases and a condensed and/or ash laden plume are present. Also a comparison of synthetic with measured spectra would be necessary to give a solid suggestion on the evaluation wavelength range for volcanic plumes.

Given these problems, the authors refrain from the incorporation of the Ring effect in given presentation of the visualization tool. Once the appropriate tools are established in the future, a comprehensive study including advanced radiative transfer modelling and measured data will be done.

To address this issue in the manuscript, the following sentences were added:

"For a correct assessment of the Ring effect however, an extensive study including advanced radiative transfer modelling and comparison with measured data would be

necessary. Up to date, the tools are missing to calculate the Ring effect in a 3-dimensional atmosphere in order to perfectly simulate the effect when probing volcanic plumes. Furthermore, retrieval wavelength ranges yielding highly erroneous SCDs without considering the Ring effect will not yield true SCDs when the effect is included."

(P4203 L7)

Comment:

2) There is virtually no discussion about the criteria of choice to optimize a DOAS fit window. The only statement to the matter seems to be found in the conclusion section (P4222, L6-10). This does not seem to justify the word 'optimization' in the title. A better substitute might be 'visualization'?

Answer:

The authors agree that visualizing the results over a set of wavelength ranges is the main focus in the publication. However, if the user draws any conclusion from the results, it will lead to an optimization and/or justification of fitting parameters. The criteria for choosing a certain DOAS retrieval wavelength range may vary depending on instrument and application. Since the main focus in the publication is on the visualization and the tests act only as examples on the optimization strategy, the publications name is changed as suggested.

The abstract was changed accordingly to

"Here we present a novel tool to visualize the effect of different evaluation wavelength range. It is based on mapping retrieved values in the retrieval wavelength space and thus visualizing the consequences of different choices of spectral retrieval ranges caused by slightly erroneous absorption cross sections, cross correlations and instrumental features. Based on the information gathered, an optimal retrieval wavelength range may be determined systematically."

(P4906, L21-25)

Comment:

3) A significant risk consists in the lack of attention to the variability between the subset of wavelength ranges based on traditional criteria, as those have been applied in the DOAS community for decades. Further, Table 1 seems incomplete. The combination of significance criteria for a 2-band and a 3-band evaluation of BrO by a logical 'AND', as done in Coburn et al., warrants mentioning on p4199, and the study by Prados Ramon et al. is missing, for example. More importantly, the systematic application of the 'visualization tool' creates the (wrong?) impression that DOAS measurements are unreliable. The reviewer sees considerable risk that this might propagate to give DOAS a bad fame for no good reason. In reality, the application of the tool to the first scenario confirms conclusions that had been reached by authors that did not use the tool previously (Aliwell et al., 2002). For the second scenario in a volcanic plume, the visualization tool does not lead the authors

to draw any conclusion. While the reviewer appreciates the benefit to ‘documenting sensitivities in the fit’, what is the benefit over traditional methods? At the very least, the amplitude in the variability of results from sensitivity tests should be discussed in context of the variability for the subset of fit scenarios that reflect ‘choices made in the past’ (reflected in Table 1, for example). The results from such a comparison might be worth mentioning in the abstract, and could be expanded on in the conclusion section.

Answer:

The authors agree with some of the reviewer’s points and understand his/her concerns. Table 1 may be extensive but is not meant to be a complete overview over all BrO wavelength retrieval ranges, which is also stated in the text. However, both studies have been added to the table since the study by Coburn et al. adds a new wavelength evaluation interval and the publication by Prados–Ramon is a valuable addition because the table is missing a reference to airborne measurements of arctic BrO. The authors have refrained from a description or discussion of the significance criteria in Coburn et al. as mentioned by the referee (the combination of 2-band and a 3-band evaluation of BrO by a logical AND), because it is not described in that publication. Coburn et al. have used that criteria in their publication nevertheless (personal communication), and a note has been added in the caption of Table 1 to indicate this.

By including the citations in Table 1, the indices denoting different evaluation wavelength ranges were adjusted and changed in Figures 1, 3, 4, 7, 8, 9, 13 as well as references made in the text.

The authors can understand the Referee’s concern that the visualization tool might give the false impression that the DOAS technique is unreliable to a reader without any further knowledge of the technique. However, this cannot be an argument against its application. It is common knowledge in the DOAS community that certain retrieval intervals will yield highly erroneous results, depending on the measurement setup and/or instrumental issues (e.g. described zenith DOAS measurements of stratospheric BrO). By using the presented tool, the application of misleading retrieval intervals can be prevented and the error of DOAS measurements reduced. So the tool will actually prevent misleading results and thus bad fame for no good reason.

That the conclusion drawn by Aliwell et al. without the tool is the same as drawn here by applying the tool strengthens the result, but cannot be used as an argument against the presented tool. The wavelength retrieval ranges in previous publications were certainly chosen with great care. However, in most publications systematic explanations are missing why a certain retrieval wavelength range has been chosen, and the mentioned “traditional” methods rarely make it into the respective publications. The reader is usually not able to verify that the base on which the data is retrieved is valid.

To give an example, which is not included in the manuscript because it cannot be verified without an additional study of the measured data: Aliwell et al. suggested the use of 346-359nm instead of 345-359nm because of a better general stability of the fit. If one compares this explanation with Fig. 1, it may be speculated that this may have been induced by shifts in the wavelength to pixel mapping of the spectrographs. The retrieval wavelength maps show a strong gradient for the 345-359nm range, which is not present for 346-359nm.

The following lines were added at P4220 L6:

"If one compares this explanation with Fig. 1, it may be speculated that the observations may have been induced by shifts in the wavelength to pixel mapping of the spectrograph. The retrieval wavelength maps show a strong gradient for the 345-359 nm range, which is not present for 346-359 nm."

Comment:

4) Finally, the paper reads rather repetitive, is long, and in parts contradictory. For example, the definition of active and passive DOAS is found in the abstract, and again on p4198, l1, and again in l9 of the same page. Also, is the ambition of the paper a qualitative (p4196, l21) or a quantitative discussion (p4199, l5; and again p4200, l4) - which is correct? A quantitative discussion would be more useful. Finally, various combinations of sensitivities that affect the retrievals are given in different combinations and in different locations. Without ambition of completeness, a selection of locations are (1) p4196, l15, (2) p4198, l27, (3) p4200 l18, (4) p4201, l8, (5) p4221, l5, (6) p4221, l15, (7) p4221, l27. Only a subset of the mentioned parameters is actually being probed (see also point #1). Also, of the four parameters mentioned on p4221, l15, only the first three seem to be discussed, while the fourth is mentioned but not further discussed? A semi-quantitative justification of why some parameters were chosen, while others were neglected should be included. Text should be synergized, and shortened to focus on results.

Answer:

The authors would like to thank the referee for his/her comments and suggestions. Because the presented tool can be used to study any parameter of a DOAS retrieval, more parameter are mentioned in the text than actually discussed. Also, the main focus of the manuscript is to present the novel tool with examples and not an extensive study. Limitations of the approach and synthetic spectra, Ring effect, etc, have already been discussed in the previous answers to the Referee's comments.

The manuscript was carefully reviewed to synergize and shorten the text. An extensive description of the changes made is given in the following:

<u>Page 4198:</u>

The sentence in Line 9 was shortened to

"Passive instruments can be constructed very compact and of low power consumption since they do not have the necessities of an additional emitter and reflectors." (P4198 L9)

<u>Page 4209:</u>

In an effort to reduce repetitions, the authors have moved discussions of results to from section 4 to section 5. Consequently, in the title of section 4 ("Results and discussion…") the word "discussion" has been deleted.

(P4209, L18)

Page 4210:

Parts of the discussion in Sec.4.1.1 were merged with the comparison of both measurement scenarios in Sec. 5.1. and Sec 5.4:

(P4210 L9-12 to P4218 L6):

"The observed deviations … without presence of other absorbers."

"again is an indication of" replaced with *"indicates"*

(P4210, L19)

Page 4211:

Parts of the discussion in Sec.4.1.1 was merged with the comparison of both measurement scenarios in Sec. 5.1. and Sec 5.4:

(P4211 L8-13 to P4220 L5):

Deleted *"The previous study by Aliwell et al. (2002) recommended the use of a retrieval wavelength interval between 346 nm and 359 nm (#9 in Fig. 1 and 3) due to greater stability of retrieved SCDs in measured spectra. This evaluation wavelength range is well studied and validated (e.g. Theys et al., 2007). However, if strong O3 absorptions are present, care must be taken to apply a valid I0 correction to the RCSs, otherwise the retrieval may overestimate the true BrO SCD."* (P4211 L8-13)

Merged to

"For zenith-sky DOAS, the tests confirmed the evaluation wavelength range 346-359 nm as suggested by Aliwell et al. (2002) due to greater stability of retrieved SCDs in measured spectra in comparison to 345-359 nm. This has also been validated by Theys et al. (2007). At this known example, the novel tool confirms that this retrieval wavelength interval of BrO offers least the dependency on the I0 effect although an I0 correction of RCSs is still mandatory." (P4220 L5)

Deleted because it is mentioned in the description of Test 2:

"Note that only I0 corrected RCSs are used in the fitting algorithm."

(P4211 L18)

Deleted:

"The differences shown result from a combination of slightly erroneous I_0 correction (the original SCDs are used, $I_{K;0}$ in Eq. 2 neglects presence of other absorbers) and

possible cross correlation of absorption cross sections, which are not resolved in this test."

(P4211L28 – P4212L3)

Page 4212:

Deleted since it is already mentioned in 5.2 (see also comments from Referee #1):

"The observed deviations from the true SCDs are most likely resulting from an insufficient correction of the I0 effect of the strong O3 absorptions. Indications are the structures observed already in the plots for varying O3 strengths."

(P4212 L9-12)

The following sentences were deleted because a description of the figure can be found in its caption:

"In order to obtain significant results, retrievals were performed at each individual wavelength interval with 100 different noise spectra. The first column shows the results if uncorrected RCSs are applied together with unfiltered noise, whereas the following columns depict fits applying I0 corrected RCS with unfiltered Gaussian noise, followed by low pass filtered Gaussian noise with a binomial filter of 10 and 50 iterations, respectively (for examples, see Fig. 2). The top row gives the mean of resulting BrO SCDs, the middle row shows the standard deviation for the respective wavelength retrieval interval and the bottom row gives the correction factor defined by Stutz and Platt (1996), which is the ratio of standard deviation of results and the mean fit error."

(P4212, L16)

Instead, only a short reference to Fig 2 was added:

"A sample of the different noises is shown in Fig"

Page 4213

Replaced:

"The noise only leads to an increased scatter of results … systematic wavelength dependent features." (P4213 L1-5)

"With an increase in noise structure (column 2 till 5), an increase in standard deviation of results is observed."

Page 4214

Parts of the discussion in Sec.4.2.1 was merged with the comparison of both measurement scenarios in Sec. 5.1. and Sec 5.4:

(P4214 L8-12) -> (P4218 L 7-9)

Deleted: *"Compared to the zenith-sky DOAS scenario applying I0 corrected RCSs (Fig. 1), the combined SO2 and O3 differential absorptions are still an order of magnitude smaller than the combined O3 differential absorptions in the zenith-sky*

DOAS scenario, which reduces the deviations of BrO SCDs due to an insufficient I0 correction." (P4214 L8-12)

Merged to *"In the case of the scenario of BrO in volcanic plumes, the combined SO2 and O3 differential absorptions are still about two orders of magnitude smaller than the combined O3 differential absorptions in the zenith-sky DOAS scenario at wavelengths < 320nm. Therefore deviations of the retrieved BrO SCDs are much smaller than for the zenith-sky DOAS scenario."* (P4218 L 7-9):

Page 4215

Parts of the discussion in Sec.4.2.2 was merged with the comparison of both measurement scenarios in Sec. 5.2.:

Deleted: *"However, these results stand in contrast to findings using measured spectra, where much higher anti-correlations can be expected (Vogel, 2011). It can be speculated, that cross correlations between HCHO and BrO are observed when systematic residual structures are present (see also Sec. 5 and App. A)."*

(P4215 L26 – P4216 L3)

Page 4216

Replaced

"As already observed for the scenario of zenith-sky DOAS … applying I0 corrected RCSs are still concealed by the noise." (P4216 L14 – 18)

with

"As already observed for the scenario of zenith-sky DOAS, sec. 4.1.3, BrO SCDs are comparable to evaluations without noise (see Fig. 7, 8). Possible minor deviations from the true BrO SCDs for evaluations applying I_0 corrected RCSs are still concealed by the noise." (P4216 L14)

Page 4217

The last two paragraphs in Sec. 4.2.3 (P4217 L3-16) were modified to since parts are discussed in 5.3:

Replaced *"The calculated correction factor… due to an insufficient I0 correction of RCSs are negligible."* (P4217 L3-16) with

"The calculated correction factor shows a clear transition at a lower limit of 320 nm for uncorrected RCSs, changing from below unity to an average value of 1 for all other retrieval wavelength intervals. For I0 corrected RCSs, the correction factor only shows a small wavelength dependence. For unfiltered noise, standard deviation and measurement error do not differ significantly. For low pass filtered noise correction factors of ~3 and ~4.5 (10 and 50 iterations of the binomial filter, respectively) need to be applied to calculate the true standard deviation from the fit error."

Page 4218

Replaced the following sentences (P4218 L25 – P4219 L2) due to merging of text from Sec. 4.2.2:

“Their source can be, … observed in this theoretical study.” (P4218 L25 – P4219 L2)

Replaced with:

“One such example is the anti- correlation between BrO and HCHO observed in measurements of volcanic plumes (Vogel, 2011), which occur despite the negligible correlations described in Sec. 4.2.2 and only minor anti-correlations found in App. A. For field measurements of volcanic plumes, systematic spectral structures are likely induced by wavelength dependent radiative transfer effects which are not fully considered in a standard DOAS retrieval.”

<u>Page 4219</u>

Removed *“of a significant number”* (P4219 L6), because it is explained earlier.

Replaced *“These findings … broad band structures.”* (P4219 L7-8) with

“These findings also remained true in general when noise spectra were calculated with additional, random broad band structures. However, the deviations from the true BrO SCD were slightly increased with increasing broad band structures of the noise in case of the zenith-sky DOAS scenario for reasons yet unclear.”

Removed *“One has to keep in mind that*” (P4219 L20)

Minor comments:

Comment:

Abstract, lines 1-18: this reads like an introduction. Indeed much of this text is being repeated several times in the manuscript. Consider removing here. The abstract fully captures the essence of the paper if it was to start on line 19.

Answer:

The autors have condensed the abstract considerably, reducing line 1-18 to:

"Remote sensing via differential optical absorption spectroscopy (DOAS) has become a standard technique to identify and quantify trace gases in the atmosphere. Due to the wide range of measurement conditions, atmospheric compositions and instruments used, a specific challenge of a DOAS retrieval is to optimize the retrieval parameters for each specific case and particular trace gas of interest. Of these parameters, the retrieval wavelength range one of the most important ones."

(P 4196, L1)

Comment:

Abstract, line 16: the reviewer agrees the Ring effect should be an important consideration. It is mentioned here, but not further discussed in the paper. Since passive DOAS applications are discussed, this seems to be a major limitation of the paper. There is arguably little practical use for this paper without a thorough discussion of the Ring effect.

Answer:

Mentioning of the Ring-effect has been removed from the abstract (see answer to the first minor comment above). Regarding further discussion on Ring-effect in the manuscript, the authors would like to refer to their answers in this matter in the major comments.

Comment:

What are the criteria 'to determine the optical evaluation wavelength range'? They seem to be the essence of any ambition for 'optimization', yet are not spelled out in the abstract?

Answer:

The authors describe a novel tool and as examples certain tests which can be used in a strategy to find the right DOAS retrieval parameters. However, due to the variability of the instruments and measurement geometries, different tests may be necessary. Thus the authors refrained from a detailed description of a strategy and applied the novel tool to set of tests which may only act as examples. Furthermore, the authors addressed the concern of the referee by replacing “*optimize*” with “*visualize*” in the title (see major comment 1)

Comment:

What is the difference between ‘interference’ and ‘cross correlation’? Unless there is a reason to make this distinction, it would make for an easier read to pick on terminology and stick with it throughout the manuscript.

Answer:

Throughout the manuscript, interference is replaced by cross correlation

Comment

P4209, l10: How is the correction factor defined?

Answer:

A short definition has been added:

“…similar to the error calculation study by Stutz and Platt (1996). A correction factor is defined in the study which is the ratio of standard deviation of results and the mean fit error.” (p. 4209, l. 9)

Comment

P4220, l15: Is the I0 correction crucial or not? Are the authors saying that I0 correction is insufficiently well possible?

Answer:

The I0 correction is still necessary. Because of the varying conditions when measuring volcanic plumes, it is important to choose a retrieval wavelength range with a low dependency on the I0 effect to minimise possible artefacts from erroneously assumed trace gas SCDs in the I0 correction. The authors have changed to the paragraph to better express this necessity:

“Whereas the fit applying I0 corrected RCSs shows a good agreement with the true BrO SCD at most wavelengths, BrO SCDs retrieved with uncorrected RCSs can differ by more than 10%. In the field, volcanic emissions can vary greatly on short time scales. Also, changing O3 SCDs in early and late hours of the day have to be considered. Therefore, a retrieval wavelength range with a low dependency on the I0 effect and cross correlations to other absorbers is needed rather than one that 590 can be well corrected under stable conditions. In an evaluation wavelength range with a lower limit between 320-335nm the deviations from the true BrO SCDs are

below 5% applying uncorrected RCSs. Given the variability of strong absorbers at lower wavelengths, i.e. SO_2 and O_3, and the increased cross correlations observed for lower wavelength limits <325nm (sec. 4.2.2), evaluations should be performed at the upper range of suggested interval.”

(P4220, L13-20)