Dear Dr. Ma,

We would like to thank the reviewers for their constructive and helpful comments, which helped us to significantly (in our opinion) 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 we were able to address all reviewers' questions and that the revised manuscript is now adequate for publication in ACP.

In the following we reproduced the reviewers' comments (in black) together with our responses (in red). Our responses to the interactive comments can be found at the end of this document.

With very best regards,
Jonas Gliß

General remarks by the authors

Before addressing the individual comments of the reviewers, we would like to summarize the most important and general changes applied to our manuscript. These are a result of the really helpful comments of the reviewers and we are convinced, that all reviewers as well as the editor accept our revised article with its improvements:

1. **Detection limit and error discussion, discussion of trends**
   One main point of criticism was whether in certain cases the BrO and OClO data are significantly different from zero and further, the question of the validity of discussing trends based on the data which appeared to be below our detection limit. We would especially like to thank reviewer 3 for his helpful suggestions to use statistically robust results (i.e. plume evolution analysis).

2. We reconsidered the list of most important outcomes of our study, i.e. those representing a new contribution to the scientific community:

   a. **Observation of OClO and BrO formation in a young volcanic plume**
   b. **Estimation of Cl-concentrations and CH4-depletion due to volcanic chlorine**
   c. **Direct observation of the photochemical formation of BrO (OClO) in the early morning**

   We agree with the reviewers, that the discussion about individual measurement points close to or below our detection limit was partly delicate and difficult. Therefore,

   I. we reduced the discussion of plume cross section profiles of BrO and OClO (i.e. the question of enhanced ratios at the edges of the plume) to a small paragraph, stressing, that only indications of enhanced BrO/SO2 and OClO/SO2 ratios at the edges of the plume were found, since the corresponding values appeared to be below our (conservative) detection limit.
   II. we largely reduced the discussion of individual plume evolution scans

3. **All reviewers felt that section 2 (Methods and study area) is too long, therefore we**
   a. shortened the discussion of the plume age determination and moved the (rather detailed) discussion about the corresponding uncertainties to the appendix
   b. moved details on the Ring4 calculation to appendix

c. moved details on the DOAS error treatment to appendix
d. shortened and rephrased Sect. 2.4.1 (Evaluation routines) and moved parts to the appendix (second OClO evaluation range).
e. moved large parts of the stratospheric BrO correction to appendix
f. shortened and rephrased Sect. 2.5 (BrO, OClO concentration estimation)

Response to the individual reviews

Anonymous Referee #1, Received and published: 30 October 2014

Remark: page numbers etc. in this first review refer to the initially uploaded manuscript pdf file and not to the discussion paper pdf file.

OClO and BrO observations in the volcanic plume of Mt. Etna - Implications on the chemistry of chlorine and bromine species in volcanic plumes Gliss et al. reported on halogen oxides observations at Mt Etna using MAX-DOAS measurements. This paper is interesting and report on new measurements and should be published after addressing the points below.

General comments:

1. Overall, the methodology is valid and the quality of the results is good. However, the scientific significance of this study is somehow questionable. From the title and the introduction, a reader will have the impression that new conclusions on volcanic halogens formation and chemistry will come out of the paper but in fact it is not really the case. The measurements presented here largely confirm findings from past studies. The only exceptions are the results for young plumes and the discussion on formation time and the results for OClO. My main comment on this study is for the presentation quality.

   Answer: The authors disagree with the reviewer in this point, especially concerning the scientific importance of the findings.
   It is true, that the discussion of e.g. cross section profiles (i.e. enhanced BrO/SO2 and OClO/SO2 ratios at the edges of the plume) might not be fully supported by our data and – as a result – we drastically reduced this part in the revised document, since it basically confirms previous findings (e.g. General et al. 2014) and is not of major importance for this study.
   However, as the reviewer already mentioned, the observation of the detailed BrO and OClO formation in a very young plume, has never been published to our knowledge up to today. Furthermore, both the estimation of chlorine atom concentrations in the gas phase and from that, the potential – chlorine induced – depletion of atmospheric methane were – to the authors knowledge – not yet reported or discussed in any published literature and therefore represent an important and new contribution. From our point of view, these topics represent a step forward regarding the understanding of halogen chemistry in volcanic plumes, especially with regard to chlorine chemistry.

2. The abstract and conclusions should be rewritten. Especially the conclusions part is only a summary of what was presented in previous sections (with a lot of numbers and statistical values, not really necessary). Instead it should reflect what this paper brings compared to previous studies.

Answer: Abstract and conclusions have been re-written, especially the latter was changed following the suggestions from reviewer #3 by shortening the summary of our results and by shifting the analysis of Cl concentrations and CH4 depletion into the Conclusions part.

Changes to the manuscript:
- Abstract was rewritten
- Reorganization of "Results" and "Conclusions" chapters
- Conclusions were rewritten

3. The paper is quite long. The section 2 (methodology) contains a lot of details and are often not very linked with each other. I am worried the reader becomes a bit lost and feels disconnected to the objective of the paper (first results come at page 11!). I am not pushing to revised the complete manuscript structure because it is difficult but I think there are some subsections that could be either simplified, suppressed (section 2.9) or moved to section 3. E.g., section 2.5 could be summarized in five lines, not more. Several other sections could be simplified as well, for instance, on DOAS evaluations and alternative fitting windows. In my opinion, section 2.7 is really where the text is too long. It would be enough to say that tau =l/v and that it has been determined using wind vector an viewing angles (basic trigonometry). The error on tau is calculated by simple error propagation on l and v. I think Fig 4 is not necessary. As an alternative, the authors might want consider to transfer some details of Section 2 in an Annex, to improve the readability of the paper.

   Answer: The authors agree with the reviewer in this point and shortened section 2 drastically. For details, see "General remarks by the authors", point #3

4. English could be improved.

   Answer: We attempted to improve the readability by careful English proof-reading

5. Throughout the section3, the author pays a lot of attention to refer to section 2 e.g. for a term definition but I think it is too frequent and it becomes hard to read.

   Answer: We reorganized the manuscript, especially section two to improve the readability of the article (see also bullet point 3 above and our general remarks).

Minor comments

1. p2,l76-83: as it is stated now, the study of volcanic emissions seems to be useful mostly for predicting eruptions and for climate impact. I think it is not what you meant. I suggest to reformulate this sentence and underline the importance notably for ozone/oxidant chemistry.

   Answer: We like to thank the reviewer for this helpful comment. We rephrased this paragraph and included a sentence underlining the importance of volcanic emissions related to ozone/oxidant chemistry.

   Changes to the manuscript: we added a sentence in Sect. 1
   "In addition, the environment of volcanic plumes provides an unique possibility to study details of

complex chemical reaction mechanisms related to atmospheric ozone/oxidant chemistry in the presence of reactive halogen species (RHS).”

2. p2, l103-104: “In addition, we found evidences of the photochemical nature of the reactions involved.” I don’t understand this sentence. What else than photochemistry could possibly explain your observations? Please reformulate.

   Answer: The intention of this sentence was with regard to our observation of the early morning formation of BrO and OClO, which was attributed to the photochemistry involved in the formation of BrO (OClO).

   Changes to the manuscript: We removed this sentence, since it would need more detailed explanation to make the point, which was not supposed to be given in this part of the manuscript.

3. p3, sect 1.1.2, first paragraph: The release of chlorine and bromine in the gas phase is driven by Cl-/Br- ratio. I think it is an interesting part but it would be useful to give information (if available) on what could possibly determine this ratio (aerosols type, etc)

   Answer: We agree with the reviewer, that this is an important point related to halogen activation in volcanic plumes and in fact, it is one of the central questions we address. Namely, that the activation of chlorine is much weaker compared to the bromine activation, which is indicated by the comparatively low Cl and ClOx abundances we found (relative to the BrO ratios). In other words ClO/HCl is much smaller than BrO/HBr. In our opinion the main reason for this phenomenon is the fact, that Br-oxidation (conversion of bromide to Br+BrO) is a self-amplifying process (the bromine explosion) while Cl-oxidation has no such properties. The reason why Br “explodes” but Cl does not is due to the relatively fast reaction of Cl-atoms with CH4, details can be found in Platt, 2000 (Water, Air, and Soil Pollution, 123: 229-244, 2000) or Platt and Janssen, 1995 (Platt, U. and Janssen, C., 1995: Observation and role of the free radicals NO3, ClO, BrO and IO in the troposphere, Faraday Discuss. 100, 175-198). In addition the release of halogens may be influenced by the nature of the aerosol in the plume, therefore our aim is to motivate further investigations to study the dependencies of volcanic aerosols, plume acidity, etc. on the release of Cl and Br from the condensed phase. However, studying these processes would demand detailed studies of the release mechanisms of both species (e.g. in controlled laboratory experiments). These could for example be similar to the studies performed by Fickert et al. 1999 but with focus on volcanic aerosols and volcanic plume conditions. However, this is not within the scope of this study. Rather, we use existing knowledge (see e.g. Fickert et al. 1999) and typical values for Mt. Etna (e.g. Wittmer et al. 2014) and our measurement results, to show, that the release mechanisms in volcanic (represented by the abundances of BrOx and ClOx) are most likely very similar to those found in Polar Regions.

   Changes to the manuscript: We slightly changed the first paragraph in Sect. 1.1.3 (Volcanic chlorine) and added the following text:
   “Apparently, the activation of chlorine is much weaker compared to bromine. This is indicated by the comparatively low Cl and ClO_x abundances we found (relative to the BrO ratios). In other words ClO/HCl is much smaller than BrO/HBr. In our opinion this phenomenon is mainly due to

the fact, that Br-oxidation (conversion of bromide to Br, BrO) is a self-amplifying process (the bromine explosion) while Cl-oxidation has no such properties. The reason why Br "explodes" but Cl does not is due to the relatively fast reaction of Cl-atoms with CH_4 (Platt and Janssen, 1995, Platt, 2000). Moreover, the dissolved chloride ions are, however, less reactive compared to bromide ions (see R4) (von Glasow et al., 2009). Thus, Cl-release is rather likely…"

4. P4, section 2.2: it would be good to mention already here why measurements have been performed at different places. Why not at only one site?

   Answer: We agree with the reviewer and added an explanatory sentence:

   Changes to the manuscript: *"One of the main objectives of this study was to investigate the temporal evolution of oxidised halogens in the volcanic plume. Therefore, the measurements were performed at different locations in order to cover a large variety of different plume ages in the spectra."*

5. p5, l388: "saturation effects"? what do you mean?

   Answer: We would like to thank the reviewer for this hint and apologize for being unclear in this point: here, spectral saturation effects of the individual species are meant (details can be found in Platt and Stutz, 2008,). The functionality to apply this correction is provided by the software package DOASIS. We used typical SCD amounts for the convolution of the literature cross sections.

   Changes to the manuscript: We changed this sentence in Sect. 2.4 accordingly to read:
   "During the convolution, the sigma_i were corrected for the solar I0 effect and for spectral saturation (Platt and Stutz, 2008) using the corresponding functions in DOASIS. The latter was performed assuming a typical SCD for the respective species (e.g. S_{SO2}= $2x10^{18}$ molecules cm^{-2})"

6. p6, Table 1: it is not looking as a table.

   Answer: This issue has already been changed in the published version of the discussion paper

7. Figure 3: features from the Ring effect are clearly visible in the residuals.

   Answer: Ring features might be visible in the residuals and this is strongly dependent on the individual measurement conditions and the strength of the ring effect and we don't claim to be able to correct and evaluate our spectra perfectly. **However, please also note, that the optical density of this residual structure (which might be due to the Ring effect) is much smaller compared to those of BrO and OClO.**
   Nevertheless, sensitivity studies were performed to analyse possible cross influences of the fitted Ring optical densities with the retrieved OClO and BrO SCDs, no significant cross dependencies could be found (please also see Sect. 2.4.1 in the revised manuscript or Vogel et al. 2013). However, the fact, that in some cases the residuals might have been influenced by structures shows the importance of our conservative approach for estimating the corresponding fit uncertainty.

Changes to the manuscript: None

8. p7, l 514: “radiation transport effects” is vague. “Non-linear retrieval effects” would be more appropriate. The sentence l516-519 is quite odd, please reformulate.

   Answer: This whole section (SO_2 evaluation details) was reformulated in the revised manuscript and the part dealing with the evaluation problems now reads as follows:

   Changes to the manuscript:
   “… .In order to avoid the well known evaluation problems related to strong SO_2 absorption in this ``lower'' wavelength range (see e.g. Kern et al., 2010; Bobrowski et al. 2010), $SO_2$ was evaluated in a second, ``upper'' wavelength range of Delta_lambda$^{uwr}{}_{SO2}$ = 349.8-372.8 nm for SO_2-SCDs exceeding $3x10^{18}$ cm^{-2} (Hörmann et al., 2013). These problems – originating in the non-linear nature of the Beer-Lambert law – lead to an underestimation of the SO_2-SCDs in the “lower” wavelength range. This is clearly visible in the scatter plot of the SO_2 retrieval in both evaluation ranges shown in Figure A2 (i.e. flattening of the trend at large SO_2-SCDs).”

9. p10, section 2.8: a stratospheric BrO column of 7.2xE13 cm-2 is definitely too high for a mid-latitude site as Etna. Sinnhuber et al., 2005 showed such high values but it was for the total BrO column at high latitudes (hence including a contribution from polar BL BrO). However, a typical mean value of 4 xE13 cm-2 seems reasonable.

   Answer: We agree with the reviewer, which is why we did not choose the values of our own observations (which were only a few data points and showed a rather large variation) as mentioned in the text. However, since we rather followed the published results of Sinnhuber and Schofield to estimate a reasonable stratospheric BrO column, we decided to leave out the presentation of our own attempts to fit the stratospheric BrO column directly using plume free Fraunhofer reference spectra (FRS).

   Changes to the manuscript: We removed the part regarding our own attempts to directly retrieve $V_{str,BrO}$ from FRS, since it bears a too large uncertainty and variation. (Please also note, that most of the details regarding the stratospheric BrO discussion was moved from Sect. 2.8 into the appendix A5 in the revised manuscript).

10. Figure 6: I don’t understand how a BrO or OClO measurement is classified as below/above the detection limit. I would have thought that the detection limits would be fixed SCD values (BrO or OClO)

    Answer: We defined our detection limit from the DOAS fit uncertainty for each fit individually following Stutz and Platt, 1996, as introduced in section 2.4 (revised manuscript). Therefore, the detection limit varies in between individual measurements

11. p11, l839-841: this statement is untrue because only the measurements within the plume are shown here.

    Answer: We would like to thank the reviewer for this hint. In our improved version, we plotted the data including all spectra of the field campaign.

    Changes to the manuscript: New plots including all spectra (Fig. 6)

12. Table A1. For scans with only a few spectra, the statistical parameters are meaningless. I would not present them at all.

    Answer: We agree with the reviewer and would like to remark, that table A1 was removed completely in the new version of the manuscript (see also General comments, point #1.I)

13. Figure 9b. the drop of OClO after 150 s is due to dilution of the plume (low BrO and low ClO concentrations)

    Answer: We thank the reviewer for this hint, which is a very good explanation for this slight decrease.

    Changes to the manuscript: We added a sentence in the corresponding paragraph in chapter 3.1.3: *"Indications of such a decrease could also be observed in some of the individual scans and it is likely due to plume dilution (decreasing BrO and ClO concentrations)."*

14. Figure10: I'm not convinced by Figure 10 (BrO). The diurnal photochemical variation of stratospheric BrO is small for SZA 70-83_ but it is still of about 15% or so and would propagate to the observed SCDs by an AMF quite large (twilight measurements). Even if the stratospheric diurnal variation of BrO is zero, an error on stratospheric column (assumed 4e13molec/cm2) would also propagate with a dependence on SZA through the AMFs used. Sensitivity tests that include realistic stratospheric diurnal variation should be undertaken to verify the results.

    Answer: We would like to thank the reviewer for this comment. This point was considered beforehand and was found to be negligible in this case. This is because the fitted BrO-SCDs in this example are comparatively large (around 6e14cm^-2). Therefore the impact of the relatively small stratospheric contribution is rather small. However, it is true, that the stratospheric column varies for this SZA range by a factor of approximately 15% (according to Schofield (Figure 8)) for the corresponding SZA range (~83 – 79°) in which we observed increasing BrO/SO2-ratios. However, we performed sensitivity studies for this dataset and even for a stratospheric BrO VCD varying by 50% (i.e. letting the VCD linearly increase from 3e13 to 4e13) in this SZA-range (first 5 measurement points) we still clearly observed the increasing trend. Nonetheless, we agree with the reviewer, that it is important to keep in mind that the stratospheric BrO column slightly varies in this SZA range which can be of great importance when correcting volcanic BrO measurements for stratospheric columns, especially when the volcanic signal is weaker. Please also note, that this discussion was moved to the appendix in the revised manuscript.

Changes to the manuscript: In section 3.1.4 (revised version of the manuscript) we added the following text:
"In case of BrO, this increase (at large SZAs) was only observable due to the correction for stratospheric BrO signals, were we assumed a constant stratospheric BrO-VCD of $V_{str,BrO}=4.0x10^{13}$ *molecules* cm^{-2} *(see Sect. 2.8). However, according to Schofield et al., 2004, slight variations of about 10--20% in the stratospheric BrO load are to be expected during that time of day (i.e. 83.2>SZA>80.3°). Hence, to ensure that the observed increase can be attributed to variations in the volcanic column (rather than stratospheric variations) we performed a sensitivity study for this dataset by linearly varying the stratospheric VCD from 3.0 to* $4.0x10^{13}$ *molecules* cm^{-2} *during the time span of the first five data points. This test did not reveal any significant change and still clearly showed the increasing trend of the BrO/*SO_2*-ratio before 05:32 UTC. This is mainly due to the comparatively strong volcanic BrO signal of several* 10^{14} *molecules* cm^{-2} *during this measurement."*

15. Figure 10: adding SZA in a 2nd x-axis would be helpful. A third panel with OClO/BrO as a function of time could be interesting as well

    Answer: We thank the reviewer for this comment, and we agree that adding the SZA is a really good idea and was therefore included in the figures. The trend for the OClO/BrO ratio looks very similar to the OClO/SO2 trend, so therefore in this point we did not follow the reviewers suggestion, since including a third panel showing OClO/BrO would overload the figure and would distract from what we aimed to discuss/show.

    Changes to the manuscript: Top axis SZA was included in Fig. 9

16. p16, l1131-1134: I don't see how it 'underpins' the theory of bromine explosion. It simply shows the importance of local photochemistry on halogen oxides.

    Answer: We agree and removed this sentence in the revised manuscript

17. p16, l1151: '(since OClO is likely formed via the "BrO + ClO"- reaction and BrO & ClO via reaction of Br & Cl with O3).' is not necessary

    Answer: We agree and removed this sentence in the revised manuscript

18. p16, section 3.1.3: a concentration of 2.7 ppb of BrO is larger than any other published estimates.
    (1) An error bar (likely dominated by the estimated plume diameter) should be provided.
    (2) On Fig 11, error bars are shown but it is not mentioned what they represent.
    (3) I think the fact that OClO is not visible after Tau>4 is to be expected: as the plume ages, the dispersion of the plume makes the concentration of BrO and ClO lower and OClO drops below detection limit very quickly (production rate is non-linear: k[BrO][ClO]). This should be underlined.

Answer: We thank the reviewer for this helpful comment and agree that a BrO concentration of 2.7ppb is quite large.
(1) We included the corresponding uncertainties (which are – in fact – mainly determined by the uncertainties in the plume diameter estimation) in the text.
(2) The uncertainties were determined using Gaussian error propagation of DOAS fit errors and uncertainties in the plume diameter estimation.
(3) The discussion about the drop in the OClO/ClO ratio at tau=6min was removed (only one measurement point, large uncertainty, see also review 3, comment #25).

Changes to the manuscript:
- Uncertainties of reported minimum/maximum values of the derived concentrations were included
- Details about the determination of the error bars (Fig. 11) were included in the caption and in the respective paragraphs (sect: 2.5 and 2.6)
- Removed discussion about OClO drop at plume age of 6 min

19. p18, section 3.2: the detection limit of IO is an order of magnitude better than for OIO and OBrO, and after looking at the absorption cross-sections, it is clear that it is due to the different performances (SNR) of the instrument in the UV and Visible. This should appear in the text.

    Answer: We agree with the reviewer and added an explanative sentence

    Changes to the manuscript: We added a sentence:
    "Note that the UV spectrograph showed a better performance (S/N-ratio) than the VIS spectrograph, which is indicated by the lower detection limits for IO compared to OIO and OBrO."

Typos

We would like to thank the reviewer to call attention to the following typos which were corrected in the revised version of the manuscript.

1. p2, l75: "difficulties often are associated" ! "difficulties often associated".
2. p2, l133: I wonder whether footnotes are allowed in ACP(D). I suggest you include a sentence on BrO/SO2 ratio directly in the text.
3. p3, l156: "aquatic" ! "aqueous"
4. p3, l170: R4f ! R4
5. throughout the manuscript, the term "radiation transport" is used but in usually "radiative transfer" is preferred by the scientific community.
6. for all numbers provided decimals (e.g. correlation coefficients, slope of linear regression), only two digits are needed.

7. p12, l899: “tropospheric ozone O3 “ ! “tropospheric O3“

Anonymous Referee #2

Received and published: 4 November 2014

This manuscript presents results about the chemistry of halogens in volcanic plumes, focusing on the formation of reactive halogen species (RHS, e.g. BrO, ClO, OClO) from the primarily emitted species (e.g. HCl, HBr) and their evolution in the ageing plume. This very important topic was initiated when bromine monoxide (BrO) was detected in the plume of Soufriére Hills volcano, Montserrat (Bobrowski et al., 2003). Up to now BrO was detected in plumes of many volcanoes. Most of the authors of published papers agree that numerous aspects of photochemistry of RHS are still not properly understood due to difficulties of the measurements, sporadic nature of the studies conducted and at last but not least the complexity of the chemical processes related with RHS genesis and transformations. The experiments in this study have been conducted by means of multy axes DOAS, which is probably the best way to investigate RHS in volcanic plumes. However, the descriptions of experimental technique and some discussions in this manuscript are rather poorly justified and sometimes misleading, in particular for the ever increasing number of DOAS users in the volcanology society. The manuscript is an interesting contribution to the topic of RHS photochemistry and deserves to be published in the journal Atmospheric Chemistry and Physics pending some moderate to major revisions. See attached pdf for the full series of comments and suggestions.

Review of J. Gliß et al., OClO and BrO observations in the volcanic plume of Mt. Etna – implications on the chemistry of chlorine and bromine species in volcanic plumes

General Comments and Recommendation

1. The description of the formation of BrO in volcanic plumes is not full – e.g. the reaction involving ultraviolet radiation is missing. This reaction is the basis for the explanation of the increase of BrO early in the morning . A very good description of formation of RHS in volcanic plumes is presented by L. Sulf et al. (this journal 14, 23639-23680). At the same time the formation of BrO is regularly explained in all papers reporting BrO in volcanic plumes and in the original papers of Wennberg, von Glasow and others. Why not just provide a reference?

   Answer: We would like to thank the reviewer for this comment. We added the Br2 photolysis reaction to complete the description of the bromine explosion. We think it is important to provide these reactions in this context, since we quite often refer to them in the article. References to the original papers (Lehrer, 1997, Wennberg 1999) were already included in the originally submitted version of this article (P. 25217, L. 16), the reviewer might have overlooked those.

   Changes to the manuscript: We included the Br_2 photolysis reaction (R5, Sect. 1.1.2)

2. The estimation of BrO and OClO concentration is based on the assumption of circular plume but all cross sections reported in the manuscript (c.f. figures 7 and 8) are strongly suggesting that plume has a form quite different from the circular. Thus the reported values are rather not realistic.

Answer: In this point, the authors disagree with the reviewer and we wish to remark that all these figures (apart from Fig. 8f [i.e. Fig. 7f in the revised version of the manuscript]) show plume evolution scans, were we scanned along the plume propagation axis. The plume cross section scan shown in Fig. 7f (revised manuscript) is perfectly consistent with a circular plume cross section. As clearly described in the document, we only used plume cross section scans to estimate the plume diameter. Thus, we are convinced that our reported values are realistic.

3. The statement that it is possible to measure and to estimate corresponding mean and standard deviation of some parameter below the detection limit is nonsense from statistical point of view (c.f. figures 7, 8, and 10). This means that the threshold definition is wrong or threshold limit itself is not estimated properly.

   Answer: Strictly speaking, the reviewer is right in this point. This issue (of discussing trends etc. of measurement points below our detection limit) is discussed in our general remarks (at the beginning of this document) and we revised the text in the current version of the manuscript accordingly. However, we want to emphasize again that our threshold definition is conservative (as the reviewer suspected), hence they are in the range of the largest, but still justifiable errors (see Stutz and Platt, 1996).

   Changes to the manuscript: We made changes to the manuscript as described under “General remarks by the authors”

4. The reported increase of XmYn/SO2 (BrO/SO2 and OClO/SO2) ratios at the edges of volcanic plumes is a tendency that needs further verification at different atmospheric conditions and in plumes of different volcanoes. The reported results are not totally convincing. Plume edges in figure 8 look rather as tails of the plume caused by its drifting due to the wind variations. The quite long time required for collection of a single spectrum (2.5 minutes) and the scanning angle increase by 4 degrees are also prompting for probable missed plume structure. Also, in cases when it was possible to access plume edge by scans perpendicular to plume direction, an increase of BrO/SO2 is observed only in 30±18% of the cases whilst decrease or no change in 16% and 8% respectively. This means that it is possible to talk about tendency only and further investigations are necessary.

   Answer: Here we agree with the reviewer and again refer to our general comments were the changes related to our discussion of plume cross section scans is explained

   Changes to the manuscript: See “General remarks by the authors”

5. The reported stratospheric BrO column amounts are up to two times larger that the mean values reported previously by other authors. Is it possible that this fact is compromising the reported variation of BrO early before sun rise?

   Answer: This issue was already dealt with in point 9 of the answer to Review #1 (Minor comments)

Changes to the manuscript: For the reasons explained in point #9 in Review #1, our own attempts to fit the stratospheric BrO column from FRS were removed in the revised manuscript.

6. The description of DOAS retrieval will arise many question by DOAS users. I suggest that part of the manuscript should be significantly improved by paying particular attention to the following:

6.1. It is stated that the used spectrographs is Avantes 5 AvaBench-75-Ultra Low Straylight. Probably the authors refer to AvaBench-75-ULS-2048. This means there are about 6 pixels per instrumental slit function in UV (0.51 nm) and VIS (0.31 nm). These numbers are on the limit when it is necessary to account for undersampling effect. Please elaborate its ignoring.

Answer: We like to thank the reviewer for this correction. We corrected the spectrometer name to "Avantes AVA AvaBench-75-ULS2048x64" for the UV and "Avantes AVA AvaBench-75-ULS2048L" for the VIS spectrometer. An adjustment of the spectrometer was performed to achieve a constant spectral resolution over the spectral range within 10% and to have a relative symmetric line spread function, optimised for DOAS applications. It is correct that the sampling is ~6 channels and thus above the limit of the minimum of 5 channels to avoid undersampling (for details see e.g. Platt and Stutz 2008). As the instrument function is very symmetric and similar in shape to a gaussian function, this sampling is sufficient to avoid undersampling effects.

Changes to the manuscript: We corrected the spectrometer names

6.2. Please explain how the absorption cross sections have been corrected for saturation effect.

Answer: The software package DOASIS provides a saturation correction when convolving a high resolution literature cross section with the line spread function (instrument function) of the spectrograph. To do so, an estimate of the expected column amount of the trace gas species has to be provided (for details see Platt and Stutz 2008, ch. 8.4.2). These were chosen for each species according to the typical amount to be expected (e.g. 2e18 molec/cm^2 for SO_2)**.**

Changes to the manuscript: We added one explanatory sentence in Sect. 2.4 :
"During the convolution, the sigma$_i$ were corrected for the solar I_0 effect and for spectral saturation (Platt and Stutz, 2008)) using the provided function of DOASIS. The latter was performed assuming typical SCDs for the respective species (e.g. 2e18 molec/cm^2 for SO_2)."

6.3. Why it is necessary to perform Io-correction when convolving all absorption cross sections (especially the strongest SO2 one) included in the fit. Originally the Io-correction was used to correct the fit of weak absorbers (stratospheric BrO).

Answer: Measurements of weak absorbers in volcanic plumes require the same I_0 correction of strong absorbers as stratospheric measurements. The strong SO_2 absorption has to be accounted for precisely in order to correctly evaluate the weak absorbtions due to BrO and OClO. When evaluating stratospheric species the situation is similar just that O_3 (rather than SO_2) is the strong absorber and it is therefore recommended to be corrected for the I0-effect (see e.g. Aliwell et al., 2002: *Analysis for BrO in zenith-sky spectra: An intercomparison exercise for analysis improvement*).

Changes to the manuscript: None

6.4. The origin of R4 Ring effect and the improvements achieved by its usage.

Answer: The R4 spectrum is a first order correction (in addition to the "usual" Ring spectrum) to account for multiple scattering events, or scattering on aerosols, cloud particles etc., which is not considered in the determination of the Ring spectrum (see also Wagner et al. 2009, Appendix B). We found that inclusion of the R4 spectrum in the fit improves the fit results further.

Changes to the manuscript: We reworded the paragraph regarding the R4 spectrum (now in the Appendix A1) to read:
"The R4-spectrum accounts for influences due to multiple scattering and/or scattering on aerosols and cloud particles which are not considered in the determination of R."

6.5. Explain necessity of using two O4 absorption cross-sections (table 2).

Answer: Different cross sections show different accuracy for different spectral regions. We found that different cross sections for the UV and visible spectral range give best results.

Changes to the manuscript: we added a sentence in Sect. 2.4.1 (revised manuscript):
"Note, that in case of O_4 two different literature cross sections were used because we found that different cross sections for the UV and VIS spectral range give best results."

6.6. The used absorption cross sections are measured by different authors and are loaded with individual errors (especially with respect to wavelength calibration). As a result linking the shift of all cross sections included in any particular fit to the shift of the strongest one could be a quite arguable decision. Please elaborate the reasons.

Answer: We agree with the reviewer that the different literature cross sections from different authors can have different errors on the wavelength calibration, although these errors are very small for modern cross sections. However, all cross sections should have a fixed true relative wavelength position in relation to each other. It makes physically no sense to allow a free shift of the different absorbers to each other. It is a typical source of error in DOAS evaluations to allow too much degrees of freedom and this should be avoided. However, we evaluated whether we could improve the quality of the fit by introducing a relative shift between the literature cross sections, but found the best results for relative wavelength shifts of zero using consistently air wavelength. Thus the relative shift was set to zero and all literature cross sections shift together.

Changes to the manuscript: None

6.7. Explain the meaning of zero-order polynomial and the improvements achieved by its usage. Is this actually the offset polynomial?

Answer: Yes, this is the offset polynomial fitted in intensity space (as it is already mentioned in the text). The offset polynomial improved the quality of our fit results.

Changes to the manuscript: We added the corresponding sentence in Sect. 2.4 (revised manuscript) to read: *"An additional 0th-order polynomial residing in intensity space was included (in literature often also referred to as offset polynomial) to account for intensity offsets in the spectra (e.g. due to stray light, for details see Kraus, 2006, Platt and Stutz, 2008)."*

6.8. Why formaldehyde is included in the fit. Explain the origin of H2CO in volcanic plumes.

Answer: Formaldehyde is a normal component of the air, in addition it is likely to be formed in a well known reaction mechanism initiated by the oxidation of methane (in volcanic plumes by the reaction of $Cl+CH_4$, see R10 in the conclusions of our manuscript) and in the presence of nitrogen oxides (see e.g. Platt and Stutz 2008). Thus, H_2CO could very well be formed within a volcanic plume.
In fact, H_2CO was often significantly visible in our measured spectra, for instance when the measurements were performed within cities (e.g. 19.9) or even partly at the observatory, when the diesel generator was running.

Changes to the manuscript: None

6.9. The three gases of interest SO2, BrO and OClO are fitted in three different fitting windows but these gases are abundant in the same plume at the same time instance, i.e. the retrieved SO2 column amount has to be the same in all fitting windows. To my knowledge only WinDOAS and Q-DOAS are capable to perform the fit in this manner. How this issue was resolved when using DOASIS.

Answer: DOASIS can handle the situation that column densities (SCDs) are equal in different fitting windows, e.g. by prescribing SCDs. However, the point here is another one. The derived column densities are not necessarily the same for different fitting windows. First, the light paths can be different as radiative transfer is changing significantly in the UV spectral range. Second, strong saturation effects can arise at large SO_2-SCDs (which is why we defined a second SO_2 evaluation range for large SO_2-SCDs). Thus, slight differences in the column are expected, and using the same column as fixed value in other fit scenarios in different wavelength regions would produce significant errors.

Changes to the manuscript: None

6.10. The radiative transfer effects (RTE) are totally ignored in this work. According to figure 1 some measurement locations were more than two kilometres from the Etna's craters. The distances to the plume have to be reported for each location and the neglecting of RTE has to be explained in details. Please refer to Kern et al., 2008, who proved the necessity to account for RTE in all DOAS retrievals. The fact that RTE effects are ignored in this manuscript may be accepted in a very wrong way – recommendation just to ignore them as unnecessary complication when interpreting the retrieval results.

Answer: We agree with the reviewer in the point, that RTE is an important topic and can have significant impacts on DOAS retrievals and other remote sensing techniques such as SO_2-cameras (as discussed by Kern in several articles), which aim to estimate absolute values (e.g. SO_2-flux rates). In both techniques, multiple scattering (due to aerosols) in and around the plume as well as the – in recent literature often mentioned – light dilution effect affect the results.

However, the discussion of our results relates mostly to ratios of BrO and OClO to SO_2. The corresponding wavelength evaluation ranges are very close to each other and impacts on the retrieved and discussed ratios caused by differences in the RT between different evaluation ranges were found to be smaller than the errors and uncertainties in the DOAS retrieval (see also Lübcke et al. 2014, BrO/SO2 molar ratios from scanning DOAS measurements in the NOVAC network, Solid Earth , 5, 409-424, 2014).

Furthermore, it is wrong, that RTE were completely ignored (as explained in the manuscript) since SO_2 was evaluated in two different wavelength ranges (one at shorter and one at longer wavelengths compared to the BrO and OClO retrieval). Looking at Figure A2 (scatterplot of SO_2 retrieval in both wavelength ranges) it is clearly visible, that any potential differences in the retrieved SCDs in both ranges are smaller than the corresponding DOAS errors. Only the case of large SO_2-SCDs, were – as discussed in the manuscript – SO_2 directly influences the RT, differences in the SO_2-SCDs become significant, which shows the importance of our approach to avoid using the falsified values from the lower evaluation range when the SCDs exceed several 10^{18} molec/cm^2.

Only for the estimation of absolute concentrations (Sect. 2.5 in the revised manuscript) RTE might impact to a certain degree and this issue is discussed in the corresponding section 3.1.5 of the revised manuscript were we are discussing the results of our retrieved mixing ratios. However, we agree that – for the derived concentrations – this is an important issue and needs some more explanation, therefore we included a small additional paragraph in Sect. 3.1.5. addressing these uncertainties and furthermore providing the maximum plume distances both for data from the observatory and for the data collected during the other days of the campaign. In our discussion of these potential effects (see below) we mainly rely on Kern et al. 2012, in particular their discussion of RTE in the conclusions section therein, where they found errors between 20% for plume conditions as shown in Fig. 9a therein and 90% (Fig. 9b respectively). In our revised document we thus estimate the corresponding error to be smaller than 100% (factor of 2), please also note Fig. 1 in our revised document, showing a photo of the slightly condensed plume, as it was during most of the measurements performed in September 2012.

However, we want to remark that for the discussion of our main results (i.e. young plume increase, formation times, Cl atom concentrations, methane depletion) we only refer to the data collected at the observatory close to the plume, where at least light dilution effects should be small due to the proximity to the plume. Therefore, we do not see any additional outcome in providing detailed information about individual plume distances and we think, it is enough, to provide the maximum distances for the observatory data (as was done).

Changes to the manuscript:

Regarding the ratios, we added a sentence in section 2.9.:
"Furthermore, compared to the SCDs, the X_mO_n/SO_2*-ratios are much less affected by radiative transfer effects (RTE) such as light dilution or multiple scattering (Lübcke et al., 2014)."*

Regarding the absolute concentrations, we added a small paragraph in Sect. 3.1.5.:
"The comparatively large errors of the derived mixing ratios (see Fig. 10) are due to our conservative estimation of the SCD-errors (for details see Appendix A2) and the uncertainties in the plume diameter estimation (e.g. due to deviations from the circular shape). We want to remark, that radiative transfer effects (RTE, e.g. multiple scattering, light dilution, for details see Kern et al., 2010; Kern et al., 2012) were ignored in the determination of the mixing ratios. However, for the observatory data (11--13 September 2012, i.e. tau<4 min range in Fig. 10, we assess potential deviations due to RTE to be smaller than 100% (factor of two), relying on the findings of Kern et al., 2012. This is due to the fairly good measurement conditions (i.e. low plume condensation, see e.g. Fig. 1) and furthermore, because of the proximity to the plume (mean distance to plume: d = 2:03 km; dmax < 3:2km) and the high altitude at the measurement location (i.e. 2.800 m a.s.l., i.e. lower scattering probability).

However, the measurements performed in the aged plume (i.e. data points at tau > 4min in Fig. 10) are likely influenced by the light dilution effect since they were partly performed at sea level and at greater plume distances (up to 17 km). Thus, the observed decrease of the BrO mixing ratios in the ageing plume (see Fig. 10) is most likely not solely caused by decreasing concentrations (due to plume dilution) but to a certain degree also due to light dilution."

Specific Comments

1. Provide reference for MS-DOAS software or describe it briefly.

   Answer: We added a short explanation about the features of MS-DOAS.

   Changes to the manuscript: Sect. 2.1: *"MS-DOAS was developed by U. Frieß at the Institute of Environmental Physics in Heidelberg and is designed to control standard hardware components used* *in DOAS instruments (e.g. spectrographs, motors, temperature controller, gps receiver). Furthermore, it includes a scripting feature making it easily possible to automate measurement and scanning routines."*

2. Explain how a UV camera may be used to estimate the wind direction – UV camera is registering 2D-projections.

   Answer: This issue has already been clarified as to be a result of the first review. We did not use the SO_2-cam to derive wind directions, but only velocities, the wind directions were retrieved from satellite pictures, own observations/field notes and later also using a meteorological station.

   Changes to the manuscript: The sentence was reworded in Sect. 2.7 (revised manuscript) to read: *"Wind velocities were partly retrieved from simultaneously performed SO_2-camera measurements and from own observations."*

Anonymous Referee #3

Received and published: 12 November 2014

In this manuscript, the authors present the results MAX-DOAS measurements targeting halogen oxides in the plume of Mt. Etna. What sets these measurements apart from most previous ones is that they were performed in geometries specifically targeting the spatial distribution and temporal evolution of halogen oxide concentrations within the plume. The results are interesting, as is the discussion about chemical formation mechanisms and implications for atmospheric chemistry at large (specifically methane destruction). In my opinion, the manuscript has one fairly major overarching deficiency. Throughout the entire paper, spatial and temporal trends are interpreted that appear to be statistically insignificant. In several places, the authors argue that the trends might still be significant, even though the values either lie below the detection limit of their measurement technique, or the observed trends are smaller than the errors associated with the individual measurements. Such argumentation does not hold up to scientific standards and needs to be revised. Please see the supplementary material for additional comments, specific corrections and suggestions for improvement.

Review of

OClO and BrO observations in the volcanic plume of Mt. Etna – implications on the chemistry of chlorine and bromine species in volcanic plumes

J. Gliß, N. Bobrowski, L. Vogel and U. Platt

General comments

I feel that there are two avenues for improvement, one or both of which could be explored to improve the manuscript.

1. For one, the error treatment could be improved. Section 2 is already quite extensive, and clearly the authors have put much thought into accurately assessing the errors associated with their measurements. This is very important, as much of the measurement results are close to the detection limits of the instrument. However, perhaps the error assessment is overly conservative? In any case, it stands in contrast to the interpretation of the results that occurs later on. Improving the methodology for determining realistic errors might help consolidate this apparent conflict. The other potential path towards consolidation is a reduction of the data into larger sample sizes. As it currently stands, the authors first evaluate trends found in individual plume scans, then evaluate trends in the aggregate of all their measurements. Due to the improved statistics, the interpretation of the aggregate dataset is significantly better constrained. The question then arises whether an interpretation of individual scans is even necessary, and what value it adds to the paper. It appears the authors could arrive at most of their conclusions without the need for unfounded interpretations of individual scans. Since the manuscript is quite long already, either removing the discussion of individual scans or moving it to an appendix could streamline the study, moving the scientific findings more into the foreground.

Answer: We really like to thank the reviewer for these helpful comments (as well as the follow up comments related to the topic of data appearing to be statistically insignificant), which helped us to restructure the presentation and discussion of our results by largely removing misleading discussions based on individual scans and trends derived from data apparently below the detection limit.

However, in our opinion, the error estimation (i.e. the threshold definition) is conservative, but not overly conservative, rather it is in the range of the largest justifiable errors (following Stutz and Platt 1996, Fig. 10 therein). This is a result of the limited resolution of the instrument and the presence of fit residual structures in some of our measurements. Following a conservative approach (which we wish other authors would follow as well), we therefore chose to use fit correction factors between 3-4 rather than 2-3. Due to the large number of data-points, it was unfortunately not possible, to analyze each fit residual individually which could be a promising method to estimate the fit correction factor for each spectrum individually and which most likely would reduce the estimated errors in some of the individual scans (this actually was the reason of our delicate discussion about relative trends, absolute errors etc. in the previous version). In our opinion, a method to analyze all residuals individually would be one way to estimate the fit errors more accurately for each individual measurement. However, as the reviewer already suggested, the method of larger samples is another possibility to reduce uncertainties and we followed these suggestions in the revised manuscript. For further explanations related to the new document structure we refer to our general comments at the beginning of this document.

Other than this conflict between error assessment and data interpretation, I only have two other relatively minor general comments.

2. The organization of the manuscript might be improved by more clearly separating measurement results from conclusions. As it currently stands, the conclusions section 2 really just repeats the previously described results. One example is the estimation of Cl atom concentrations and relatively slow CH_4 depletion – this is more of a conclusion than a measurement result, and this section could be moved.

   Answer: This issue is also addressed in our "general comments" at the beginning of this document. We reformulated the conclusions and moved the discussion of Cl atom concentrations and CH_4 depletion into the conclusions.

3. The readability of the manuscript could be improved by careful English language proof-reading.

   Answer: We attempted to improve the readability by careful proof-reading

Specific comments

1. P25215 L26 – Here you mention volcanic risk assessment and prediction of eruptions. These are two different things. Risk assessment is the assessment of potential risks to populations, e.g. certain areas could be affected by lahars, others by ash fall. Hazard maps are a good example of risk assessments. Please explain how gas emissions and plume chemistry can be helpful for risk

assessments. Do you mean direct risk to populations from toxic gases? If so, please cite an appropriate reference. With regard to eruption prediction (better: eruption forecasts), there are examples where gases helped a great deal. The references you cite here may not be the best. Especially Carroll and Holloway (1994) is a book that, as far as I am aware, does not deal with risk assessment or forecasting at all. But perhaps I am wrong? Please either cite the chapter you mean or give a better reference.

Answer: We would like to thank the reviewer for this comment and remark, that in the revised manuscript, this part of the manuscript was rephrased, more focusing on atmosphere/climate and chemistry. The phrase "Risk assessment" was removed, it was not our aim to resolve details related to this topic, rather we wanted to give a motivation for our studies.

Changes to the manuscript: The introduction was rephrased accordingly.

2. P25217 L7 – You mention that photochemistry is involved in BrO formation, but do the references that you cite really "confirm" this fact? An increase in BrO/SO2 ratio during plume evolution doesn't really imply a photochemical reaction at all, or does it? Perhaps the active LP-DOAS measurements performed by Kern et al (2009) at Masaya (which you mention later) are more relevant in this context?

   Answer: We agree with the reviewer, that Kern et al 2009 is an important article related to this topic and we followed the suggestion and included the corresponding citation.

   Changes to the manuscript: Please note, that this whole paragraph was slightly reformulated, for details see "General remarks by the auhors".

3. P25218 L15 – Is a release of BrCl really only found for Cl/Br ratios of the order of 1e4? What about larger ratios? Perhaps better to say the release is only effective for Cl/Br > 1e4?

   Answer: We like to thank the reviewer for this attentive comment and followed his suggestion.

   Changes to the manuscript: We modified the text accordingly in Sect. 1.1.3 (revised manuscript).

4. P25224 L14 – How does DOASIS calculate the Ring spectrum? Why are two Ring spectra needed? If only R4 accounts for the wavelength dependency of the Rayleigh cross-section, why is R needed?

   Answer: DOASIS calculates the Ring spectrum from the measured FRS (Kraus, 2006). It is calculated according to the given information in DOASIS by: Bussemer M.,Der Ring Effekt: Ursachen und Einfluß auf die Spektroskopischen Messungen Stratosphaerischer Spurenstoffe, Thesis, IUP, University of Heidelberg, 1993.
   Details on the necessity of the R4 spectrum and changes applied to the manuscript can be found in our answer to Review #2, point 6.4 the corresponding literature reference is Wagner et al. 2009.

   Changes to the manuscript: See Review #2, point 6.4

5. P25225 L10 – I believe you mean an “additive polynomial in intensity space”.

   Answer: Yes, this is correct, to make it more clear we changed the sentence in Sect. 2.4

   Changes to the manuscript: *“An additional 0th-order polynomial residing in intensity space was included (in literature often also referred to as offset polynomial) to account for intensity offsets in the spectra (e.g. due to stray light, for details see Kraus, 2006, Platt and Stutz, 2008).”*

6. P25225 L13 – Section 2.4.1 is very important for the rest of the manuscript, as this is where the error treatment is derived. Citing Stutz and Platt (1996), you state that the measurement error is not given by the photon noise of the optical measurement, but is instead related to absorption structures of the trace gases. Then, a seemingly arbitrary choice of correction factors U is introduced whereby U is related to the peak-to-peak value of the residual. It does not become clear from the text why these values for U were chosen. Stutz and Platt (1996) derived a relationship between the frequency of the residual, the frequency of the respective absorption cross-sections, and the correction factor U. They did not derive a relationship between the peak-to-peak value of the residual and U. Any such relationship therefore needs to be justified in the text. For the sake of the later interpretations, it would probably be useful to discuss both accuracy and precision here. If the authors feel that the precision is greater than the accuracy of the measurement, a separate method for deriving the measurement precision should be investigated. This could possibly be based on the magnitude of high frequency shot noise in the measurement residual. In any case, the discussions in this section need to result in an adequate and well-motivated method for deriving the overall accuracy of an individual SCD (how close to the true SCD?), the precision of individual SCDs to one another, and the detection limit. By definition the detection limit is understood to be the limit above which a positive detection is obtained (perhaps, as you say, with 95% confidence). By definition, all measurements below the detection limit are non-detections, meaning that the SCD is equal to some unknown value below the detection limit. All measurements below detection limit are equal in this sense, and investigation of trends below the detection limit doesn’t make much sense.

   Answer: We like to thank the reviewer for this comment and would like to refer to our answers related to this topic in the previously discussed reviews #1 and #2 and to our “general remarks” in the beginning of the document. To summarise these points: regarding the selection of the fit correction factors, we followed Stutz and Platt, 1996, taking into account the optical resolution of the instrument (FWHM of the line spread function (LSF)) and the typical width of residual structures, which could be found in some of the measurements (resulting in a worst case correction factor of U=4, see Fig. 10 Stutz and Platt, 1996). Choosing a conservative approach (because there are not much OClO measurements yet and we wanted to ensure to avoid “false” detections) we thus decided to use the largest – but still reasonable – correction factors between U=3-4. These were selected in dependence of the peak-to-peak values of the residual, because they were found to be correlated with the presence/abundances of fit residual structures (see e.g. fit example Fig. 4 in the revised document). This conservative approach was assessed to be sufficient for our data/instrument and we reformulated the paragraph providing some more explanations on how these correction factors were chosen/justified.

Unfortunately, to our knowledge, there is no other published literature related to volcanic MAX-DOAS measurements using another method to derive their errors for each measurement individually, so we followed the common approach by using a fixed fit correction factor (see e.g. Donovan et al. 2014) with the only difference, that we varied these in dependence of the peak to peak residual (but still staying in the conservative regime). However, we agree with the reviewer, that investigations to derive more precise individual fit correction factors for each measurement (i.e. as suggested by the reviewer, in dependency of the shot noise in the residuals) are very promising. Unfortunately, it was not possible, to investigate this issue (develop and verify an easy to implement and individual fit correction estimation procedure for each measurement) within the scope of this study which is why we followed the approaches used in other published literature (e.g. Donovan et al. 2014).

However, in the revised manuscript, we largely reduced the discussion of trends etc. of individual scans above or below this detection limit (following the general suggestions of the reviewer) and rather argued on the basis of our more robust statistical analysis (see also general comments at the beginning of the answer to the comments of reviewer #3).

Changes to the manuscript: We reformulated the paragraph on "Error treatment" (which was moved into the Appendix A1 in the revised document). Furthermore, we reformulated the corresponding paragraph in the revised document to read:
"Following Stutz and Platt, 1996, the retrieved fit errors (sigma$_{fit}$) were multiplied with a factor of U = 4 to have a conservative estimation of the measurement uncertainty sigma$_{meas}$ = U x sigma$_{fit}$. In case of good fit results (i.e. low peak-to-peak values in the fit residuals) the correction factor was reduced down to U = 3 (still a conservative error estimation, details are discussed in Sect. A2). The corresponding detection limits were defined to be twice the measurement uncertainty (2 x sigma$_{meas}$) thus, representing a detection certainty of 95 %."

7. P25227 L12 – I recommend removing Section 2.4.3. and figure A1. If this alternate wavelength region gave less reliable results, there is really no reason to discuss it further. If the authors feel strongly about mentioning the fact that this range was found to be less suitable, then a single sentence in section 2.4.2. would suffice.

   Answer: This issue was discussed in our "General remarks" (at the beginning of this document) and changes were applied accordingly. We moved section 2.4.3 into the appendix A3. However, we decided to keep the corresponding scatterplot Fig. A1 due to the fact, that not much reports on volcanic OClO are published in literature yet and because it is well known, that interferences between different absorbers and/or Fraunhofer lines in the DOAS retrieval can lead to significant deviations in the DOAS fit of a certain species in different wavelength regions and/or fit scenario settings. Furthermore, this information might be interesting in the light of the few other studies related to volcanic OClO measurements, since Theys et al. 2014 (DOI: 10.1002/2013GL058416) for example used this upper wavelength range for their OClO retrieval.

   Changes to the manuscript: The paragraph 2.4.3 was moved into the appendix

8. P25230 L15 – Radiative transfer effects can only be neglected for these two species if their optical depths are small, i.e. they are both "weak absorbers". This is the case for you data, but should also be mentioned in this context.

   Answer: We removed this paragraph in the revised document and refer to the short discussion of possible influences of radiative transfer effects (RTE) in Sect. 3.1.5.
   However, the author might have misunderstood our initial intention, namely to stress, that we did not consider RT effects at all here, which are unfortunately not always negligible even if the absorbers are weak (e.g. light dilution, multiple scattering in the plume).

   Changes to the manuscript: None, because this paragraph was removed in the revised version of the manuscript

9. P25231 L25 (footnote) – Why must vertical plume propagation be negligible for your approach to work? I don't understand how vertical plume rise (be it convective or buoyant) would affect the age of a plume measured at a well-defined horizontal distance from the vent. Is this because you are assuming a varying vertical wind profile?

   Answer: We like to thank the reviewer for this comment, we agree with the statement and thus, we removed this sentence in the revised version of the manuscript.

   Changes to the manuscript: The corresponding sentence was removed in the revised version of the manuscript.

10. P25233 L21 – It is unclear how SO2 camera measurements can be used to accurately derive wind speed and wind direction, given that the images always represent a projection of the 3D scene into two dimensions. Please explain how this was done.

    Answer: We apologise for being unclear in this point: we did not use the camera data to derive wind directions but to derive wind velocities when the wind direction was known or could be estimated. As being part of a re-structuring of the part about plume age determination, this issue was explained more clearly.

    Changes to the manuscript: We re-structured this part in Sect. 2.7 to read:
    "Wind velocities were partly retrieved from simultaneously performed SO_2-camera measurements and from own observations."

11. P25235 L2 (Eq 7) – I'm not sure why gamma is introduced here. This is simply the difference in stratospheric AMF between measurement i and measurement j. Consider using ?AMFij or similar.

    Answer: The authors do not agree with this suggestions and decided to keep using gamma here, since AMF is rather the acronym for "air mass factor" than a mathematical symbol and should, in our opinion, not be used in formulae, plot labels etc.

A similar example is the acronym “SCD” for slant column densities, were we strongly feel, that rather the symbol “*S*” should be used in the plots and formulae.

Changes to the manuscript: None

12. P25235 L6 to P25236 L17 – I was not able to follow the argumentation in this section. First of all, I don’t understand how the range of stratospheric BrO VCDs was arrived at. Deriving a VCD according to Equation 7 assumes that this VCD is constant over the time between measurement i and measurement j. In principle, any permutation of i and j is possible, even spanning completely different days. Is this how the VCDs were determined? Or were only consecutive spectra evaluated against each other? In other words, how was the subsample of spectra used for this calculation determined, and how were the individual spectra paired? And why was this combination chosen? In the second part of the text, a sensitivity study of stratospheric BrO VCDs on the measurements is attempted, as shown in Figure 5. However, it is a bit unclear why plotting dSstr/Smeas is useful here. Wouldn’t it be better to discuss the potential errors in the BrO SCDs caused by an inaccurate stratospheric correction? For example, one might say that, based on the range of retrieved stratospheric BrO VCDs, the 4e13 molec/cm2 VCD assumed for the correction has an approximate error of ±2e13 molec/cm2. Then, one can calculate how such an error would influence the stratospheric correction of a given BrO SCD, and adjust the previously derived SCD error appropriately in all plots. This does not appear to be the route the authors have taken here, and I do not understand their approach.

    Answer: We would like to thank the reviewer for this comment and would like to refer to review #1, points 9 and 14, where we already handle this issue. As a result, we removed the presentation of our own attempts to derive the stratospheric VCD completely and instead used the values provided by Sinnhuber and Schofield. In our opinion, our presentation of the impact of stratospheric BrO (i.e. Fig. 5) is appropriate to visualize the relative contribution of an assumed constant stratospheric BrO column of $4x10^{13}$ cm^{-2}, as it gives directly the percentage amount and visualizes the larger impact on smaller measured SCDs compared to large measured BrO-SCDs. Sure, this is only an approximation, but we could show that it can cause non-negligible deviations compared to not correcting at all. The sensitivity studies performed show, that any potential uncertainties in our assumption (e.g. varying BrO-VCD) are still within our errors and therefore we would like to keep our presentation as it is now (however, please note the changes implemented due to the above mentioned points of review #1).

    Changes to the manuscript: See answer to review #1, points 9 and 14

13. P25237 L25 – If BrO was only detected within the plume, does this mean that any potential error in the stratospheric correction smaller than the BrO detection limit?

    Answer: No, but in order to detect a significant amount of BrO in a spectrum of radiation, which has not penetrated the plume at all, this spectrum has to be recorded at a quite different SZA than the corresponding FRS (see also previous point). This was only the case in the really early morning or late afternoon measurements. In case of our dataset (presented in the corresponding scatterplot, Fig. 6) all spectra recorded at these conditions show large SO_2 columns, hence were solely recorded within the plume and therefore actually also include a large volcanic BrO contribution.

Changes to the manuscript: None

14. P25238 L18 – Wouldn't errors in the wind speed cause a stretch/squeeze of the dataset, not a shift?

    Answer: We like to thank the reviewer for this comment, we agree and changed the text as suggested (please note, that – due to restructuring – the corresponding section 3.1.1 was renamed to "Results from individual scans")

    Changes to the manuscript: We made the appropriate changes to Sect. 3.1.1 "Results from individual scans".

15. P25238 L19 to P25239 L2 – The given discussion of Figure 7 is a good example of over interpretation of uncertain data, as mentioned in the general comments above. The authors write "Figure 7 shows an increase of the OClO/SO2 ratio up to a plume age of 120 s and a slight decreasing trend afterwards". I would argue that, as depicted in Figure 7, OClO was not detected for plume ages shorter than 120 seconds, and was then constant within the uncertainty of the measurements up to an age of 200 seconds. This is a significant difference. In fact, in the presented plot, it appears that the non-detection of OClO for ages shorter than 120 s might be simply a result of a poorer detection limit caused by lower SO2 columns measured in this part of the plume. Therefore, as it stands, the data shown in figure 7 is in principle consistent with a constant OClO/SO2 ratio in the young plume. I'm not implying that I believe this to be the case, but based on this particular example dataset, one cannot rule it out. The authors go on to state that the depicted errors also include systematic errors. This may be true, but in the absence of a way of quantifying how much is systematic and how much is random, it is not possible to interpret figure 7 in the way they have done. This again points to the need to either improve the error analysis or increase the statistics by additional averaging. Or both (see general comments).

    Answer: As mentioned before we like to thank the reviewer for these helpful comments and his suggestions, especially related to our error analysis and the discussion of those. As stated in our general comments, this issue has been attributed in the revised manuscript (by following the reviewers' suggestions to rather discuss our results using the statistical approaches).

    Changes to the manuscript: see "General remarks by the authors"

16. P25239 L3 to P25241 L13 – In this section, the individual scans perpendicular to the plume are evaluated. Again, I feel the data is over-interpreted. The data shown in figure 8f is essentially consistent with a constant BrO/SO2 ratio throughout the plume, perhaps with the exception of one point measured at about 54 degrees elevation. The data shown in table A1 and described in the text is similarly inconclusive, if viewed one scan at a time. Out of the 10 scans listed in the table, only 2 have statistically relevant differences in their BrO/SO2 ratios. In all other cases, the ranges given by

Mean1, Std1 and Mean2, Std2 overlap (by the way, line 9 is missing some data). Therefore, it is questionable whether the statement “The BrO/SO2 ratio showed an increase towards the edges in 76% of all analyzed scans” is true or not. Couldn’t one just as easily say that the BrO/SO2 ratio only showed a statistically significant increase towards the edges in 20% of the scans?

Answer: As being part of overall restructuring, the discussion of plume cross section scans was largely reduced and put into relation (see “General remarks by the authors”, previous point, etc.**)**

Changes to the manuscript: See “General remarks by the authors”

17. P25242 L22 – The discussion of Figure 8d is again difficult because all data is below the detection limit. As per definition, this means that OClO could not be detected. Therefore, you cannot argue that there is an increasing trend. Either the definition of detection limit must be revised or this discussion removed.

    Answer: Based on our statistical analysis we detect a significant OClO trend, for a detailed response, we agree and refer to our general remarks at the beginning of this document.

    Changes to the manuscript: See “General remarks by the authors”

18. P25242 L8 – “This could be the result of a superimposed vertical profile of BrO” What does this sentence mean? Please clarify.

    Answer: This sentence was removed in the restructured document since we largely reduced the discussion of individual scans. However, the original idea was, that this trend could be caused by the fact, that this scan (along the plume propagation axis, see Fig. 8f) probably started at the edges of the plume, where the BrO/SO2 ratios are probably larger due to the cross sectional (“vertical”) profile of the BrO/SO2-ratio. Reconsidering this discussion, we agree, that this could be an over-interpretation and furthermore, it does not contribute to our scientific findings at all, thus we removed this part.

    Changes to the manuscript: The corresponding sentence was removed in the revised manuscript.

    P25243 L1 – This statistical analysis is exactly what I mean by reducing the data to improve statistics and derive statistically relevant trends. In my opinion, this result is by far more robust than the previously shown results and the authors should consider showing just this plot (figure 9). Note that in this plot, there is not difference in the formation time of BrO and OClO.

    Answer: We like to thank the reviewer for these very positive comments, which we followed. See our “General remarks” at the beginning of this document.

    Changes to the manuscript: The discussion of a potentially increased formation time of OClO with respect to BrO was removed in the revised document.

19. P25243 L20 – It is, however, important to mention that the “slight decreasing trend” in OClO/SO2 ratios with distance is not statistically significant.

    Answer: We agree and changed this sentence to read:

    Changes to the manuscript: *“…rather seems to follow a slight - but statistically not significant – decreasing trend.”*

20. P25244 L10 – The statistically more robust dataset does not show a difference in formation time between BrO and OClO. So does your data really support such a difference?

    Answer: No, it does not and this discussion of variations in the formation time has been removed completely in the revised document.

    Changes to the manuscript: see “General comments”

21. P25245 L14 – “an increase of the OClO/SO2 ratio might be observable”. Again, if all these values are below the detection limit, then deriving a trend is probably not valid.

    Answer: Again, we refer to our general comments at the beginning of this document.

22. I also don’t understand why the detection limit is so constant over time (particularly for BrO). Since the measurements were taken so early in the morning that the incident UV radiation was quite limited, wouldn’t one expect at least some improvement of the detection limit as the more UV light becomes available?

    Answer: This depends on how the spectra are recorded. In our case, we always added a similar amount of spectra (typically between 500-1500 scans), and the integration time was adapted to reach always the same amount of collected photons. This means, that the expected error (for photon noise dominated measurements) should be the same even when comparing measurements during noon with early morning measurements. The latter simply only require a longer time to be recorded.

    Changes to the manuscript: None

23. P25246 L14 to P25246 L25 – Here the authors write an entire paragraph about a single, extremely uncertain point of data (why is the uncertainty range not given for 0.25?). This type of excessive discussion of extremely uncertain data is contra-productive to the overall message of the paper. This point can be mentioned, but I a maximum of 2 sentences would suffice to put it in perspective.

    Answer: We agree with the reviewer and want to remark, that the discussion of this point was removed completely, since (as the reviewer points out) it is only one point with large uncertainty.

24. P25247 L1 – I very much enjoyed this section. Perhaps consider moving it to the conclusions though?

Answer: We are glad the reviewer liked this part which was, as suggested, moved to the conclusions which were completely rewritten and restructured (see also "General remarks by the authors").

25. P25247 L21 (Eq. 10) – I believe you need to specify that [ClOy] on the right side of equation 10 needs to be evaluated at t = t0, i.e. [ClOy](t0).

    Answer: We thank the reviewer for this attentive observation. The text was changed as suggested

26. P25250 L10 – Please motivate why these correction factors were chosen. Simply stating that they are large doesn't help very much. In particular, why were different values chosen for different species, even though their cross-sections appear to have similar frequencies?

    Answer: We like to thank the reviewer for this legitimate comment. As part of restructuring, we moved the presentation of the fit correction factors for IO, OIO and OBrO from this section (3.2) to section 2.4.1 (Evaluation routines) in the revised document. We added a small paragraph in the introduction of 2.4.1 explaining, why we chose to be as conservative (U=5) with the VIS data.

    Changes to the manuscript: A paragraph was added in Sect. 2.4.1 to read:
    "The focus of this study was on the evaluation of the data collected with the UV spectrograph (i.e. the evaluation of OClO, BrO, SO_2, IO). Therefore, detailed sensitivity studies were performed including contour plots of the DOAS fit results in dependency of the fit wavelength range ("Retrieval wavelength mapping", for details see Vogel et al., 2013) to find the optimum evaluation range for each species. For the VIS data (i.e. OBrO and OIO evaluation) these sensitivity studies were not performed since this data was of secondary interest for this study. We therefore estimated the corresponding measurement uncertainty very conservative using a fixed fit correction factor of U=5 (for details see Sect. A2)."

27. P25250 L5 – Please give at least the average X/SO2 detection limits for t > 3 minutes in the text.

    Answer: The corresponding figures were included in the text.

28. P25250 L13 – As it stands, the conclusions section provides no new information, instead simply summarizing what was discussed before. I recommend restructuring the manuscript and separating the observations from the conclusions (see general comments above).

    Answer: We thank the reviewer for the recommendations and we remark, that we followed this advice. We would like to refer to our general comments where we describe how the conclusions section was rewritten taking into account these points (29 and 30) from the reviewer.

29. A number of points of contention are mentioned in the conclusions, but they are repeats of points mentioned earlier and I will not repeat my comments here. Just note the following:

    29.1. I'm not sure that the "OClO/SO2 ratio showed a strong increase in the first three minutes after release"

29.2. I'm not sure the "OClO/SO2 increase could be observed in 6 individual scans on two different measurement days"

29.3. If the apparent difference in formation time is "probably due to uncertainties in the plume age determination", but the evaluation of individual scans results in a 70% longer formation time for OClO, then either the uncertainty in plume age is about 70%, or the comparison of individual scans is not statistically robust

29.4. only 20% of the scans given in Table A1 have BrO/SO2 ratios that are not consistent (within 1 standard deviation) with a constant ratio throughout the plume.

29.5. If only 8% of the measurements are affected by uncertainties in stratospheric BrO, couldn't those just be omitted for all calculations except the photochemistry sunrise experiment? Then you wouldn't have to worry about that problem elsewhere.

29.6. Mentioning the single measurement of OClO/ClO at longer plume age is questionable, because if I'm doing the math right, then the range for that point is 0.06 - 1.6.

Answer: See previous point (29).

Minor corrections

P25214 L5 – In the first sentence you define abbreviations in parenthesis (e.g. SO2). In the next sentence you use parenthesis to present values obtained for different species, e.g. OClO (BrO). This is confusing to read.

Answer: This issue was changed in the revised manuscript accordingly

P25214 L8 – Recommend ending sentence after "OBrO", starting new sentence with "None"

Answer: This issue was changed in the revised manuscript accordingly

P25214 L19 – "… showed A BrO/SO2 ratio…"

Answer: This issue was changed in the revised manuscript accordingly

P25215 L12 – "CONSIDERABLY SMALLER THAN THE ATMOSPHERIC LIFETIME"

Answer: This issue was changed in the revised manuscript accordingly

P25216 L14 – "oxides of nitrogen" = "NITROGEN OXIDES"

Answer: This issue was changed in the revised manuscript accordingly

P25218 L14 – Recommend removing the dashes before and after “Cl releasing” as they are unnecessary.

Answer: We removed the dashes as suggested

P25219 L19 – Please start the sentence with “A key parameter…”

Answer: This issue was changed in the revised manuscript accordingly

P25221 L4 – Replace “due to” with “USING”

Answer: Done

P25222 L20 – “GAS-FREE”

Answer: This issue was changed in the revised manuscript accordingly

P25224 L4 – “… background spectrum FROM LITERATURE as an FRS…”

Answer: This issue was changed in the revised manuscript accordingly

P25231 L2 – “slightly slower THAN stratospheric OClO…”

Answer: This issue was changed in the revised manuscript accordingly

P25232 L14 – what does “rather linear” mean? I would say uncertainties in the wind velocity have a linear effect on the plume age uncertainty.

Answer: This issue was changed in the revised manuscript accordingly

P25232 L18 and figure 8 – if you refer to this contribution as ?tvwind in the text, please use the same notation in the figure.

Answer: This issue was changed in the revised manuscript accordingly

P25233 L26 – “These data WERE used…”

Answer: This issue was changed in the revised manuscript accordingly

P25234 L18 – “… that the STRATOSPHERIC air-mass-factor…”

Answer: This issue was changed in the revised manuscript accordingly

P25236 L4 – “… ratio of these species TO the retrieved…”

Answer: This issue was changed in the revised manuscript accordingly

P25237 L2 – "improved sensitivity"? Improved over what?

Answer: This sentence was removed in the revised manuscript

P25237 L3-4 – Please be more specific with regards to exactly what days the measurements were performed.

Answer: We stated on what days the measurements were performed in the restructured version of this paragraph.

P25240 L2 – What does "suited in terms of their SO2-plume coverage" mean?

Answer: This sentence was removed in the revised manuscript since the whole discussion of cross section scans was revised. However, to answer this question: The scans had to cover both spectra from the edge as well as from the centre of the plume which was assessed using the SO_2-SCD retrieval.

P25242 L21 – "… performed on different days and at different times."

Answer: This issue was changed in the revised manuscript accordingly

P25244 L8 – "…start leveling off" is not precise enough. Please be more specific in your definition.

Answer: This sentence was removed in the revised version of the manuscript as a result of the general changes applied (see general comments)

P25246 L1 – Throughout this section, please replace "concentrations" with "mixing ratios" as you are reporting relative mixing ratios, not absolution concentrations.

Answer: Actually, we determined absolute volume concentrations (in units $1/cm^3$ according to Sect. 2.5 and 2.6). Only for the discussion of our results, these were converted into mixing ratios. We changed the structure to make this clearer.

Changes to the manuscript: A sentence was added in sect. 3.1.5: *"The corresponding number densities were converted into mixing ratios…"*

P25246 L2 – "determined AVERAGE BrO and OClO …"

Answer: This issue was changed in the revised manuscript accordingly

P25246 L8 - Replace "whereas" with "with"

Answer: This issue has been resolved as being a result of restructuring this paragraph

P25247 L8 – Positive or negative temperature dependence?

Answer: The dependency is positive.

Changes to the manuscript: The sentence was changed accordingly (Sect. 4.0.1 in the revised version): *"…a strong positive temperature dependence"*

P25247 L12 – I assume you mean "All other Cl-sink reactions…"?

Answer: Yes, the sentence was changed accordingly

Changes to the manuscript: *"All other Cl-sink reactions…"*

P25249 L8 – The typical O3 background IS 60-80 ppb, not "should be".

Answer: The sentence was changed accordingly

P25249 L12 – Maybe also cite some measurements of O3 depletion, not just modeling work? For example, Kelly et al 2013, Rapid chemical evolution of tropospheric volcanic emissions from Redoubt Volcano, Alaska, based on observations of ozone and halogen-containing gases, JVGR. This would also be good in the context of discussion what "really low" O3 concentrations would be, see line 24 on this page.

Answer: We thank the reviewer for this hint and added the suggested reference.

P25249 L28 – What are conditions "more favorable to Cl-activation"?

Answer : This is obviously unclear since we do not really understand the Cl release mechanism. We think that for instance higher Cl/Br ratios, low NMHC concentrations, and the presence of volcanic particles (more effectively) catalyzing chloride oxidation could constitute conditions "more favorable to Cl-activation"

Changes to the manuscript: We removed this statement in Sect. 4.0.1 and replaced it with the following text:
"… . Nevertheless, we want to remark that our calculations are based on the volcanic conditions at Mt. Etna in September 2012 and we therefore want to stress, that it is absolutely possible, that CH_4 depletion may become detectable in plumes of other volcanoes or at different conditions (e.g. due to varying volcanic activity, stronger chlorine emissions, larger Cl^-/Br^--ratios, low NMHC (nonmethane hydrocarbons) concentrations or the presence of volcanic particles favouring the chloride oxidation)."

P25250 L1 – "… IO (in the UV spectral range), OIO and OBrO (in the VIS spectral range)…"

Answer: The sentence was changed accordingly

P25250 L2 – I recommend not mentioning the second spectrograph here. The fact that your instrument has 2 spectrometers was already discussed earlier.

Answer: We followed this suggestion and removed the corresponding text

Response to interactive comments

1. Interactive comment on “OClO and BrO observations in the volcanic plume of Mt. Etna – implications on the chemistry of chlorine and bromine species in volcanic plumes” by Gliß et al.
   J. Orphal
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   Received and published: 2 October 2014

   The reference for the OBrO spectrum is Fleischmann OC, Meyer-Arnek J, Burrows JP, Orphal J. The visible absorption spectrum of OBrO, investigated by Fourier transform spectroscopy. J Phys Chem A. 2005 Jun 16;109(23):5093-103.

   Answer: This issue was changed in the revised manuscript accordingly