Dear Dr. Ma,

We would like to thank the reviewers for reading our revised manuscript carefully and for providing further comments, which helped us to further improve the manuscript. We can agree with most of the reviewers' comments and suggestions, however we sharply disagree with several statements and have to reject accusations on certain points as explained in detail below. In response to the points raised by the reviewers' we made the according changes to the manuscript or modified the text for more clarity. 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 comments and 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).

With very best regards,
Jonas Gliß

Response to the Review report #2

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, D. Pöhler and U. Platt

General comments and recommendations

1. The estimation of BrO and OClO concentration is based on the assumption of circular plume. In authors' reply to the reviews it is stated: "*plume cross section scan shown in Fig. 7f (revised manuscript) is perfectly consistent with a circular plume cross section*". OK, here is Fig. 7f – the only one example proving circular structure of plume. Obviously plume is grounded and quite prolonged above 45°. I would suggest the authors should provide better proof of circular structure, report how many times they observed it and at last but not at least, estimate confidence intervals for the reported mean BrO and OClO concentrations. It will be very convincing to provide a figure where observed plume's cross section is fitted by a curve corresponding to circular plume with Gaussian distribution of concentration, c.f. Wark and Warren, Air Pollution its Origin and Control. Without convincing proof of the circular structure of the plume the reported methane depletion in volcanic plume is meaningless.

   Answer: We thank the reviewer for this attentive comment. However, we cannot agree in all points here. Especially we strongly disagree with the statement, that our estimation of a potential methane depletion would be "meaningless" unless there was a proof of a circular plume cross section. First, we like to stress, that in the estimation of ClO_Y (which determines the Cl atom concentrations, see Eq. 6) only the OClO concentrations carry a potential uncertainty due to the plume shape assumption. The estimates of the ClO concentrations (which equally contribute to the ClO_Y estimations, for details see Sect. 4, Eq.3f) however, do not carry this uncertainty since they rely on the ratio of the BrO and OClO SCDs (see Sect. 2.6) and are thus largely independent of the particular plume shape.
   Furthermore, again we would like to remind the reviewer that throughout the whole manuscript we largely argue with results retrieved directly from the column densities and/or ratios of those with SO_2-SCDs without making any assumptions about the plume shape (for details on this topic,

please see the discussion of point 2 and 3). For the concentration estimation itself we only aimed a rough estimate of these plume averaged concentrations i.e. the order of magnitude also because we did not deal with any RTE effects, as pointed out and – in our opinion – properly discussed in the corresponding section 3.1.5.
The only point where we used these absolute concentration estimations is the CH_4 degradation in the plume which – in turn and already mentioned above – equally depends on the estimated OClO concentrations and on the determined ClO concentrations (which are independent of the plume shape as pointed out above as well as in the manuscript, see Eq. 1 Sect. 2.6 and Sect. 4). However, in order to perform this rough estimation of the plume dimension, we think it is sufficient to assume a circular plume cross section (as it was done in the citet literature, e.g. Bobrowski et al. 2003, Lee et al., 2005) and based on that the corresponding diameter from the solid angle spanned by the scan and the calculated distance to the plume.
A plume might deviate from a circular shape becoming more and more elliptical in the ageing plume (assuming a Gaussian plume). There are three main reasons for non-circular plume shapes:
a) Large-scale turbulence distorts the plume
b) Chemical processes (e.g. higher O3-levels in the surrounding air) cause lateral inhomogeneity
c) Differences in the turbulent diffusion coefficients in vertical and horizontal directions can cause "elliptical" plume shapes

However, all three processes rather apply for the aged plume (for this, please see **Changes to the Manuscript** below) and might influence the corresponding estimations by a certain factor. In our opinion, this factor is most likely smaller than two for the majority of measurements performed in the young plume (see also the photo in Fig. 1 in the revised document), which is the data our results are based on.
Moreover, situation b) would not really influence our estimation, since we only estimate the plume extend (i.e. outer borders of the plume) and based on that, mean concentrations which do not depend on the concentration distribution within the plume (for instance a "hole" in the plume due to depletion of halogen oxides near the plume center).
All of our discussed and interpreted results rely on the young plume data, especially the estimation of the methane depletion which – in addition and as already pointed out above – is only marginally influenced by uncertainties in the plume diameter carried by the estimated OClO concentrations (i.e. $[Cl] \propto [ClO_y]=[ClO_{mean}]+[OClO_{mean}]$).
Furthermore, as pointed out in the manuscript, the derived Cl concentrations (at plume age 142 s) prevail only for a short time as the plume disperses, thus the volume of this effectively CH_4 depleting environment is small, which puts things even more in relation. Moreover, one should keep in mind, what the retrieved SCDs (let's say in this context the OClO-SCDs) actually represent: namely, the integral of an unknown concentration distribution along an unknown absorption light path, or, the mean concentration of an unknown concentration distribution along a certain “effective” absorption light path. Having this in mind, one might see, that this does not affect our findings regarding the total mass of methane destroyed since this information is already intrinsic in the retrieved SCDs itself. Therefore, we are convinced that our discussion of the methane depleting potential of the plume is still valid.
The reviewer suggests to estimate potential deviations from the circular cross section by fitting the retrieved SCDs to simulated SCDs assuming a Gaussian distribution of concentration. This is a very good idea but in our opinion, this is extremely difficult (if not impossible) with a single MAX-DOAS instrument. Tomographic measurements with two or more instruments would help here. Regarding our results, we want to point out here, that we did not claim to know the true plume shape (or a deviation from a circular one) nor did we discuss or present it like that. We clearly

discuss in the manuscript, that these *numbers are based on the assumption of a circular plume cross section (i.e the numbers one would find, if the plume shape would be circular and if the effective absorption light path would be a straight line through the plume and if light dilution between instrument and plume would be negligible, for details on the latter two points, see comments #2 and #3 below).*
In our opinion this is a valid approach and we think, that these potential deviations (e.g. due to an elliptical shape) should be within a factor of two for the young plume data from the observatory (see also discussion of uncertainties in Sect. 3.1.5, where we also address the RTE discussion). For this estimate, we refer to the fundamental laws of physics governing the plume dispersion (see above) and moreover, we rely on our own observations during the campaign (plume photos and field notes).
For the aged plume, these uncertainties could be larger in case of pronounced elliptical shapes (e.g. factor of six at 20 km distance from the craters, see revised manuscript Sect. 3.1.5). To make this clearer, we included a small paragraph in Sect. 3.1.5 discussing the effects of a potential eccentricity in the old plume (and corresponding uncertainties) though this is not of much importance for the interpretation and discussion of our data (which mostly bases on young plume data and on ratios with SO_2). As clearly discussed in the manuscript, our motivation is to estimate the order of magnitude of the plume average concentrations. However, again we refer to our applied **Changes to the manuscript,** which clarify these issues even better.

Gaining more knowledge about the actual plume shape and maybe even about the distributions of concentrations (especially O_3 and reactive halogens) within the plume is very desirable and yet not trivial and is part of ongoing studies. However, as discussed above, addressing this issue is in our opinion not possible by fitting something (e.g. a simulated angular SCD profile for instance based on the assumption of a Gaussian plume) to the measured SCD profile considering the individual uncertainties in the SCDs and the low spatial and temporal resolution of a plume cross section scan (i.e. usually 20-40 min and 5 to 15 spectra sampling the plume).

To conclude, we aimed to roughly estimate mean concentrations of the measured species and from that the overall potential of an effective CH_4 depletion in the plume and we are convinced, that we discussed this properly including potential uncertainties and that our findings are robust. We did not attempt to spatially resolve individual areas within the plume, for which a much better knowledge of the plume shape and the radiative transfer would be necessary (and probably more than one instrument). We are surprised about the very negative comment of the reviewer our estimation of the methane depletion would be “meaningless” unless there was a proof of a circular plume cross section and we showed clearly above, that this is definitely not the case!
We nevertheless followed the reviewers’ suggestions and provide the corresponding number of 61 cross section scans, where we successfully retrieved an estimation of the plume diameter (in Sect 3.1.5).

Changes to the manuscript: We more clearly state the above dependencies in the corresponding Sections 2.5 and Sect. 3.1.5 and Sect. 4 (CH_4 depletion)
Sect 2.5: *”This was done assuming a circular plume cross section and straight line absorption light paths through the plume. Any potential deviations due to radiative transfer effects (RTE, e.g. multiple scattering, light dilution, for details see e.g.*
Kern et al., 2010, Mori et al., 2006) or deviations from the assumed circular shape were neglected in this estimation.”

Sect. 3.1.5: *"The plume diameter could be estimated in 61 (from in total 90) cross section scans performed during the campaign. […]*
Furthermore, only measurements during clear meteorological conditions were included to avoid potential impacts on the radiation light path, for instance caused by clouds or high background aerosol concentrations. […]
The comparatively large errors of the derived mixing ratios (see Fig. 10) are due to our conservative estimation of the SCD-errors and the uncertainties in the plume diameter estimation.
More detailed radiative transfer effects (RTE, e.g. multiple scattering, light dilution, for details see Kern et al., 2010; Kern et al., 2012) were neglected in the determination of the mixing ratios as well as potential deviations from the circular plume cross section. Hence, the reported numbers are rather an estimate of the order of magnitude of the average abundances of these species in the plume. Nonetheless, for the observatory data (11–13 September 2012, i.e. $\tau < 4$*min range in Fig. 10) potential deviations due to RTE are most likely smaller than a factor of two, relying on the findings of Kern et al., 2012 and Mori et al., 2006. 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;* $d_{max} < 3.2$ *km) and the high altitude at the measurement location (i.e. 2.800 m a.s.l., i.e. lower scattering probability).*
Moreover, a strong eccentricity of the plume (i.e. pronounced elliptical plume shape) is unlikely in this plume age regime (see e.g. Turner, 1970).
The measurements performed in the aged plume (i.e. data points at $\tau > 4$*min in Fig. 10) are most likely stronger influenced by deviations from the assumed circular cross section and 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 due to the decreasing concentrations (plume dilution) but to a certain degree also influenced by light dilution and elliptical plume shapes. However, in most cases the latter two effects should counteract each other to a certain degree since light dilution induces a decrease in the "true" signal whereas the lengths of the effective light paths through the plume are most certainly overestimated. The latter is due to the pronounced elliptical shape of the plume (i.e.* $\sigma_{hor} > \sigma_{vert}$*, for typical conditions) and large plume viewing angles (i.e. close to 90°). Hence, rather* σ_{hor} *is estimated from the scan and as a result, the individual lengths of the absorption light paths*
(leff,i) are overestimated. A rough estimation assuming slightly stable conditions (i.e. Pasquill stability class E, see e.g. Turner, 1970) would approximately yield a factor of $\sigma_{vert}/\sigma_{hor}=0.16$ *at 20 km distance from the source, yet underestimated concentrations up to a factor of six."*

Sect. 4: *"The OClO concentrations (used to estimate* ClO_y*) might carry potential uncertainties due to RTE or non-circular plumes. However, as discussed in Sect. 3.1.5, these deviations should be small (i.e. <=2) for the majority of data points recorded in the young plume and should not significantly influence the outcome of this analysis."*

2. The radiative transfer effects (RTE) are not considered in this work. In reply to the reviews the authors speculate that "*the discussion of our results relates mostly to ratios of BrO and OClO to SO2. 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*". There is no proof of this statement. Below is given a plot of plume transmittances caused by SO2 (two wavelength ranges, the right Y-axis correspond to lower SO2 range), BrO and OClO at maximum values of column amounts present in the manuscript. Let's consider plume

dilution as it was explained firstly by Millán Millán, secondly confirmed experimetally by Mori and finally modelled by Kern et al. Fitting windows 349.8-372.8nm and 330.6-356.3 are closely situated and this means the scattered radiance (caused by aerosol and Rayleigh scattering) entering the plume along the field of view in both intervals do not differ too much as a quantity (spectral content differs due to Fraunhofer lines). The dilution originates from the photons scattered within the telescope field of view between plume and telescope. These photons produce the harmful radiance which is practically the same for SO2, BrO and OClO. This means that the dilution or harmful effect will depend strongly on the transmittance, i.e. will be quite different for the three considered gases – stronger for SO2 and OClO and weaker for BrO. I suppose the authors should reconsider RTE in more details before publishing the manuscript. Otherwise they have to outline that reported molar ratios are estimated without consideration of RTE.

Answer: Before responding to this comment we would like to complete (blue marked) the reviewers above citation of our previous answer: "*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)*".
Further, we assume, that with "plume dilution" the reviewer means "light dilution". We also assume that the reviewer means the *harmful effect* would be stronger for SO_2 in the lower wavelength range "*lwr*" (minimum transmittance of 0.7) and should be the same for SO_2 *uwr*, OClO and BrO, since here the optical densities are small (10^{-3}-10^{-2}) and thus the transmittances close to unity even at the largest measured SCDs.
It is true, that we did not directly prove the above statement since we mostly rely on the findings of Lübcke et al., 2014 and the further published literature on that topic (e.g. Mori et al., 2006, Kern et al., 2010 etc.) and convey their findings to our specific measurement conditions. However, to make this a bit clearer, we will review these points in detail here:
Lübcke et al., 2014 found (by modelling rather than by back-of-the envelope calculations as the reviewer did) that the retrieved ratios in these wavelength regions are only marginally influenced by light dilution effects. They modelled up to lateral distances of 7 km at an instrument altitude of 4.5 km (plume at 6 km) and found maximum deviations of ~6% (at 6.5 km lateral distance in a Rayleigh atmosphere). Granted, our measurements were performed at lower altitudes, however considering the measurements performed at the observatory (which is the important data in our report) at 2.8 km altitude (and the plume between 3 and 4 km) the effect is still small for these data as the following consideration proves. If the light dilution is Rayleigh dominated (which is the case for our measurements due to the good meteorological conditions, visibility, see e.g. Fig. 1), the effect should be slightly larger in our case for a given lateral distance. The difference in light dilution due to the different altitude can easily be estimated from the air density in case of a Rayleigh atmosphere between plume and instrument and should be around 20%. Hence, considering the maximum plume distance for the observatory data (<3.2 km) the dilution should be increased by about 20% compared to Lübcke et al., 2014.

At 3 km lateral distance, they found a deviation of about 3%, which roughly yields an impact of 3.6 % in our case. This is a very small uncertainty compared to our comparatively large measurement uncertainties carried by ratios itself, none of which had an S/N-ratio larger than 20 (i.e. corresponding to a uncertainty of 5 %). Rather, the average S/N ratio of BrO/SO_2 in our retrieval was 4.5 (corresponding to 22% uncertainty). Thus, compared to Lübcke et al., in our case the impact of RT on the ratios would have to be enhanced by a factor of about 5-6 in order to exceed the uncertainties related to the DOAS retrieval itself.

It is true, that the plume transmittance in the different wavelength ranges has a certain effect as it determines the "spectral input" of radiation into the scattering air mass, which causes the dilution of this input. This is an important point, which can become significant for cases of large plume optical densities (i.e. low plume transmittances) in combination with a strong light dilution effect in a certain wavelength range. However, as the reviewer correctly remarks, the overall impact of light dilution is still directly proportional to the lateral distance of plume and instrument and strongly depends on the number densities of scattering particles and can thus assessed in case of a known distance and a pure Rayleigh atmosphere. In case of large aerosol concentrations (e.g. clouds) between plume and instrument or when the plume itself contains a significant amount of scattering aerosols, the treatment of plume dilution becomes difficult, though even under these difficult conditions, the impact on the ratios appears to be small according to Lübcke et al., 2014 (i.e. table 1 & 2 therein).
For our lower SO_2 range (314.8-326.8 nm) and at a maximum SCD of $S_{SO2}=3x10^{18}$ molec/cm^2 the optical densities (OD) vary between (0.35 and 0.015) hence corresponding to plume transmittances T=exp(-OD) of (0.705 and 0.985) in the specific *"lower"* wavelength range. Thus, this fit range covers both, wavelengths where the transmittance might play a role (if there would be a strong light dilution effect) and wavelengths, where this transmittance effect is more than negligible (as it is the case for the BrO, OClO range and the SO_2 upper range with ODs of the order of 10^{-3}-10^{-2}).

Following the reviewers suggestion we further wish to review the findings of Mori et al., 2006. Looking at these, two things become very clear. To discuss this issue, we first would like to refer to the transmittance plot provided by the reviewer, which we modified such, that the lower border of our standard SO_2 retrieval wavelength range becomes a bit more clear (see Fig. R1, end of document) since the reviewer plotted the calculated transmittances down to wavelengths we did not consider in our evaluation and because this is rather important for the following discussion. Moreover, we want to show three figures from Mori et al., 2006 (see Fig. R2a, b, c ath the end of this document).

Mori et al., 2006 showed that the impact of the light dilution starts to become significant once wavelength regions below 315 nm are used for the SO_2 evaluation. However, there appears to be little effect for the 315 nm band (W3 band in Mori et al. 2006, see Fig. R2, b) which is the lowest band we fitted (and even less for the absorption bands at higher wavelengths included in this lower fit range, see also discussion above). Mori et al., 2006 showed, that even at distances of 2.5 km, the decrease in the W3 band due to the measured dilution (which includes this transmittance effect) is not significant. Please also note, that all of our discussed results (i.e. young plume increase, methane depletion etc.) are based on measurements performed at the Etna observatory and (as discussed) at maximum plume distances of 3.15 km. Furthermore, we measured at higher altitudes (~3000 m a.s.l) compared to the measurement site of Mori et al. (~1100 m a.s.l). Hence in our case, the Rayleigh dominated light dilution should generally be smaller (by about 20%). Furthermore, looking at the case studies performed by Kern et al. 2010, for all curves shown, the wavelength dependency of the respectively discussed phenomena flattens at wavelengths above 315 nm, apart from the single example of extremely opaque plumes (Fig. 6 therein). However, such low visibilities could not be observed during our campaign in September 2012, rather the measurement conditions were fairly good during the majority of our measurements (see e.g. Fig. 1 and/or the discussion of RTE in Sect. 3.1.5.). Furthermore, Kern et al simulated a plume at 500 m altitude.

Taking into account all these facts, we assessed any potential deviations in our discussed ratios due to light dilution to be negligible (having in mind the large intrinsic uncertainties in the ratios itself).

However, to make this point a bit clearer we included an explanatory sentence in the corresponding section of the manuscript where we point out (as suggested by the reviewer) that we did not consider RTE in determining the ratios since we assess these to be negligible for our measurements.

Changes to the manuscript: We added a small paragraph in Sect. 2.9 to read:
"Furthermore, compared to the individual 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) and we therefore neglect any potential influences of these effects on our retrieved trace gas ratios. The discussion of our results mostly relates to the measurements performed at the Etna observatory. Especially for these data, potential influences due to RTE on the retrieved ratios should be negligible because of the proximity to the plume, the relatively high altitude (i.e. low plume dilution, see e.g. Mori et al., 2006, Kern et al., 2010) and the fairly good visibility during most of the measurements (i.e. low aerosol scattering, for details see Sect. 2.2)."

3. Further I would like to present here another part of reply to reviews. It is also related to the question about RTE. "*Furthermore, it is wrong, that RTE were completely ignored (as explained in the manuscript) since SO2 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 SO2 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 SO2-SCDs, were – as discussed in the manuscript – SO2 directly influences the RT, differences in the SO2-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 1018 molec/cm2.*"
The above phrase sounds as a confession that RTE corrections extensively discussed in a number of published papers are not necessary at all. I do not agree with such implication. Above is given

the figure A2. By the way the retrieval results in both fit widows coincide for column amounts 2×1018 - 4×1018 molecules/cm2, i.e. in this interval the RTE burdens are coinciding in both fit windows. More over from statistical point of view the coincidence of two estimates is not a proof of their accuracy. Something is wrong and additional elaboration is required.

Answer: The authors do not quite understand the reviewer in this point especially regarding the SO_2 retrieval. However, we try to address these issues as best as we understand the reviewers' comments. In any case, we reject the accusation, that our arguments would imply the statement, RTE considerations were unnecessary or that we would *confess "that RTE corrections extensively discussed in a number of published papers are not necessary at all"*.
In fact, the opposite is the case and if this accusation by the reviewer would be close to any truth we would probably not have mentioned and discussed these effects at the relevant parts of our manuscript (e.g. Sect. 3.1.5). We fully agree that a fundamental elaboration of potential RT effects is extremely important. Both, the Editor and the reviewer(s) can be assured that these issues were intensively discussed before submitting this article. However, one has to keep in mind, that RT simulations strongly depend on a priori knowledge of the atmospheric state introducing other potential uncertainties (i.e. type and size distribution of aerosols, topography, scattering properties of potential aerosols (i.e. phase functions, ssa), surrounding atmosphere...). By using the simplistic approach of SCD ratios, the radiative transfer effects are effectively minimised for the observed measurement conditions and provide a robust estimate as has been explained in our answer to the previous reviewer comment and as discussed is in the cited literature.

Regarding our use of the two SO_2 evaluation ranges, we do not really understand the point of criticism here and especially not, why *"Something is wrong and additional elaboration is required"*.
As the reviewer correctly remarks the SO_2-SCDs show a good agreement up to SCDs around $4x10^{18}$ cm^{-2} (please also note the rather large fit uncertainties in the upper range which are due to the lower ODs).
We agree, that in general coincidence is not a proof of accuracy however, we did neither used nor attempted to estimate any "true" SO_2-SCDs throughout our whole manuscript (leaving for the moment open, what "true" in fact means regarding this issue). Furthermore, this statement is misleading as will be lined out in the following.

One could argue that a coinciding SO_2-SCD in two different wavelength ranges does not imply coinciding mean optical light paths through the plume and the same amount of light scattered into the field of view between plume and instrument. Standing-alone, this statement is certainly true. However, our approach is nevertheless valid and the introduced error negligible (please also see previous comment). However, let's review the following general facts (e.g. see also Platt & Stutz 2008, Kern et al. 2010, 2012, Bobrowski et al. 2010):

a) At lower wavelengths, a slightly higher reduction of measured SCDs must occur between plume and instrument due to increased Rayleigh scattering (see also Fig. A3).
b) Multiple scattering in the plume may occur, which can lead to over- or underestimation of the true SO_2 column.
c) Saturation effects in the plume yield an underestimation of the SO_2-SCD in the lower range.

Having these facts in mind, we do not understand the reviewer, why the retrieved SO_2-SCDs in both ranges should not coincide. In general (assuming a Rayleigh atmosphere in between plume

and instrument at 3.2 km distance to the plume) the SO_2-SCDs should be about 10% lower in the *lwr* range (based on the findings of Vogel et al., 2011 Appendix A) due to increased light dilution and indeed, the upper SCDs appear to be slightly larger compared to the *lwr* range in our case (by ~3E17 cm^{-2}, see Fig. A3, however, please still keep in mind the large intrinsic uncertainties due to the DOAS fit). Any differences in the light path due to potential multiple scattering events in the plume should be small due to the $\lambda^{-1.3}$-dependency of the aerosol scattering. Saturation is negligible for BrO, OClO and SO_2 *uwr* but might have played a certain role in the lower SO_2 range even at SCDs equal or below $3x10^{18}$ cm^{-2}. However, here the maximum optical densities (i.e. at $3x10^{18}$ cm^{-2}) are still at a moderate level (maximum 0.35 => transparency > 70%).
We are convinced, that for our relevant data (i.e. short plume distances, low degree of plume condensation, no clouds, high atmospheric visibility), these potential and small deviations are in no relation to the uncertainties carried by the measured quantities itself. Namely, the previously mentioned average error in the SCDs and ratios (e.g. 22% for BrO/SO_2 and even larger for $OClO/SO_2$ with 33%). Furthermore, one should keep in mind, that in the ratios the RTE are effectively minimised as extensively discussed in the previous comment.

For these very reasons, we disagree with the reviewer that *“Something is wrong and additional elaboration is required”*. Once more, we would like to refer to the published articles of Mori et al. 2006, Kern et al. 2010, Vogel et al. 2011, Kern et al. 2012, Lübcke et al. 2014, which we did consider in the first place. We related these findings to our measurement conditions and we addressed the relevant points in the discussion of our measurement results (see e.g. Sect. 2.4, 2.5, 2.9, 3.1.5 in our manuscript). Moreover, to our best understanding, none of these articles shows any indications, that RTE (including potential wavelength dependent light dilution effects, transmittances, saturation, multiple scattering …) should significantly influence the ratios analysed in this study at the prevailing measurement conditions.
In this context, we assess the reviewers comments and accusations to be more than inappropriate especially as many of the co-authors of this article have published on that very topic many times before (e.g. Vogel et al., 2011, Kern et al., 2010, Bobrowski et al., 2010), even partly being co-authors in articles the reviewer suggests (e.g. Kern et al. 2010). Thus, the statement we would state *“that RTE corrections extensively discussed in a number of published papers are not necessary at all*” is not correct at all.

We would like to add some last remarks on the accuracy of the measured SCDs and the question of the “true” SO_2-SCD: let’s assume the instrument would be placed directly behind the plume, so any light dilution effects shall be negligible for now. Now consider a background distribution of scattered sunlight behind the plume entering it from multiple different directions, being multiply scattered and strongly wavelength-dependently absorbed within the plume and at some point being scattered into the FOV of the instrument. Let’s also assume, the considered wavelengths are longer than 315 nm. The SO_2 absorption signal measured in a certain wavelength range now corresponds to the absorption along the average light path, which contributes most to the signal (assuming wavelength dependencies of this average path due to strong absorption to be negligible in this example). The length of this path within the plume might deviate strongly from a straight-line path through the plume (in literature e.g. denoted as the vertical column (VCD), Kern et al. 2010 &2012) due to multiple scattering events caused by aerosols in the plume (Mie theory, flat wavelength dependency).
In this case, one could say the ***true SCD*** is the ***straight line SCD*** *(*which might deviate strongly from the measured SCD). The straight line SCD is an important parameter e.g. for estimating SO_2 fluxes using UV cameras but was of minor interest in this study (apart from the estimation of mean concentrations however, for these we discussed the corresponding simplifications and

uncertainties appropriately, see point #1 and/or Sect. 3.1.5 in the manuscript).
However, one could also argue that rather the ***measured SCD*** is the ***true (i.e. more accurate) SCD*** since it represents the total absorption along this unknown light path (as long as the DOAS assumption of a weak absorber is fulfilled or in other words that the linearization of the Beer-Lambert-law is valid). In any case, as soon as the instrument is placed in a distance to the plume, both signals will be diluted and thus falsified. However, if this dilution is negligible (and if the DOAS assumption of a weak absorber is fulfilled in the corresponding wavelength range) it is more than justified to call the retrieved SCD an accurate measure of the corresponding quantity (for more information see Platt and Stutz, 2008) though it might still strongly deviate from the straight line column.

Changes to the manuscript: See comment #2.

4. I also suggest that it is necessary to improve Fig. 4 by presenting whole picture of retrieval results as it is done in (General-2014) and (Bobrowski-2007). This approach will permit to discuss the significance of usage of both ring effects (R and R4), fitting of formaldehyde, significance of Io-correction and may be used to explain detection threshold calculation.

   Answer: We followed the reviewers suggestion and replaced Fig. 4 by an fit example showing all fitted species. Furthermore, in order to better explain our decision of the fit correction factors as well as the effect of the *R4* spectrum, we included one further fit example (from the $SO_{2,uwr}$ range) in the appendix (Fig. A2). As a result, the appendix now includes one more section "***A4:** Details regarding the SO_2 evaluation"* (basically framing Fig. A2 and A3) including this fit example which we use to visualise and justify our decision of the used fit correction factor of *U*=4. However, we do not understand the reviewer regarding the suggestion to discuss the significance of the I_0-correction based on a fit result file. Hence, regarding the latter point no changes were applied. Furthermore, both examples do not show a significant CH_2O signal, since we rather chose these examples with focus on typical fit examples for BrO and OClO at the observatory (i.e. usually no CH_2O in the background air) itself and in case of the other fit example (i.e. from the SO_2 upper range, Fig. A2) to be able to discuss the uncertainties and show the improvements due to the R4 spectrum. The fit of CH_2O is thus only relevant in background air to avoid cross interferences to the other fitted cross sections if CH_2O is present (which was the case for our downwind data).

   Changes to the manuscript: Replaced Fig. 4 by a fit example including all species. Furthermore, we provide a second fit example in Fig. A2 (from the SO_2 upper range), which we use to discuss the R4 approach and the choice of our fit correction factors.

Specific comments

1. Notations σ_{meas} and σ_i of fit errors and absorption cross-sections are a bit confusing. Better use different letters for presenting these quantities instead.

   Answer: We like to thank the reviewer for this attentive hint. We agree and changed it accordingly (using δ now instead of σ for the fit uncertainties).

2. In paragraph 1.1 “Initial plume composition” it is necessary to provide information on HCl emissions form Etna, e.g. (Schäuble-2012) and (Voigt-2014).

   Answer: We thank the reviewer for this helpful comment. We followed this suggestion and included the relevant numbers in section 1.1.1. which we also slightly reformulated regarding other gases (CO2, H2O, sulphur gases).

   Changes to the manuscript: Sect. 1.1.1: “
   The main constituents of volcanic plumes are H_2O, CO_2 and sulphur gases dominated by SO_2, H_2S. Apart from these species, volcanoes also emit a certain amount of halogen species which is largely dominated by chlorine emissions (e.g. Textor et al., 2004).
   […]
   In case of Mt. Etna, SO_2/HCl-ratios between 2-7 were found in past measurements (e.g. Francis et al., 1995, La Spina et al., 2010, Voigt et al., 2014). SO_2 appears to dominate the total sulfur emissions of Etna with SO_2/H_2S-ratios of the order of 10^1-10^3 (Jaeschke et al., 1982, Aiuppa et al., 2005).”

3. The paragraph 1.1.2 “Formation of RHS in the plume - the bromine explosion” may be omitted because its content has been published many times elsewhere and its content is mentioned a few times but not used in the rest of the manuscript.

   Answer: Regarding this point, we disagree with the reviewer because and in our opinion it is important to provide these details here, since it appears, that the chlorine activation is (or in some cases could be) strongly dependent on the discussed release mechanisms (i.e. by-product of the bromine explosion). Further, one of the main objectives of this study is the young plume formation of RHS, we therefore like to discuss these processes in the current detail and provide the necessary information.

   Changes to the manuscript: We slightly shortened and rephrased paragraph 1.1.2 to read:
   “A certain amount of RHS (e.g. Cl, Br) can be produced in the hot initial plume via high temperature oxidative dissociation processes as suggested by model studies (e.g. Gerlach, 2004; Martin et al., 2006). Furthermore, Br can be formed via the reaction of HBr with OH in the very young plume (Roberts et al., 2009). However, the corresponding amounts are by far too small to explain the BrO amounts observed. In fact, the largest part of BrO is formed in atmospheric reactions including the photolysis of Br_2 and BrCl (e.g. Oppenheimer et al., 2006; Bobrowski et al., 2007; Kern et al., 2009). This is further supported by direct observations showing a strong increase of the BrO levels in the young plume (e.g. Bobrowski et al., 2007; Bobrowski and Giuffrida, 2012) and the virtual absence during night-time (Kern et al.,2009).
   Nowadays, the underlying chemical reaction processes are mostly understood and likely driven by a heterogeneous and partly auto-catalytic reaction mechanism often referred to as “bromine explosion” (e.g. Lehrer et al., 1997; Wennberg, 1999), which includes the following reactions (note that the subscript “aq” denotes species in the aqueous phase on particles):
   >
   <R1-R6>
   >
   The “bromine explosion” encompasses the uptake of hypobromous acid (HOBr) from the gas into the aqueous phase. After reaction of HOBr with bromide, Br2 is released into the

gas phase where it is rapidly photolysed forming BrO in reaction with O_3. Once formed, the self reaction of BrO induces a catalytic destruction of O_3. Noteworthy in this context are the similarities to observations of bromine emissions in polar regions (e.g. Barrie et al., 1988; Simpson et al., 2007).
Measurements performed at Mt. Etna and Stromboli volcano (Aeolian islands, Italy) indicate that up to 11% of the total emitted bromine is converted into BrO already within the first five minutes downwind (Wittmer et al., 2014)."

4. Provide explicit explanation why it is necessary to include formaldehyde in the fit.

   Answer: we included a small paragraph in Sect. 2.4.1 (BrO and OClO evaluation):

   Changes to the manuscript: *"Formaldehyde (CH_2O) was included in the fitting routine in order to account for potential background abundances. In addition, CH_2O could also be formed in the volcanic plume itself, for instance via CH_4 oxidation (in the plume most likely initiated by the reaction with Cl atoms) or in the presence of nitrogen oxides (Platt and Stutz, 2008)."*

5. Explanation of threshold estimation (lines 280-290) is a bit vague and has to be elaborated in more details.

   Answer: We agree with the reviewer and rewrote parts of section 2.4 (Data evaluation) and **A2** (DOAS error treatment). In Sect. A2 we included a concrete explanation, how and why we chose these factors (between 3-4) based on the (newly included) fit result of the SO_2 upper range given in Fig. A2 of the revised manuscript.

   Changes to the manuscript: Changes in Sect. 2.4:
   "The measurement uncertainty (δ_{meas}) was estimated conservatively by multiplying the retrieved fit errors (δ_{fit}) with a factor of U=4 to account for potential abundances of fit residuals structures (Stutz and Platt, 1996, see e.g. Fig. A2). In case of good fit results (which were assessed by the peak-to-peak values of the fit residuals Δ_{res}) the correction factor was reduced down to U=3 (i.e. for $\Delta_{res} <= 1.2 \times 10^{-3}$, see e.g. Fig. 4). Details regarding the error treatment are discussed in Sect. A2."

   Changes in Sect. A2:
   The fit residuals often show distinct structures which are mainly a result of the limited optical resolution of the instrument or due to uncertainties in the absorption spectra of the fitted species. In this case, the DOAS fit yields underestimated measures of the true fit uncertainty since it is based on the assumption of individual radiance measurements in each pixel on the detector. Thus, in case of structured fit residuals, this underestimation has to be accounted for. This can be done by multiplying the retrieved DOAS fit errors with a certain factor (here denoted with U) which can reach values of up to six according to Stutz and Platt, 1996. The choice of U for a given measurement is mainly dependent on the spectral width of the fitted absorption lines and on the width of potentially abundant residual structures (in channels on the detector, see Fig. 10 in Stutz and Platt (1996)). Since we could observe such residual structures in some of our measurements (see e.g. Fig. A2), we followed Stutz and Platt, 1996 and corrected our retrieved DOAS fit errors with a factor of U = 4. We remark, that this constitutes a conservative estimation of the measurement uncertainty. Therefore, in case of good fit results (i.e. low peak-to-peak value of the fit residual), this factor was reduced as follows:

"…"

We found a good correlation between Delta$_{res}$ and the width of structures in the residual. However, we want to point out, that this approach constitutes only a rough – but easy to implement and still conservative – implementation of the interpretation of the retrieved DOAS fit errors (e.g. Donovan et al. (2014) used a fixed correction factor of U = 3 for their OClO and BrO evaluation). In Fig. A2 such an example of a structured residual is shown (one residual structure is marked and has a width of W=20–30 channels on the detector). Typical absorption lines of the fitted species cover between 15–30 channels on the detector of our spectrograph. Considering these typical widths, we decided to use fit correction factors between three and four, based on the findings of Stutz and Platt, 1996 (see especially Fig. 10 therein)."

Figures

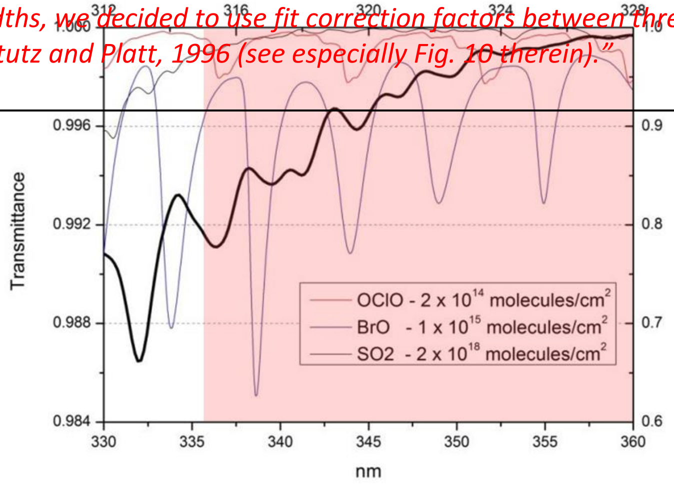

Fig. R1: modified transmittance plot

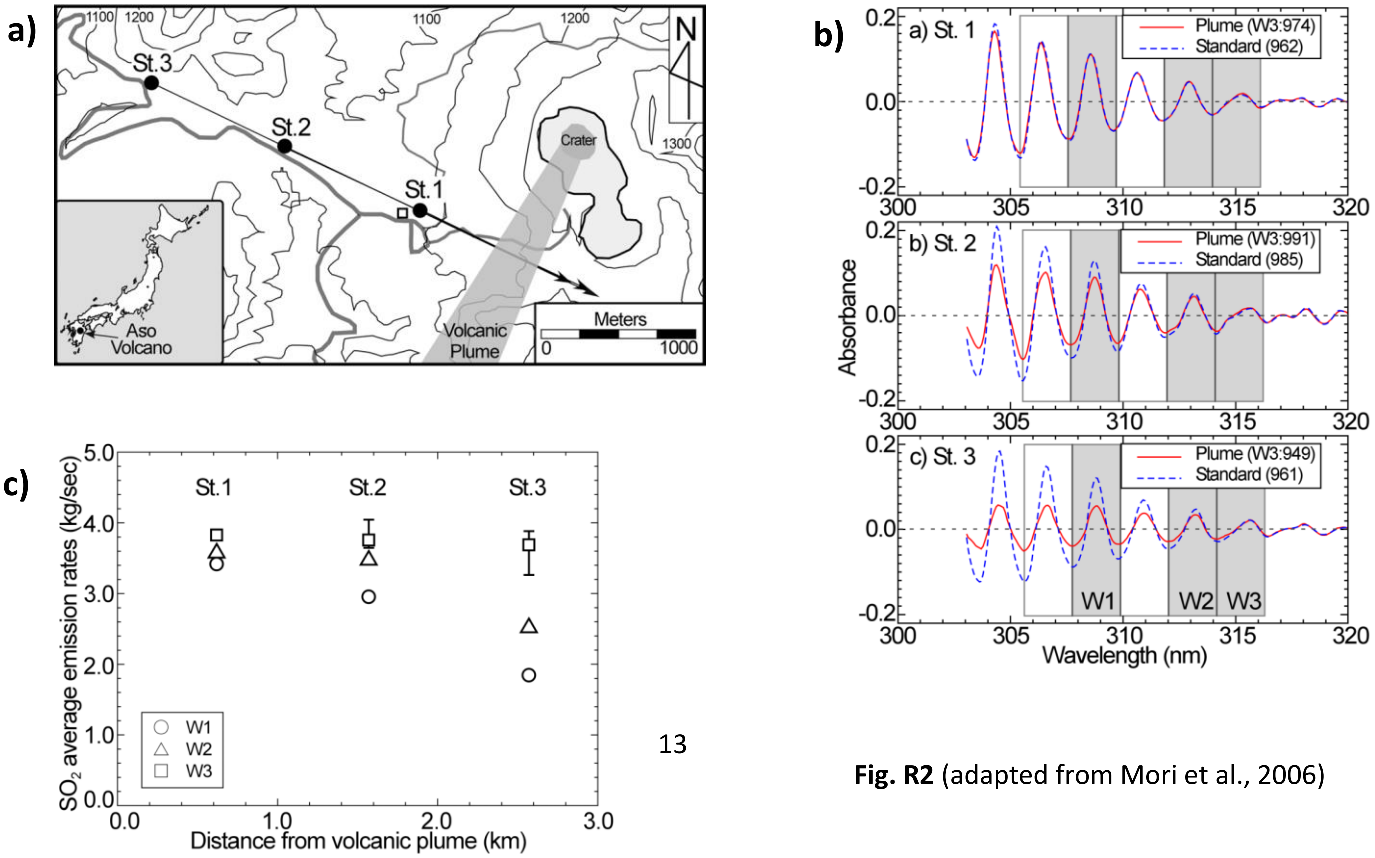

Fig. R2 (adapted from Mori et al., 2006)