Letter to Editor

Author Response: Review process of manuscript acp-2016-619: "Space based observations of volcanic iodine monoxide"

Dear Martyn Chipperfield,

first of all we would like to thank you for the extension of the review period for manuscript acp-2016-619. We have now taken into account the comments, corrections and suggestions of the two Reviewers and we prepared a revised version of the manuscript accordingly.

In the revised manuscript it is made clear that the effect of the observed volcanic iodine is in the first place a regional effect (Section 4). However, the strongly affected region may be dislocated from the erupting volcano as the volcanic plume may be moving at large horizontal speeds. Distributed evenly over the entire globe, the impact of iodine on UTLS or stratospheric chemistry is considerably smaller than the immediate effect in the volcanic plume just a few days after the eruption. The dilution is around or more than three orders of magnitude, considering the area of the Kasatochi emission plume in comparison to the area of the entire globe.
The detailed impact of volcanic iodine on ozone concentrations needs to be investigated by future studies using chemical transport models that include the most recent knowledge on iodine chemistry. Such a model exercise is out of scope of our study, but we encourage respective research in the future stimulated by our satellite observations. Model studies will also help to quantify the total reactive iodine emitted by an individual volcanic eruption, while current satellite retrievals yield the amount of iodine monoxide as major part of the entire reactive iodine. Our study thus gives a lower limit for reactive iodine by using the observations of IO.
Due to some shifted paragraphs from other sections, the discussion part is now somewhat longer.
The revised manuscript also incorporates all of the language related corrections and suggestions of Reviewer #1 (and some more).

The thoughts of Reviewer #2 concerning formation of aerosol particles by iodine, as well as on the chemical conversions within the volcanic plume that may affect the temporal evolution of IO have been incorporated into the analysis of IO and BrO amounts (Section 3.3) and the discussion (Section 4).

In the Author Comments we respond to each of the reviewers' comments individually. In addition, we prepared a revised version of the manuscript in which all changes are tracked. Deleted text is shown in red and is struck out. Newly added text is shown in blue and is underlined.

In addition to the Reviewer Comments, a colleague commented internally on some aspects including 1. an additional reference, 2. the potential influence of vibrational Raman Scattering on the retrieval, as well as 3. the applied O_4 cross section in the GOME-2A fitting window. According to these points of discussion, we added some statements here, and some additional information is given now in the revised version of the manuscript.

Attached to this letter, you find the two Author Comments regarding the Reviewer Comments #1 and #2, the statements and changes to the manuscript triggered by discussion with a colleague, as well as the marked-up revised manuscript.

After the according revision, we feel that our study has improved and we hope that it will now be accepted for publication in ACP.

Thanks a lot for your support.

Best regards,
Anja Schönhardt

Author Comment on „Space based observation of volcanic iodine monoxide“ by A. Schönhardt et al. (acp-2016-619)

Referring to the Interactive Comment of Referee #1, from 16 August 2016.

We are grateful for the comments, corrections and suggestions of Referee #1.

In the following, we address all the comments. Original comments are shown in black italics, our answers in black normal font and new text for the manuscript in blue.
All page and line references refer to the original ACPD online version, i.e. passages of changed text or locations for added text. Surely, the page/line numbers are different after revision.

1. Major Comments

Comment 1.1
When assessing the implications of detected iodine mass on stratospheric ozone, then I strongly recommend to consider the following scenarios for possible IO mixing ratios

a.) first a lower limit given by the largest amount of the air mass into which iodinated air is eventually mixed into, i.e. by assuming the emitted iodine is uniformly mixed into whole the atmosphere located above the maximum emission height (~150 mbar).
b.) second an intermediate scenario an upper limit (the area of plume and layer of 4 km thickness), just in way as presented in the manuscript.
c.) third an upper limit, where all iodine is mixed into lowermost stratosphere with the upper altitude located at 12 km, and a lower altitude given by the tropopause

If you chose option b.) and/or c.) then the correct notion for the implications for ozone are that effects of volcanic iodine are 1.) regional, and restricted to the 2.) (subtropical?), midlatitude and high latitude UT/LS.

Answer to Comment
A global effect of IO can only be estimated if the emitted IO is spread over the entire atmosphere. In the manuscript we concentrate on the situation shortly after the volcanic eruption, therefore option b.) is our choice. We agree with the reviewer’s comment that the implications for ozone derived from the observed amounts of iodine are regional - and in addition also temporally restricted. The impacted region may be, however, dislocated from the volcano as the volcanic plume is transported over considerable distances within a short time of a few days.
After mixing and dilution of the emitted iodine, the volume mixing ratio (vmr) will be much smaller. Assessing a more global effect of the emitted iodine from the single volcanic eruption under consideration, the main influence is the large horizontal area over which the iodine is spread. The area of the volcanic plume is around $5x10^5$ km², while the entire globe has a surface area of around $5x10^8$ km², i.e. three orders of magnitude larger than the volcanic plume. For homogeneous mixing of iodine over the entire globe, the resulting vmr is a factor of 10^3 smaller than the derived 3 pptv within the volcanic plume a few days after the eruption. This yields a global averaged vmr of 0.003 pptv. Additional vertical mixing will take place which on the one hand further decreases the vmr, and on the other hand yields increasing vmr due to thinner air at higher altitude. All in all, the horizontal dilution is the main factor in this estimate.

Iodine chemistry in the atmosphere is likely to have a non-linear impact. For the revised manuscript we prefer to describe the regional and instantaneous impact, when considering the iodine within the volcanic plume. In addition we emphasize the fact that the implications for ozone are regional and in the first place affect the lower stratosphere or UTLS region. It is still important that the volcanic plume may move rather quickly so that the effects of iodine on the regional chemistry may be located at large distances from the erupting volcano.
Furthermore, we mention that for global estimates the horizontal dilution will enter with a factor of three orders of magnitude, so that on average the additional iodine vmr (resulting from the single

volcanic eruption under consideration) will be around 3 orders of magnitude smaller. The following paragraph is added to Section 4 in the revised version.

The above estimated IO vmr of 3pptv in the Kasatochi plume will be diluted with time. Spreading the released trace gas amount over the area of the entire globe decreases the vmr at the given altitude by three orders of magnitude as compared to the plume area. Consequently, strong implications for ozone depletion through iodine from a single volcanic eruption are probably mainly regional and restricted in time. Primarily, the lower stratosphere or UTLS region is affected. However, the region impacted by the emitted iodine may be dislocated from the erupting volcano due to the quickly moving volcanic plume covering distances of typically around several hundred km per day.

In addition, we change the wording in the summary adding the restriction of a „regional“ reduction of ozone concentrations (p.12. ll. 19-20), cf. suggestions made by the reviewer in Comment 3.6.

Iodine volume mixing ratios of around 3 pptv may have substantial impact on the atmospheric composition, e.g., through regionally reducing the ozone concentrations.

Comment 1.2

Without further explanation (including chemical modeling), it is however unclear how the authors conclude from measured BrO, and IO vertical column amounts to the volcanic emission ratio of both halogens.

Answer to Comment

Certainly, the ratio of IO/BrO is not necessarily equal to the I/Br ratio. To our knowledge, the chemistry of iodine oxides within volcanic plumes is not yet implemented in chemical modelling systems. However, after the presented observations of large amounts of IO within the Kasatochi eruption plume, chemical modelling studies of volcanic iodine oxides are strongly encouraged.
The manuscript therefore concentrates on the observations and numbers of IO molecules. Nevertheless it is an interesting fact, that similar to other studies showing typically a one order of magnitude difference between bromine and iodine species in volcanic material (sediments, gas filter samples etc.), our measurements yield a one order of magnitude difference between gaseous BrO and IO in the emission plume.

Assuming that chemical conversions from halogens to halogen oxides are on a similar order of magnitude for iodine and bromine, then our satellite observations agree with these previous studies. While the observation of IO column amounts of only one order of magnitude smaller than BrO column amounts is an interesting fact by itself, the comment about the I/Br ratio is rather an additional thought. As stated in our manuscript, a detailed conclusion about how much iodine is emitted from Kasatochi certainly cannot be drawn from IO measurements alone without model calculations. However, the development of volcanic iodine chemistry for modelling purposes is out of scope of the present manuscript which focuses on observations. The above considerations and restrictions are therefore made more obvious and explicit in the revised manuscript.

(p.8, ll. 11-13)
Consequently, the emitted mass of iodine (3.9 to 10.8 t) can be regarded as a lower limit for the iodine content in the Kasatochi emission plume because this range is derived directly from the IO observations. Detailed chemical modelling would be needed to derive the total amount of reactive iodine in the volcanic plume from the observed IO column amounts by taking into account the other iodine species and all known chemical reactions that are taking place in the hot exhaust of the individual volcano. Such a modelling exercise is however out of scope of the current study.

(p.9, l.32)
Modelling of the halogen chemistry within the volcanic plume would be required to calculate the iodine and bromine amounts from the IO and BrO column observations. These estimates are performed under the given restrictions, and the present observations of volcanic emissions of IO shall

encourage including chemistry of iodine and iodine oxides in volcanic halogen chemistry modelling in the future.

Also in the summary, one sentence has been changed, to remind readers of the restriction that only IO and BrO are measured but not the total iodine and bromine content in the plume.
(p.12 ll. 7-8)
Judging from the IO and BrO column amounts alone, this indicates a three order of magnitude difference with respect to the seawater ratio between iodine and bromine in agreement with previous filter measurements of volcanic samples at arc volcanos.

2. Minor Comments

Comment 2.1

I largely doubt that recent paper of Saiz-Lopez et al. (2015a) provide any cogent reference for stratospheric iodine, because

- a.) *Their definition of the TTL (see Figure 2, lower boundary 12 km upper boundary ~16 km) largely departs from the one given by Fueglistaler et al., 2008 (lower boundary 150hPa/355 K/14km, upper boundary 70hPa/425K/18.5km). A correct definition is very important in this context, since only air masses reaching altitude above the level of zero radiative heating (about 14.5 km, i.e. at the lower boundary of the Fueglistaler's TTL definition) may eventually enter the stratosphere.*
- b.) *the reported aircraft measurement of IO did not vertically extend into Fueglistaler's definition of TTL. Nevertheless they nicely complement previous iodine oxide measurements previously performed in the stratosphere (e.g., Pundt et al., 1998, Bösch et al., 2003, and 1998, Butz et al., 2009) to the upper troposphere.*
- c.) *the modelling in the study is at least in one aspect flawed, i.e. to correctly model the photolysis frequency and hence the ratio of IO/I_y at larger SZAs i.e., for the solar illumination when the balloon (solar occultation!) observations were made (inspect Figure S4, http://onlinelibrary.wiley.com/doi/10.1002/2015GL064796/full)*
- d.) *it missed to mention the study of Murphy et al., (2000) which claimed that iodine ions were found in the analyzed stratospheric aerosol. Evidently, if true the role 'reactive' iodine for stratospheric ozone may even further reduced.*

Accordingly I recommend you change the sentence (first page, bottom page) from….
Recent measurements and modeling studies conclude that iodine injection into the stratosphere is currently underestimated (Saiz-Lopez et al., 2015a), and that stratospheric amounts of reactive iodine lie between 0.25-0.7 parts per trillion by volume (pptv). ..to .. A recent study of most Saiz-Lopez et al., 2015a most optimistically estimate that stratospheric iodine may range between 0.25-0.7 parts per trillion by volume (pptv).
Here you also need to skip the notion reactive from the sentence, because the reported measurements detected a good deal of the total reactive iodine at daytime, i.e. (citation from the papers) [IO] ~ 0.17 ppt (at 12.5 km) on the aircraft (Dix et al., 2013, Saiz-Lopez et al., 2015a) and in Butz et al., (2009) …. 0.09 to 0.16 (+0.10/−0.04) ppt in the tropical lower stratosphere (21.0 km to 16.5 km) and 0.17 to 0.35 (+0.20/−0.08) ppt in the tropical upper troposphere (16.5 km to 13.5 km).

Answer to Comment

The evaluation of the reviewer regarding the study of Saiz-Lopez et al. (2015a) is understood. The addressed sentence (p.1, ll.25-26) in our manuscript will be changed in the revised version. In addition, the upper limits and observed values of the IO volume mixing ratio and estimates of total gaseous iodine derived by Pundt et al. (1998), Butz et al. (2009), as well as Volkamer et al. (2015) are now explicitly referred to.

From balloon borne observations, an upper limit for stratospheric iodine monoxide, IO, of 0.1 parts per trillion by volume (pptv) was determined in the tropics (Butz et al., 2009), while upper limits for IO of 0.2 pptv at 20 km, or 0.1 pptv at 15 km (Pundt et al., 1998) were derived in the mid and high latitudes. Butz et al. (2009) conclude upper limits of total gaseous iodine of about 0.09 to 0.16 pptv in the tropical lower stratosphere (21.0 km to 16.5 km) and 0.17 to 0.35 pptv in the tropical upper troposphere (16.5 km to 13.5 km). A recent study by Saiz-Lopez et al. (2015a) estimates that stratospheric iodine may range between 0.25-0.7 pptv. This is based on, e.g., new aircraft observations in the tropics from which volume mixing ratios of IO between 0.1–0.2 pptv at altitudes up to 14 km were obtained (Volkamer et al., 2015).

Comment 2.2

Further the authors need to provide a reference to the following sentence: Even at sub-pptv levels, reactive iodine may significantly impact on stratospheric ozone chemistry….. c.f., Hossaini et al., 2015 (inspect Figure 2a), WMO (2014) and references therein ... and considering them probably it is worthwhile to rethink the notion significantly in the sentence.

Answer to Comment

Effects of iodine vmr of 1pptv as well as at sub-pptv level have, e.g., been analysed by Solomon et al., 1994. Although some reaction rates were not known at that time, conclusions are that stratospheric iodine may play a role in ozone depletion. Also Hossaini et al., 2015, find an influence of very-short lived iodine species on stratospheric ozone levels when considering the small amount of 0.15 pptv of iodine. Although the overall importance of iodine is less that of bromine, which has much larger stratospheric abundances, the iodine effect on ozone is still noticeable. As suggested, the notion “significantly” will be omitted from the respective sentence in our current manuscript. In addition, references to (Solomon et al., 1994) and (Hossaini et al., 2015) are added.

(p.2, ll. 1-2)

Even at sub-pptv levels, reactive iodine may impact on stratospheric ozone chemistry (Solomon et al., 1994; Hossaini et al., 2015).

3. Recommended editorial changes and typos

The manuscript contains are larger number of oddities with English, proof-reading of the manuscript by a native English speaker is highly recommended.

Comment 3.1

Examples of oddities with the grammar/style/notation (a selection)

3.1 on page 21 (and at many other places): The GOME-2A data show higher noise levels than the respective SCIAMACHY measurements. Consequently, for the analysis of GOME-2A data, the use of more spectral information from a larger fitting window was (is!!) investigated. So please consider the coherence in the grammatical tense i.e., I largely recommend that you use the simple presence in all sentences we you do not explicitly refer to past, or future event, and that something started in the past and is still ongoing et cetera….

>> Done. (page 4)

More example:

- *Page 4 line 24: ….was investigated → is investigated*

>> Done.

- *Page 4 line 24: For SCIAMACHY, the 3T retrieval had not been successful (Schönhardt et al., 2008) → For SCIAMACHY, the 3T retrieval was not successful (Schönhardt et al., 2008)*

>> Done.

- *Page 4 line 30: For all IO retrievals, a daily averaged Earthshine spectrum was used as reference background → For all IO retrievals, a daily averaged Earthshine spectrum is used as reference background.*

>> Done.

- *Page 7, line 21: For IO, values in that region were lower so the effect is less pronounced. …. IO vertical column amounts are lower in this region, accordingly this effect (and please name the effect it properly!) less pronounced.*

>> The sentence is changed to:
For IO, values in that region are lower. Consequently, the influence of the precise plume shape on the calculation of the integrated amount is less pronounced.

- *Page 8, line 24: Previous satellite studies have observed that → Previous satellite studies reported that often BrO……*

>> Done.

- *Page 30, line 30: The IO and BrO data from within a rectangular latitude-longitude box enclosing the entire volcanic plume has been investigated individually for each day between August 08 and 12…-> The IO and BrO vertical column amounts enclosing the entire volcanic plume with rectangular in latitude-longitude is investigated for each individual day between August 08 and 12, 2008.*

>> (Page 8) The sentence now reads:
The IO and BrO vertical column amounts that are observed within a rectangular latitude-longitude box which encloses the entire volcanic plume are investigated for each individual day between August 8 and 12, 2008.

- *Page 10, line: Hydrothermal experiments have been used to analyse the compositions of hydrous fluids and silicate melts with respect to the different halogens (Bureau et al., 2000) ….-> Results of hydrothermal experiments were used to analyse the compositions of hydrous fluids and silicate melts with respect to the different halogens (Bureau et al., 2000). (were…. Since Bureau et al., 2000 used it once in the past)*

>> Done.

- *Page 10, line 26: For several days following the major eruption of Kasatochi volcano in August 2008, iodine monoxide was observed by satellite → Following the major eruption of the Kasatochi volcano in August 2008, iodine monoxide is observed by satellite in the volcanic plumes for several days.*

>> Done.

Comment 3.2
3.2 Wrong units and notation
Example:
On line page, line 10: The columns of IO are approximately….instead of …. The columns amounts of IO….. because IO does not tend to form columns, but a certain number of IO molecules reside in an air column, and (2) if you name and/or define thing in a manuscript, please keep the same name and/or definition throughout the manuscript in order not to confuse the reader.
>> Done (Page 1). Only vice versa:
The sentence now reads "The column amounts of IO…" instead of " The columns of IO…"

More examples:

- *Page 4, line 19: The comparably large IO columns are connected -→ The comparably large IO column amounts are detected with*

>> Done.

- *Page 5, line 10: The DOAS analysis yields the trace gas slant column values→ The DOAS analysis yields (differential) slant column amounts…*

>> Done.

- *Page 5, line 10: In order to convert these numbers ..... → In order to convert the slant column amounts.....*

>> Done.

- *Page 6, line 29: 3.3 Analysis of IO and BrO amounts → 3.3 Analysis of IO and BrO column amounts*

>> We prefer to keep the title of the section because the analysis deals with the integrated IO and BrO amounts in addition to and derived from the observed IO and BrO column amounts.

- *Page 7, line 27: The range of IO values between 4.3 and 12.1 t .....-> The integrated mass of IO ranges between 4.3 and 12.1 t*

>> See next comment.

- *Page 7, line 27: The range of IO values between 4.3 and 12.1 t corresponds to an amount of reactive iodine between 3.9 and 10.8. -> The IO mass ranges between 4.3 and 12.1 t, which corresponds to mass of reactive iodine between 3.9 and 10.8t. And!!! how are the ranges calculated? Here any reader becomes confused because a result is reported before it is outlined how the result is obtained. So there is also problem with the logical order.*

>> The method how the integrated amount of IO molecules is explained above the results given in the respective sentence. The conversion from integrated mass of IO to integrated mass of iodine refers to the iodine directly contained in the IO, and the calculation uses the molar masses of iodine and oxygen. The addressed sentence is changed to:
The integrated mass of IO hence ranges between 4.3 and 12.2 t. Using the molar masses of iodine and oxygen, this amount of IO contains an integrated mass of reactive iodine between 3.9 and 10.8 t.

- *Page 8, line 3: On August 12 an amount of 66 t of BrO remains...-> On August 12, 2008, an integrated mass of 66 t of BrO remains in the atmosphere.*

>> In order to avoid misunderstandings (as there is additional BrO in the atmosphere apart from the integrated mass of BrO in the volcanic plume), the sentence is changed to:
On August 12, 2008, an integrated mass of 66 t of BrO remains in the volcanic plume.

In addition, the sentences before and after the above addressed sentences are also changed in analogy to the analyses of the integrated mass of IO and iodine:
The integrated mass of BrO within the plume increases from 26 t on August 8 to 76 t and 79 t on August 9 and 10, and reaches a maximum of 87 t on August 11.
Directly converting the integrated mass of BrO between 26 and 87 t to the corresponding integrated mass of reactive Br, a range between 22 and 73 t is derived, using the molar masses of bromine and oxygen.

- *Page 8, line 21: ... retrieved amounts of ... instead of ...retrieved column amounts ....*

>> Vice versa. Wording is changed from “amounts” to “column amounts” in this sentence, and also in the next sentence, as well as three and five sentences further down.

Comment 3.3

3.3 A wrong comparative!

>> Probably the reviewer refers to the second sentence of section 3.3. The sentence has been changed from: … IO retrieved from GOME-2A yields a more accurate analysis of the total iodine amount and mass emitted from the Kasatochi eruption.
to: … GOME-2A IO results provide a more accurate analysis of the total iodine amount and mass emitted from the Kasatochi eruption than the IO results retrieved from SCIAMACHY.

More examples

- *Page 6, line 15: Due to the much better spatial coverage of the GOME-2A instrument, the IO plume….. Due to the much better spatial coverage of the GOME-2A instrument as compared to (the SCIAMACHY?) instrument, the IO plume…*

>> Done.

- *Page 10, line 1: A wrong comparative! … the ratio of Cl vs. I is about two orders of magnitude lower than in seawater. … the ratio of Cl vs. I is about two orders of magnitudes lower in volcanic plumes than in seawater.*

>> Done.

- In addition, we have changed the sentence on p.8, l.25:

>> For the two depicted cases, the IO column amount is also lower in the plume center than in some areas around the center.

Comment 3.4

3.4 Please provide appropriate dates in order to improve the readability of the manuscript: For example on page 7 lines, 15, 18, 19 …. i.e. August 8 to 11, 2008 instead of August 08 to 11, or August 12, 2008 instead of August 12, …

>> The day format has been changed from, e.g., August 08 to August 8, throughout the manuscript. In addition, the year 2008 has been added in most places. It has not been added to all dates though, e.g., if the range August 8 to 12, 2008, is given first and then several single dates from this range are mentioned individually. Adding the year in all of those places would again degrade readability.

Comment 3.5

3.5 Page 12, lines 9 and 10: Iodine shows a stronger preference than bromine to partition into volcanic fluids than volcanic melts in the volcanic chamber below the volcano.-> Iodine shows a stronger preference than bromine to partition into volcanic fluid than melt in the volcanic chamber located underneath the volcano. (it is necessary to erase the second volcanic before melt, otherwise the sentence is ambiguous).

>> Done.

Comment 3.6

Recommended editorial changes and typos (a selection)

- *Page 2, line 12: In the Polar troposphere, both, bromine and iodine oxides are observed ……..*
  → *In the polar troposphere, bromine and iodine oxides are both observed*

>> Done.

- *Page 4, line 31: ……………which is assumed to have small column amounts of IO..-> which is likely to contain small column amounts of IO*

>> Done.

- *Page 5: The header of Table 1 need to appear on top of the table.*

>> Done. The caption of Table 2 is also moved to the top of the table for the revised version.

- *Page 5, line 13: This is an adequate assumption for the current study as the volcanic plume is located at fairly high altitudes (Theys et al., 2009) and the relevant SZA values are below 50°. → For the current study, assuming a geometric AMF is adequate since the volcanic plume is located at fairly high altitudes (Theys et al., 2009) and the relevant SZA < 50°.*

>> Sentence changed to:

For the current study, assuming a geometric AMF is adequate since the volcanic plume is located at fairly high altitudes (Theys et al., 2009) and the relevant solar zenith angle is below 50°.

- *Page 6 line 19: The results including both GOME-2A retrievals as discussed in Sec. 2.2 are summarized in Tab. 2 and the corresponding spectral fits are shown in Fig. 3.-> .... The IO and BrO retrieval for the GOME-2A instrument is discussed in Sec. 2.2 and the results are summarized in Tab. 2. The corresponding spectral fits are shown in Fig. 3.*

>> Table 2 deals with the different IO retrievals, one from SCIAMACHY and two from GOME-2A, but not with the BrO retrieval. Therefore, the suggested changes for the addressed sentence are not appropriate. Instead, the sentence is changed to:

The comparison includes the IO from the SCIAMACHY retrieval as well as IO from both GOME-2A retrievals, and the results are summarized in Tab. 2. The IO retrieval settings are discussed in Sec. 2.2 and the corresponding spectral fits are shown in Fig. 3.

- *Page 5, line 20: Following the eruption of Kasatochi, enhanced IO amounts are visible for several days. → Post the eruption of Kasatochi, enhanced IO column amounts are detected within the plumes for several days.*

>> Accepted with slight changes in the word choice:

After the eruption of Kasatochi, enhanced IO column amounts are detected within the volcanic plume for several days.

- *Page 6 line 21: GOME-2A results also show good retrieval quality with a relative retrieval error of around 14 %, which is somewhat larger than for the SCIAMACHY examples.-> The GOME-2A spectral retrieval are also of good quality with relative retrieval errors of around 14 %. The retrieval errors is thus larger than for the retrieval of SCIAMACHY data.*

>> Accepted with slight changes, especially in the grammar:

The GOME-2A spectral retrievals are also of good quality with relative retrieval errors of around 14 %. The retrieval error is thus larger than for the SCIAMACHY retrieval.

- *Page 6, line 24: .....depending on several factors such as light intensity……. What is a light intensity. Is it a radiance 8yes) or irradiance. Accordingly you need to change the sentence to: … …..depending on several factors, such as the received skylight radiance and …*

>> Accepted, while omitting the word skylight.

- *Page 6, line 25: For the example case, GOME-2A detects slightly less IO than SCIAMACHY, however, in other collocation cases the relation is reverse.-> For the discussed (shown) examples, the GOME-2A instruments detects slightly less IO than the SCIAMACHY instrument. On other collocation events the relation is however reversed.*

>> Done.

- *Page 6, line 27: For a rapidly moving volcanic plume, in which relatively fast and complex multiphase photochemical reactions take place, some real differences in the IO amounts as seen by the two instruments are therefore expected. → For rapidly moving volcanic plumes, differences in the detected IO column amounts by the two instruments are expected, either as a matter of changing IO concentrations due to relatively fast and complex multiphase photochemical reactions, the size of the ground scene and or changing ground or cloud albedo.*

>> Done.

- *Page 6, line 30: The sampling of GOME-2A measurements is intrinsically higher than that of SCIAMACHY → The sampling of spectra by the GOME-2A instrument is intrinsically better than that of the SCIAMACHY instrument*

>> Done.

- *Page 7, lines 1 and 2: …where xx is the mean IO vertical column and xx is the standard deviation, both derived from measurements on the days before the eruption …. ->…where xx is the mean IO vertical column and xx is its standard deviation. Both parameters are derived from measurements on the days before the eruption ….*

>> Done.

- *Page 7, line 6: ……….are calculated using the data from three days with satellite overpasses before ……….are calculated using the data from three consecutive days of satellite coverage prior…*

>> Done.

- *Page 7, line 22: ….. but due to the latter observation ….-> … but due to the latter finding*

>> Done.

- *Page 8, line 13: Consequently, the amount of iodine between 3.9 to 10.8 t derived here from the IO alone needs to be considered as a lower limit.-> Consequently, the emitted mass of iodine (3.9 to 10.8 t) can be regarded as a lower limit.*

>> Done. The sentence is changed as part of the answer to Comment 1.2 and now reads:
Consequently, the emitted mass of iodine (3.9 to 10.8 t) can be regarded as a lower limit for the iodine content in the Kasatochi emission plume because this range is derived directly from the IO observations.

- *Page 8, line 113: The amount of iodine derived from the Kasatochi eruption is of the same order of magnitude determined by measurements at degassing volcanos for one 15 year, e.g. 10 t/yr of iodine at Mt. Etna, Italy, (Aiuppa et al., 2005) or 12 t/yr at Satsuma-Iwojima…-> The emitted mass of iodine inferred for the Kasatochi eruption on …. is of the same order of magnitude as previously determined for the annually integrated flux for degassing volcanos, e.g. 10 t/yr of iodine at Mt. Etna, Italy, (Aiuppa et al., 2005) or 12 t/yr at Satsuma-Iwojima…*

>> Done.

- *Page 9, line 9: As a consequence, degassing from the magma may take place at different pressure, i.e. at different depth and time, for the two halogen species. -> For the two halogen species degassing from the magma may take place at different pressures, i.e. at different depth of the volcanic abyss (erase …and time).*

>> Done.

- *Page 9 line 1 to 16: Move to the discussion section.*

>> The content of page 9, lines 1 to 9 and lines 13 to 16, is moved to the discussion section. The content of lines 10 to 13, however, describes immediate observations and the comparison of IO, BrO and SO_2 spatial distributions. This part needs to remain in the current section. Linking sentences have been included along with the two moved parts.

The following sentence has been added prior to the first moved part in the discussion section:
The spatial distributions of IO, BrO and SO_2 are described in Sec.3.4, and some differences between the three species are observed.

The following sentence has been added prior to the second moved part in the discussion section:
In addition, some clear differences between the spatial distributions of the halogen oxides and SO_2 are found.

After deleting the mentioned passages, the following closing remark is now given at the end of Sec. 3.4.

The three different trace gases observed by satellite hence show several individual aspects in their spatial distribution within the volcanic plume.

- *Page 9, line 21: The corresponding ratio for the mass of BrO to IO lies between 4.0 and 6.7 (2.8 on day August 08), using data from Fig. 4. _> The corresponding mass ratio for BrO to IO range between 4.0 and 6.7, and 2.8 on August 08, 2008…. A question: Do you refer to a mass or a number density ratio?*

>> As it says in the manuscript, the values in the addressed sentence refer to a mass ratio. (The numbers given in the sentence prior to the addressed sentence refer to the number density: "For the individual days August 9 to 12, 2008, the ratio for the integrated number of BrO to IO molecules lies between 6.7 and 10.0 (4.2 on August 08).")
The two sentences are changed to:

For the individual days from August 9 to 12, 2008, the ratio for the integrated number of BrO to IO molecules lies between 6.7 and 10.0, and amounts to 4.2 on August 8, 2008. The corresponding mass ratio for BrO to IO ranges between 4.0 and 6.7, and amounts to 2.8 on August 8, 2008, using data from Fig. 4.

- *Page 9, line 23: Data from four days August 09 to 12…-> Data from the period August 09 to 12, 2008….*

>> Changed to:

Data from the four day period August 9 to 12, 2008, is included in the comparison.

- *Page 9, line 28: The uncertainties given by the latter study are rather large, but the results agree on the difference of one order of magnitude between the two halogens. → The uncertainties in emission fluxes given by the latter study are rather large, but the two halogens the results agree within their error bars.*

>> Sentence changed to:

The uncertainties in emission fluxes given by the latter study are rather large, but the results for the halogen flux ratios agree with the present satellite observations within their error bars.

- *Page 9, line 32: This implies that the iodine vs. bromine ratio in the volcanic plume is enhanced by about three orders of magnitude judging from the IO and BrO observations. -> By considering IO and BrO observations, the iodine vs. bromine ratio is enhanced by about three orders of magnitudes in volcanic plumes as compared to sea water.*

>> Sentence changed to:

By considering singly the IO and BrO observations, the iodine vs. bromine number ratio is thus enhanced by about three orders of magnitude in the volcanic plume as compared to sea water.

- *Page 10, line 13: The temporal evolution of the observed IO and BrO amounts in the plume is of interest.-> Of interest is also to study the temporal evolution of the observed IO and BrO column amounts within the plume.*

>> Done.

- *Page 10, line 18: Different chemical pathways and time constants for IO and BrO production and destruction will influence the temporal variation in the ratios. -> The different chemical pathways and time constants for IO and BrO production and destruction also influences the temporal variation of the I/Br ratio.*

>> Sentence changed to:

The different chemical pathways and time constants for IO and BrO production and destruction also influence the temporal variation of the I/Br ratio.

- *Page 10, line 26: The retrieved number of IO molecules of around 5×1028 molecules from days August 10 and 11…-> The retrieved total number of IO molecules of amounts about 5×10^{28} molecules for August 10 and 11, 2008….*

>> Sentence changed to:

The retrieved integrated number of IO molecules of about 5×10^{28} molecules for August 10 and 11, 2008, is used as lower limit of the emitted iodine amount.

- *Page 10, line 26: The lateral plume extent on these days lies around 5×10^5 km^2.. -> On both days the plumes extents over 5×10^5 km^2*

>> Sentence changed to:

On both days the plume extends horizontally over 5×10^5 km^2.

- *Page 10, line 30: An iodine abundance of 3 pptv strongly impacts, e.g., on the ozone levels..-> Iodine mixing ratios of 3 pptv may strongly impact ozone concentrations….*

>> Sentence changed to:

Iodine mixing ratios of 3 pptv may have a strong impact on ozone concentrations….

- *Page 10, line 32: The Kasatochi plume altitude reaches into the lower stratosphere. Consequently, the satellite observations of large amounts of iodine after the Kasatochi eruption indicate, that volcanic eruptions may lead to a substantial input of iodine to the stratosphere as well as the upper troposphere lower stratosphere (UTLS) region, depending on the eruption altitude and plume rise. → The upper part of the Kasatochi plume may have reached into the lower stratosphere. In consequence, our satellite-based observations of iodine oxide indicates that volcanic eruptions may have an impact on the iodine concentrations at least regionally in the upper troposphere and lower stratosphere (UTLS).*

>> Done. Second sentence with minor modifications/corrections:

Consequently, the presented satellite-based observations of iodine monoxide indicate that volcanic eruptions may have an impact on the iodine concentrations at least regionally in the upper troposphere and lower stratosphere.

- *Page 10, line 2: In this case the lower stratosphere will be most affected -> In this case the lower stratosphere may become most affected.*

>> Done. (Page 11)

- *Comparing these numbers to the results of BrO, the ratio for BrO to IO molecules lies between 6.7 and 10.0…-> By rationing the masses of the two halogen oxides found within the plume BrO, then the BrO/IO ratio ranges between 6.7 and 10.0…*

>> This would change the original meaning of the sentence, which addresses the (number of) molecules and not the masses of IO and BrO. The sentence is clarified by:

By comparing the integrated numbers of IO and BrO molecules found within the volcanic plume, the BrO/IO number ratio ranges between 6.7 and 10.0, while the BrO/IO mass ratio lies between 4.0 and 6.7.

- *Page 12, line 20 An iodine vmr of around 3 pptv has substantial impact on the atmospheric composition, e.g., through reducing the ozone levels.-> Iodine volume mixing ratios of around 3 pptv may have substantial impact on the atmospheric composition, e.g., through regionally reducing the ozone concentrations.*

>> Done.

- *Page 12, line 22: ……………..and will be facilitated in the future…-> and in future will be facilitated*

>> Done.

4. Additional references

1. Butz, A. H. Bosch, C. Camy-Peyret, M. P. Chipperfield, M. Dorf, S. Kreycy, L. Kritten, C. Prados-Roman, J. Schwärzle, and K. Pfeilsticker, Constraints on inorganic gaseous iodine in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations, Atmos. Chem. Phys., 9, 7229 – 7242, 2009.
2. Fueglistaler, S., A. E. Dessler, T. J. Dunkerton, I. Folkins, Q. Fu, and P. W. Mote, Tropical tropopause layer. Reviews of Geophysics, Vol. 47, No. 1, n/a–n/a, 2009.
3. Hossaini, R., M. P. Chipperfield, S. A. Montzka, A. Rap, S. Dhomse, and W. Feng, Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, Nature Geoscience, DOI: 10.1038/NGEO2363, Feb. 15, 2015.
4. Murphy, D. M. and Thomson, D. S.: Halogen ions and NO+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere, Geophys. Res. Lett., 27, 3217–3220, doi:10.1029/1999GL011267, 2000.
5. Pundt, I., Pommereau, J., Phillips, C. et al. Upper Limit of Iodine Oxide in the Lower Stratosphere, Journal of Atmospheric Chemistry (1998) 30: 173. doi:10.1023/A:1006071612477

>> References 1, 2, 4 and 5 are used by the reviewer to support the evaluation of the study by Saiz-Lopez et al., 2015a. The individual points of criticism are not meant to be incorporated in the revised version of our manuscript. Reference 3 is used in Comment 2.2 as basis for the evaluation of the iodine impact on stratospheric ozone chemistry. The study by Hossaini et al. (2015) is therefore cited in the revised version as stated in the answer to Comment 2.2.
Due to their direct relation to the content of the present study, we additionally include Reference 1 and Reference 5 in the introduction, as well as Reference 4 in Sec. 4 of the revised version.

Reference 4 is also linked to a comment by Reviewer #2 about iodine forming aerosol particles. The following paragraph is included in the revised version.

The evolution of iodine species in the volcanic plume may be further affected by particle formation and heterogeneous reactions. Murphy and Thomson (2000) measured enhanced iodine content in aerosols in the upper troposphere and lower stratosphere (UTLS) region. This finding has two further implications. Particles may serve as a sink for iodine reducing the availability of reactive iodine, and on the other hand they may provide pathways for heterogeneous reactions from which reactive iodine compounds may be released again.

Further reference included in the revised version (introduction) in the context of the comments by Referee #1:

Volkamer, R., et al.: Aircraft measurements of BrO, IO, glyoxal, NO_2, H_2O, O_2-O_2 and aerosol extinction profiles in the tropics: Comparison with aircraft-/ship-based in situ and lidar measurements, Atmos. Meas. Tech., 8(5), 2121–2148, 2015.

Author Comment on „Space based observation of volcanic iodine monoxide“ by A. Schönhardt et al. (acp-2016-619)

Referring to the Interactive Comment of Referee #2, from 25 August 2016.

We are grateful for the comments and suggestions of Referee #2.

In the following, we address all the comments. Original comments are shown in black italics, our answers in black normal font and new text for the revised manuscript in blue.
Page and line references refer to the original ACPD online version, i.e. locations for added text. The page/line numbers may differ in the revised version.

Comment
The authors make the point in several places that the atmospheric chemistries of iodine and bromine (and their behaviour in the magma) are different, which probably explains why the IO and BrO do not correlate perfectly in time and space. Given that iodine oxides polymerize into particles - and bromine oxides do not - it is likely that the IO/BrO ratio is underestimated. However, it is striking that Figure 4 shows little change in the ratio as the plume ages. I find that particularly interesting, since it suggests that the higher iodine oxides are photochemically labile, thereby enabling the IO to persist in the plume. If the IO mixing ratio is around the estimated 3 ppt, then formation of I2O2, I2O3 etc. should be quite fast. This might be worth mentioning in a revised manuscript.

Answer to Comment
The reviewer mentions an important point – and an important difference between iodine and bromine. Iodine oxides in contrary to bromine oxides may polymerize to form particles. This is one of the reasons, why the observed ratio of IO/BrO may only serve as a rough estimate for the iodine/bromine ratio. We will mention this more explicitly in the revised version. As Reviewer #1 raised the point that Murphy and Thomson (2000) observed enhanced iodine content in aerosol mass spectra in the UTLS region, reference to this study is made in a new paragraph in the discussion (Sec. 4).
The observation that IO is present in the plume for a comparably long time is now emphasized in the revised manuscript, and we also mention the fact that higher oxides should be formed quickly at large IO mixing ratios.

Section 3.3, p.8, l. 12:
In addition to the presence of other iodine species, iodine oxides may polymerize into particles, while there is no evidence that bromine oxides do under atmospheric conditions. This might lead to an underestimation of the iodine to bromine ratio if only gas phase species are considered.

Section 4, p.10, l.23:
Overall, it is interesting to note that the ratio of observed IO and BrO (Fig. 4) shows little change during the aging of the plume within the five analysed days. This observation may imply that higher iodine oxides which are formed more rapidly at larger IO concentrations (cf. estimation of IO mixing ratios below) are photochemically labile inside the volcanic plume. Thereby the IO may persist in the plume for a longer time period than what would be expected from the atmospheric lifetime of IO. The evolution of iodine species in the volcanic plume may be further affected by particle formation and heterogeneous reactions. Murphy and Thomson (2000) measured enhanced iodine content in aerosols in the upper troposphere and lower stratosphere (UTLS) region. This finding has two further implications. Particles may serve as a sink for iodine reducing the availability of reactive iodine, and on the other hand they may provide pathways for heterogeneous reactions from which reactive iodine compounds may be released again.

Additional information and statements concerning the manuscript acp-2016-619 “Space based observations of volcanic iodine monoxide” - triggered by internal discussions:

1. *The study by Gliß et al. (2015) reports on MAX-DOAS measurements at Mt. Etna, Italy. Upper limits for IO slant columns were derived from their observational detection limits.*

   The measurements by Gliß et al., (2015) are performed during a phase with stable quiescently degassing behaviour in September 2012. The IO slant column detection limits of their measurements are 8.6 and 7.6 x 10^{12} molec/cm^2 for plume ages <3 min and >3 min, respectively. These results are cited in the revised manuscript.

   Comparing the findings by Gliß et al. (2015) with the IO slant columns obtained from the IO measurements in the Kasatochi plume, one needs to take into account the different geometries of the two observations as this leads to different Air Mass Factors, AMF. IO slant columns from the Kasatochi eruption in August, 2008, reach maximum values of around 4 x 10^{13} molec/cm^2 corresponding to a vertical column around 2 x 10^{13} molec/cm^2. Vertical columns are not reported in the study by Gliß et al. (2015). There is some uncertainty in the conversion due to the unknown emission plume geometry and extent. Vertical columns could be up to around a factor of 6 smaller than the slant columns. As Mt. Etna was observed during a degassing phase, IO amounts are expected to be lower than during an eruptive period. In addition, each volcano has its individual characteristics with respect to halogen contents in the emission plumes. Consequently, we do not perform a quantitative comparison between the given results, but we refer to Gliß et al. (2015) in our revised version and set the observations in relation to our measurements. In conclusion, the observation of larger IO column amounts in the plume from the Kasatochi explosive eruption are not in contradiction with the smaller upper limits reported for the plume from the Mt. Etna degassing.

2. *The wavelength region of the IO fitting window (416-430 nm) might be affected by the influence of vibrational Raman scattering (VRS) in air by N_2 and O_2 molecules.*

   In order to investigate a potential impact of this effect on the satellite IO results of our study, we have performed additional IO retrieval studies including VRS reference spectra (Lampel et al., 2015). The impact, however, on the retrieved IO slant columns is smaller than the fitting error and therefore not significant. VRS on liquid water or the liquid water absorption may also slightly influence the spectral retrieval in the wavelength region used to fit IO. However, their impact is likely to be compensated by the additional intensity offset polynomial included in the IO retrieval settings (Peters et al., 2015).

3. *In the IO slant column retrieval, the O_4 cross section is included as an additional absorber. However, in the relevant wavelength range (416-430 nm), the O_2-O_2 collision dimer has no large absorption structures. The small spectral variations in the absorption cross section differ rather strongly between the three available O_4 cross sections in the literature (Greenblatt et al., 1990; Thalman et al., 2013; Herman et al., unpublished data, http://spectrolab.aeronomie.be/ o2.htm).*

   While the O_4 cross section of Greenblatt et al. (1990) has been applied for the retrieval of IO slant columns in the present study, the inclusion of any of the three O_4 cross sections or omitting O_4 completely from the IO retrieval has no significant influence on the resulting IO slant columns. Therefore, the substantial differences between the available O_4 cross sections between 416 and 430 nm are not relevant for the results of the present study. In other cases, the inclusion of O_4 in SCIAMACHY IO retrievals improved the IO fit quality by some small degree. Most probably, some otherwise unconsidered atmospheric or instrumental effects were compensated by the O_4 cross section.

Additional or changed text for the revised version of manuscript acp-2016-619 "Space based observations of volcanic iodine monoxide" - based on the additional information above

Page and line numbers refer to the ACPD online version before revision and notify the location of additional text or the passage of changed text, respectively.

>> 1.a (p.3, l. 3):
Iodine oxides have not been previously detected in the emission plumes of volcanos. Gliß et al. (2015) report an upper limit for IO slant columns of 7.6 to 8.6 x 10^{12} molec/cm^2 based on the detection limit of their ground based DOAS observations at Mt. Etna, Italy, during a stable quiescent degassing phase in September 2012.

>> 1.b (p. 6, l.12):
The IO column amounts in the Kasatochi emission plume are larger than the upper limit for IO slant columns of 7.6 to 8.6 x 10^{12} molec/cm^2 reported by Gliß et al. (2015) for the degassing of Mt. Etna in September 2012. These results are not in contradiction with the satellite observations in the present study, as different volcanos show individual gas phase compositions, and degassing phases may differ strongly from eruptive periods.

>> 2. (p.5, ll. 7-9):
An additional additive intensity offset compensates for effects such as stray light or different types of inelastic scattering, e.g., not fully compensated Ring structures, the influence of vibrational Raman Scattering, VRS, in air (Lampel et al., 2015), and VRS on liquid water or liquid water absorption (Peters et al., 2014). Including VRS spectra of N_2 and O_2 explicitly in the IO retrieval does not change the resulting IO slant columns significantly.

>> 3. (p.5, l.2):
The absorption structures in the O_4 spectrum are small in the spectral range of the IO fitting window, and in addition these small structures differ rather strongly between the three available O_4 cross sections in the literature (Greenblatt et al., 1990; Thalman et al., 2013; Herman, C. et al). However, the inclusion of any of the three O_4 cross sections or omitting O_4 from the IO retrieval has no significant influence on the resulting IO slant columns in the volcanic plume.

Additional references according to the above changes to the manuscript:

Gliß, J., Bobrowski, N., Vogel, L., Pöhler, D., and Platt, U.: OClO and BrO observations in the volcanic plume of Mt. Etna - implications on the chemistry of chlorine and bromine species in volcanic plumes, Atmospheric Chemistry and Physics, 15, 5659–5681, doi:10.5194/acp-15-5659-2015, 2015.

Hermans, C., et al.: Unpublished data, http://spectrolab.aeronomie.be/o2.htm.

Lampel, J., Frieß, U., and Platt, U.: The impact of vibrational Raman scattering of air on DOAS measurements of atmospheric trace gases, Atmospheric Measurement Techniques, 8, 3767–3787, doi:10.5194/amt-8-3767-2015, 2015.

Peters, E., Wittrock, F., Richter, A., Alvarado, L. M. A., Rozanov, V. V., and Burrows, J. P.: Liquid water absorption and scattering effects in DOAS retrievals over oceans, Atmospheric Measurement Techniques, 7, 4203–4221, doi:10.5194/amt-7-4203-2014, 2014.

Thalman, R. and Volkamer, R.: Temperature dependent absorption cross-sections of O_2-O_2 collision pairs between 340 and 630 nm and at atmospherically relevant pressure, Phys. Chem. Chem. Phys., 15, 15 371–15 381, doi:10.1039/C3CP50968K, 2013.

Space based observation of volcanic iodine monoxide

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Abstract.

Volcanic eruptions inject substantial amounts of halogens into the atmosphere. Chlorine and bromine oxides have frequently been observed in volcanic plumes from different instrumental platforms, from ground, aircraft as well as from satellite. The present study is the first observational evidence that iodine oxides are also emitted into the atmosphere during volcanic eruptions. Large column amounts of iodine monoxide, IO, have been observed in satellite measurements following the major eruption of the Kasatochi volcano, Alaska, in 2008. The IO signal is detected in measurements made both by SCIAMACHY on ENVISAT and GOME-2 on MetOp-A. Following the eruption on August ~~07~~7, 2008, strongly elevated levels of IO slant columns of more than 4×10^{13} molec/cm^2 are retrieved along the volcanic plume trajectories for several days. The retrieved IO columns from the different instruments are consistent and the spatial distribution of the IO plume is similar to that of bromine monoxide, BrO. Details in the spatial distribution, however, differ between IO, BrO and sulphur dioxide, SO_2. The ~~columns~~ column amounts of IO are approximately one order of magnitude smaller than those of BrO. Using the GOME-2A observations, the total mass of IO in the volcanic plume injected into the atmosphere from the eruption of Kasatochi on August ~~07~~7, 2008, is determined to be on the order of 10 Mg.

1 Introduction

Halogen oxides strongly influence atmospheric composition. Catalytic reaction cycles involving chlorine, bromine or iodine, lead to ozone depletion in the troposphere. In the stratosphere, the role of chlorine and bromine released predominantly as a consequence of anthropogenic emissions of chlorofluorocarbon compounds is well established (World Meteorological Organization, 2014), and the potential importance of iodine reactions in stratospheric ozone depletion is discussed ~~(Solomon et al., 1994; Saiz-Lopez et al., 2015a).~~(Solomon et al., 1994; Hossaini et al., 2015; Saiz-Lopez et al., 2015a). Stratospheric concentrations of iodine species are much lower than those of chlorine and bromine ~~(Bösch et al., 2003). However, the~~ (Bösch et al., 2003; Butz et al., 2009). From balloon borne observations, an upper limit for stratospheric iodine monoxide, IO, of 0.1 parts per trillion by volume (pptv) was determined in the tropics (Butz et al., 2009), while upper limits for IO of 0.2 pptv at 20 km, or 0.1 pptv at 15 km (Pundt et al., 1998) were derived in the mid and high latitudes. Butz et al. (2009) conclude upper limits of total gaseous iodine of about 0.09 to 0.16 pptv in the tropical lower stratosphere (21.0 km to 16.5 km) and 0.17 to 0.35 pptv in the tropical upper troposphere (16.5 km to 13.5 km). A recent study by Saiz-Lopez et al. (2015a) estimates that stratospheric iodine may range between 0.25-0.7 pptv. This is based on, e.g., new aircraft observations in the tropics from which volume mixing ratios of IO between 0.1–0.2 pptv at altitudes up to 14 km were obtained (Volkamer et al., 2015).

The ozone destruction potential of stratospheric iodine is significantly higher than that of the other halogens. The destruction of ozone is about 60 times more effective for bromine and about 150-300 times more effective for iodine as compared to chlorine (World Meteorological Organization, 2014). The effective chain length of the catalytic cycles involving iodine and ~~iodine monoxide, IO ,~~ IO is larger than those involving the other halogens. This is in part because the temporary reservoir species containing iodine are photolysed and/or react more rapidly with stratospheric free radicals than their chlorine or bromine analogies. ~~Recent measurements and modeling studies conclude that iodine injection into the stratosphere is currently underestimated (Saiz-Lopez et al., 2015a), and that stratospheric amounts of reactive iodine lie between 0.25-0.7 parts per trillion by volume (pptv).~~ Even at sub-pptv levels, reactive iodine may ~~significantly~~ impact on stratospheric ozone chemistry (Solomon et al., 1994; Hossaini et al., 2015).

IO is formed from the reaction of iodine radicals with ozone, O_3. Catalytic cycles including IO were proposed already in the 1980s by which tropospheric O_3 is effectively destroyed (Chameides and Davis, 1980). As a result of self-reactions, iodine oxides may lead to particle formation and thereby affect atmospheric radiation balance (Burkholder et al., 2004; O'Dowd and Hoffmann, 2005; Saunders et al., 2010). These issues motivate the scientific interest in the assessment of sources, amounts and distributions of iodine species in the atmosphere.

Atmospheric iodine is of organic as well as inorganic origin, e.g., from emissions of I_2 and of halogenated organic compounds such as CH_3I and CH_2I_2 (Saiz-Lopez et al., 2012, and references therein). The largest iodine source in general are the world's oceans. Iodine compounds have been shown to be emitted into the marine boundary layer, e.g., from algae (Schall et al., 1994; Alicke et al., 1999; Carpenter, 2003) or via inorganic pathways involving the ocean surface (Garland and Curtis, 1981; Carpenter et al., 2013). In the ~~Polar troposphere, both,~~ polar troposphere, bromine and iodine oxides ~~, are~~ are both observed predominantly during spring time. Release mechanisms of iodine and bromine above sea ice areas, however, are considerably different. Bromine monoxide, BrO, is released following an autocatalytic Br activation (Vogt et al., 1999), also known as the bromine explosion mechanism. Iodine most probably takes different pathways involving the release of organo-iodine compounds (Saiz-Lopez et al., 2015b), but inorganic reactions cannot be excluded.

Volcanic eruptions are an important source of halogens in the atmosphere, especially for the free and upper troposphere and the lower stratosphere (von Glasow et al., 2009). Volcanic plumes are known to contain halogen species, initially in acidic form, e.g., HF, HCl, HBr and HI (Aiuppa et al., 2009). Bromine oxides as well as chlorine oxides have been previously observed in volcanic plumes. Volcanic BrO was first observed by Bobrowski et al. (2003) who applied the well established Differential Optical Absorption Spectroscopy (DOAS) technique (Platt and Stutz, 2008) with a ground-based Multiple AXis DOAS (MAX-DOAS) system. Volcanic chlorine oxides, ClO and OClO, were measured e.g. by Lee et al. (2005) and Bobrowski et al. (2007), also using ground-based DOAS instruments. From space, volcanic BrO was detected for the first time from the Kasatochi eruption in 2008 (Theys et al., 2009), followed by volcanic OClO from the Puyehue eruption in 2011 (Theys et al., 2014). Several further observations using ground-based measurements (Bobrowski et al., 2006; Bobrowski and Platt, 2007; Kern et al., 2009), airborne instrumentation (General et al., 2015) as well as satellites (Hörmann et al., 2013) have confirmed and further quantified the abundance of bromine oxides injected into the atmosphere following volcanic eruptions. The release mechanism of volcanic BrO is believed to be similar as for polar tropospheric BrO and is based on an autocatalytic reaction cycle involving volcanic aerosols (Bobrowski et al., 2007). Ozone depletion has been observed within volcanic plumes and is attributed to reactive halogen chemistry (Lee et al., 2005; Surl et al., 2015, and references therein).

Using filter techniques, measurements at Mt. Etna in Italy (Aiuppa et al., 2005) and at Masaya and Telica volcanos in Nicaragua (Witt et al., 2008), for example, showed that gaseous HI, I and HBr are relevant constituents in the degassing of these specific volcanos. Only a few studies are available that report on samples of volcanic gases or volcanic fluids, which have been analysed for their iodine content. Snyder and Fehn (2002) investigate the ^{129}I/I ratio in volcanic fluids in order to determine the ages of iodine species. The determined iodine ages are in agreement with the expected age of subducted sediments. An iodine accumulation takes place, as marine sediments contain concentrated amounts of organic iodine. Iodine oxides have not been previously detected in the emission plumes of volcanos. Gliß et al. (2015) report an upper limit for IO slant columns of 7.6 to 8.6$\times 10^{12}$ $\mathrm{molec/cm^2}$ based on the detection limit of their ground based DOAS observations at Mt. Etna, Italy, during a stable quiescent degassing phase in September 2012.

The composition of volcanic gases is in general strongly variable with individual characteristics changing from volcano to volcano as well as between eruption and degassing phases (Witt et al., 2008; Aiuppa et al., 2009, and references therein). Although the gas phase composition is individual for each volcanic eruption, there is a general difference between iodine and other halogens in volcanic gases at high temperatures. Around 1000° C, the main constituents are HF, HCl, and HBr for the other halogens. For iodine, however, HI and atomic I may be present in equal amounts (Aiuppa et al., 2005).

Up to the present, no detection of gaseous iodine oxides of volcanic origin has been reported, neither by in-situ measurements nor by remote sensing from ground or satellite. Iodine monoxide has been retrieved from satellite measurements of backscattered solar radiation by the DOAS technique and has previously been observed from space, e.g., in the South Polar Region (Saiz-Lopez et al., 2007; Schönhardt et al., 2008, 2012). In most cases, atmospheric amounts of IO are fairly small, so that usually temporal averages of the satellite data of at least one month are created in order to improve signal-to-noise ratio.

In August 2008, the eruption of Kasatochi volcano took place (Waythomas et al., 2010). Kasatochi belongs to the volcanic arc of the Aleutan Islands, Alaska. The violent explosions started on August ~~07~~7, 2008, in the afternoon. The Volcanic Explosivity Index (VEI) (Newhall and Self, 1982), which classifies the eruptive volume and eruption cloud height, was VEI 3-4. Large amounts of ash and sulphur dioxide, SO_2, were released to the atmosphere reaching the lower stratosphere (Waythomas et al., 2010). In total about 1.7 Tg SO_2 was emitted and spread over large parts of the globe.

In the following, the detection of IO from the eruption of Kasatochi volcano using observations of the SCIAMACHY and GOME-2A satellite instruments is presented and discussed. The applied instruments and retrieval settings are briefly described, and the IO spectral fit quality is investigated. The IO results are analysed in terms of spatial distribution, temporal evolution and integral amount. In addition, IO and BrO distributions in the volcanic plume are compared among each other and to those of sulphur dioxide, SO_2.

2 Instruments and Measurements

The only satellite borne spectrometer for which an IO product has been reported so far is the SCIAMACHY instrument (SCanning Imaging Absorption spectroMeter for Atmospheric CHartography) onboard the European Environmental Satellite (ENVISAT) (Saiz-Lopez et al., 2007; Schönhardt et al., 2008, 2012). The mission operated between March 2002 and April 2012. In this study, data from the GOME-2A (Global Ozone Monitoring Experiment) onboard MetOp-A (Meteorological Operational Satellite A) has also been successfully analysed and the signature of IO and BrO absorption has been retrieved. The IO detection ~~from~~ by GOME-2A is reported here for the first time. The DOAS method has been used for the retrieval of trace gas amounts.

2.1 Satellite instruments and data

SCIAMACHY is a spectrometer measuring direct, scattered and reflected sun light in the UV, vis and near-IR spectral regions. The spectra are measured contiguously from 214 to 1773 nm and in two spectral bands within the ranges of 1934-2044 nm and 2259-2386 nm. The operation modes include nadir, limb and occultation geometries (Burrows et al., 1995; Bovensmann et al., 1999; Gottwald, 2011). The present study uses the nadir observations. ENVISAT has a sun-synchronous, near-polar orbit with a local equator crossing time of 10:00 a.m. in descending node. Individual SCIAMACHY ground pixels in the spectral range used here have a typical size of $30\times60\,\mathrm{km}^2$. For the IO retrieval in general, spatial averaging over four ground pixels is applied to reduce noise. A further reduction in spatial resolution occurs for some parts of each orbit as a result of using the SCIAMACHY read out from cluster 14 in channel 3 (404 - 424 nm) in addition to the more commonly used cluster 15 (424 - 527 nm). Cluster 14 has partly longer integration time than cluster 15, and the integration time is adapted for the entire spectral region to achieve smoothed spectra across the cluster border. Maximum across track ground scene pixel size is 240 km.

The GOME-2A instrument observes in the UV and visible spectral regions from 240 to 790 nm and performs measurements in nadir viewing geometry. Launched in July 2006 onboard MetOp-A, GOME-2A is the first of three ~~effectively~~ nearly identical instruments. The mission officially started in October 2006 and data is available since 2007. The equator crossing time of MetOp-A is 09:30 a.m. As for SCIAMACHY, spatial averaging is applied for the GOME-2A data in order to achieve noise reduction. The typical ground pixel size of $40\times80\,\mathrm{km}^2$ is thus increased to $80\times160\,\mathrm{km}^2$. For some direct comparisons with BrO, however, the IO results without spatial averaging are used.

2.2 DOAS retrievals of IO and BrO

The DOAS method is applied to the satellite measurements in order to retrieve IO and BrO column amounts. For the SCIAMACHY IO product, the standard retrieval settings as published in Schönhardt et al. (2008) and summarized in Tab.1 are used. Two example fitting results from day August 11, 2008, are displayed in Fig. 1 showing the spectral fits for IO columns of $4.9\times10^{13}\,\mathrm{molec/cm^2}$ (top) and $2.3\times10^{13}\,\mathrm{molec/cm^2}$ (bottom). The comparably large IO ~~columns are connected to~~ column amounts are detected with rather small relative fitting errors of 5.3 and 8.3 %, respectively.

For the analysis of GOME-2A data, two alternative retrievals are used and also listed in Tab.1. The 2T retrieval corresponds

Table 1. Retrieval settings for IO from SCIAMACHY and GOME-2A observations.

Retrieval settings	SCIAMACHY	GOME-2A 2T	GOME-2A 3T
Fitting window	416-430 nm	416-430 nm	418-438 nm
Polynomial degree	2 (quadratic)	2 (quadratic)	3 (cubic)
Trace gases	NO_2, O_3 IO	NO_2, O_3 IO	NO_2, O_3, O_4 IO
Other features	Ring effect: SCIATRAN calculation (Rozanov et al., 2014; Vountas et al., 1998) Linear intensity offset correction		
Background	Daily Earthshine, Siberia (60°- 70°N, 80°-120°E)		

~~Retrieval settings for IO from SCIAMACHY and GOME-2A observations.~~

to the standard SCIAMACHY IO retrieval and therefore covers the same two IO transition bands. The GOME-2A data show higher noise levels than the respective SCIAMACHY measurements. Consequently, for the analysis of GOME-2A data, the use of more spectral information from a larger fitting window ~~was~~ is investigated. The resulting 3T retrieval covers three transition bands of the IO absorption spectrum. For SCIAMACHY, the 3T retrieval ~~had not been~~ was not successful (Schönhardt et al., 2008) due to instrument related spectral features above 430 nm. It leads, however, to an improved quality of the IO retrievals from GOME-2A measurements. If not specified elsewise, GOME-2A IO results from the 3T retrieval are used. In terms of IO amounts the results are consistent within the uncertainties between both GOME-2A retrievals, as well as between GOME-2A and SCIAMACHY, cf. ~~See~~Sect. 3.2.

For all IO retrievals, a daily averaged Earthshine spectrum ~~was~~ is used as reference background. This background spectrum ~~was~~ is generated from a reference area 60° to 70°North and 80° to 120°East, a continental region which is ~~assumed to have~~ likely to contain small column amounts of IO. So a differential slant column between the specific location and this reference region is retrieved.

The cross sections used for SCIAMACHY retrievals are NO_2 (223 K) (Bogumil et al., 2003) and O_3 (223 K) (Bogumil et al., 2003). For GOME-2A retrievals, NO_2 (223 K) and O_3 (223 K) from measurements with the GOME-2 flight model are used (Chehade et al., 2013, and P. Spietz, private communication, 2005), as well as O_4 (Greenblatt et al., 1990) in addition for the GOME-2A 3T retrieval. The absorption structures in the O_4 spectrum are small in the spectral range of the IO fitting window, and in addition these small structures differ rather strongly between the three available O_4 cross sections in the literature (Greenblatt et al., 1990; Thalman and Volkamer, 2013; Hermans, C. et al.). However, the inclusion of any of the three O_4 cross sections or omitting O_4 from the IO retrieval has no significant influence on the resulting IO slant columns in the volcanic plume. For all retrievals the IO (298 K) cross section measured by Gómez Martín et al. (2007) is applied, convolved with the slit function of the respective instrument.

BrO columns are retrieved from GOME-2A in a fitting window from 336 to 347 nm taking into account absorption features of O_3 (223 K and 273 K), NO_2 (223 K), and BrO (Begoin et al., 2010). A cubic polynomial with four coefficients is fitted for the broadband spectral effects.

SCIATRAN calculations (Rozanov et al., 2014) are used to determine reference spectra for rotational Raman scattering (Ring effect), which is taken into account in all retrievals. An additional additive intensity offset compensates for ~~stray light, remaining~~ effects such as stray light or different types of inelastic scattering, e.g., not fully compensated Ring structures, ~~or~~ the influence of vibrational Raman ~~scattering.~~ Scattering, VRS, in air (Lampel et al., 2015), and VRS on liquid water or liquid water absorption (Peters et al., 2014). Including VRS spectra of N_2 and O_2 explicitly in the IO retrieval does not change the resulting IO slant columns significantly.

The DOAS analysis yields the differential trace gas slant column ~~values~~amounts, which are the differences between two spectra in absorber concentrations integrated along the mean light path. In order to convert these ~~numbers~~ slant column amounts into vertical column ~~values~~amounts, the air mass factor (AMF), i.e. the ratio between the slant and vertical column, is computed. For both, IO and BrO, a geometric AMF is applied here which is suitable for a stratospheric absorber. ~~This is an adequate assumption for~~ For the current study~~as~~ , assuming a geometric AMF is adequate since the volcanic plume is located at fairly high altitudes (Theys et al., 2009) and the relevant ~~SZA values are~~ solar zenith angle is below 50°. The influence of aerosols on light scattering and thus on the AMF are not considered in this work. Aerosols can increase or decrease visibility of trace gases depending on several aspects such as aerosol characteristics and the relative altitude distributions. Here we concentrate on a more qualitative discussion of the observed halogen amounts.

3 Results

3.1 Observation of volcanic IO

~~Following~~ After the eruption of Kasatochi, enhanced IO ~~amounts are visible~~ column amounts are detected within the volcanic plume for several days. As a consequence of the morning overpass times of the satellite instruments, the eruption which started in the afternoon of August ~~07~~7, 2008, can be observed from August ~~08~~8, 2008, onwards. For six days from August ~~08~~ 8 to August 13, 2008, the observational results from the SCIAMACHY IO retrieval are shown in Fig. 2, left column. IO enhancements are detected on all six days, as well as enhancements of BrO (not shown, see http://www.iup.uni-bremen.de/doas/scia_data_browser.htm?gas=bro&column=strat&view=nh&year=2008&month=8&day=8). On August ~~08~~8, a loop shaped area with enhanced IO is visible, maximum slant column amounts being around 2.3×10^{13} molec/cm^2. In the same area, BrO reaches slant column values up to 4.2×10^{14} molec/cm^2. The slant column amounts on August ~~09~~ 9, are higher with 3.4×10^{13} molec/cm^2 and 5.6×10^{14} molec/cm^2 for IO and BrO, respectively. While on day August 10, the volcanic plume is situated just in between two SCIAMACHY orbits, and only slightly enhanced amounts are seen at the edges of the plume in the adjacent orbits (at 50°N, 210°E, and 55°N, 225°E), the SCIAMACHY IO amounts are largest on day August 11. Slant columns reach up to 4.9×10^{13} molec/cm^2 for IO and 5.6×10^{14} molec/cm^2 for BrO. These values correspond to vertical columns of 2.1×10^{13} molec/cm^2 for IO and 2.5×10^{14} molec/cm^2 for BrO. While these large amounts of BrO from volcanic emission have been reported before (Theys et al., 2009), IO produced from volcanic activity is observed for the first time.

The IO column amounts in the Kasatochi emission plume are larger than the upper limit for IO slant columns of 7.6 to

8.6×10^{12} molec/cm^2 reported by Gliß et al. (2015) for the degassing of Mt. Etna in September 2012. These results are not in contradiction with the satellite observations in the present study, as different volcanos show individual gas phase compositions, and degassing phases may differ strongly from eruptive periods.

3.2 IO detection with GOME-2A

Maps of IO retrieved from GOME-2A data for the six days after the eruption are shown in Fig. 2 (middle) next to the SCIAMACHY results for direct comparison. BrO amounts retrieved from GOME-2A are shown in the right column. Due to the much better spatial coverage of the GOME-2A instrument as compared to the SCIAMACHY instrument, the IO plume from the volcanic emission is clearly visible on all six days. The spatial shape of the IO enhancement agrees well with the area where higher BrO is observed.

As a comparison of the IO results retrieved from the two different sensors, an example collocation case from August 11, 2008, has been chosen. The ~~results including~~ comparison includes the IO from the SCIAMACHY retrieval as well as IO from both GOME-2A retrievals~~as discussed in Sec. 2.2~~, and the results are summarized in Tab. 2. The IO retrieval settings are discussed in Sect. 2.2, and the corresponding spectral fits are shown in Fig. 3.

The IO results of the three retrievals are consistent within their uncertainties. The GOME-2A ~~results also show good retrieval quality with a relative retrieval error~~ spectral retrievals are also of good quality with relative retrieval errors of around 14 %~~, which is somewhat~~. The retrieval error is thus larger than for the SCIAMACHY ~~examples~~retrieval. The IO detection limit for GOME-2A observations is on the order of 5×10^{12} molec/cm^2 in terms of vertical columns, and around 1×10^{13} molec/cm^2 for the retrieved slant columns, depending on several factors~~such as light intensity~~, such as the received radiance and solar zenith angle. For the ~~example case,~~ discussed examples, the GOME-2A instrument detects slightly less IO than ~~SCIAMACHY, however, in other collocation cases~~ the SCIAMACHY instrument. On other collocation events the relation is ~~reverse~~however reversed. The ground scenes of the two instruments are not identical and the measurement times differ by typically half an hour. For ~~a~~ rapidly moving volcanic ~~plume, in which relatively fast and complex multiphase photochemical reactions take place, some real~~ plumes, differences in the ~~IO amounts as seen~~ detected IO column amounts by the two instruments are ~~therefore expected.~~ expected, either as a matter of changing IO concentrations due to relatively fast and complex multiphase photochemical reactions, the size of the ground scene or changing ground or cloud albedo.

3.3 Analysis of IO and BrO amounts

The sampling of spectra by the GOME-2A ~~measurements is intrinsically higher~~ instrument is intrinsically better than that of ~~SCIAMACHY~~ the SCIAMACHY instrument, and the full volcanic plume is observed on several days. Consequently, ~~IO retrieved from GOME-2 yields~~ GOME-2A IO results provide a more accurate analysis of the total iodine amount and mass emitted from the Kasatochi eruption than the IO results retrieved from SCIAMACHY. Integration over the IO amount inside the plume is performed. For this purpose, first the plume itself needs to be defined. Here, it is determined as the area enclosing those satellite pixels with an IO column amount above a certain threshold. This threshold $VC_{\mathrm{IO,thr}}$ is defined as $VC_{\mathrm{IO,thr}} = \langle VC_{IO}\rangle + 2\sigma_{IO}$, where $\langle VC_{IO}\rangle$ is the mean IO vertical column and σ_{IO} is ~~the standard deviation, both~~ its

Table 2. IO retrieval results from the collocation case between SCIAMACHY and GOME-2A on August 11, 2008. The three results agree within their fitting errors.

Retrieval results	SCIAMACHY	GOME-2A 2T	GOME-2A 3T
window	416-430 nm	416-430 nm	418-438 nm
SC_{IO} / 10^{13} molec/cm^2	4.58 ± 0.28	4.25 ± 0.60	4.14 ± 0.59

~~IO retrieval results from the collocation case between SCIAMACHY and GOME-2A on 11.08.2008. The three results agree within their fitting errors.~~

standard deviation. Both parameters are derived from measurements on the days before the eruption as explained below. For BrO, the procedure is almost the same, but the threshold is set at $3\sigma_{BrO}$ above the mean. For IO, the weaker criterion of 2σ is necessary in order to capture the plume well. The reason for this is the larger noise as compared to that for the BrO data, i.e. enhanced IO amounts are closer to the detection limit than is the case for BrO. Mean and standard deviation values for IO and BrO are calculated using the data from three ~~days with satellite overpasses before~~ consecutive days of satellite coverage prior to the eruption (August ~~05 to 07~~5 to 7, 2008) and from within a wide area around the volcano (40-62.5°N, 183.5-231°E) enclosing all main plumes on the ~~consecutive~~ following days. Threshold values are 5.3×10^{12} molec/cm^2 and 9.7×10^{13} molec/cm^2 for IO and BrO, respectively. Only a small background IO slant column is found prior to the eruption (around $0.4\times10^{12}\ \mathrm{molec/cm^2}$ and below the detection limit), while the BrO column has a substantial stratospheric as well as free-tropospheric contribution of around $6.1\times10^{13}\ \mathrm{molec/cm^2}$ in this area.

In an alternative approach, the observed SO_2 amount (cf. Sec 3.4) is used in order to select the BrO and IO in the volcanic plume. For this SO_2 mask approach, the plume is defined by applying a 10 DU limit to the SO_2 distribution. Following the plume definition and background subtraction, the IO and BrO amounts are integrated over the selected plume area yielding an integrated number of molecules originating from the volcanic eruption. For the days August ~~08~~ 8 to 12, 2008, the results of this procedure are shown as a timeseries for IO and BrO in Fig. 4. Results from the threshold criterion are displayed and compared with those obtained using the SO_2 mask approach.

On days August ~~08~~ 8 to 11, 2008, the two methods agree within a few %, while the actual plume shape differs slightly at the edges. On August 12, 2008, the difference of the plume positions between SO_2 on one hand and BrO and IO on the other is larger. For IO, the difference does not affect the integrated value much while for BrO the results from the two different selection routines differ by 60%. Using the SO_2 mask, part of the BrO plume is missed. For IO, values in that region ~~were lowerso the effect~~ are lower. Consequently, the influence of the precise plume shape on the calculation of the integrated amount is less pronounced. In general, the two methods are in agreement, but due to the latter ~~observation~~finding, the method using the σ-level criterion is preferred.

On day August ~~08~~ 8, just after the start of the eruption, approximately 1.8 $\times10^{28}$ molecules of IO are observed in the plume, corresponding to a mass of 4.3 Mg or metric tons, t, of IO. The amount of IO increases to 7.7 t on August ~~09~~9, reaches up to 12.2 and 12.1 t (i.e. around 5.1×10^{28} molecules of IO) on the peak days on August 10 and 11, respectively, and decreases back to 7.4 t on August 12. The ~~range of IO values~~ integrated mass of IO hence ranges between 4.3 and ~~12.1~~12.2 t~~corresponds to an amount of~~. Using the molar masses of iodine and oxygen, this amount of IO contains an integrated mass of reactive iodine between 3.9 and 10.8 t.

The integrated ~~amount~~ mass of BrO within the plume increases from 26 t on August ~~08~~ 8 to 76 t and 79 t on August ~~09~~ 9 and 10, and reaches a maximum ~~amount~~ of 87 t on August 11. On August 12~~an amount~~, 2008, an integrated mass of 66 t of BrO remains ~~. Converting this range of values~~ in the volcanic plume. Directly converting the integrated mass of BrO between 26 and 87 t to the corresponding ~~amount~~ integrated mass of reactive Br, ~~amounts~~ a range between 22 and 73 t ~~are derived~~is derived, using the molar masses of bromine and oxygen. These integrated BrO amounts are larger but in broad agreement with calculations by Theys et al. (2009), who use the FLEXPART dispersion model and derive the total amount of BrO within the volcanic plume to be around 30 to 42 t. In addition to BrO, other bromine compounds contribute to the total bromine mass. In the relevant altitude between 8 and 12 km, 30-50% of the total inorganic bromine exist in the form of BrO (Theys et al., 2009). Using this relation, the integrated BrO amount corresponds to 50 to 290 t total mass of reactive bromine.

Although knowledge on iodine chemistry in a volcanic plume is limited, other iodine compounds such as I_2, I, HI , HOI, OIO and higher iodine oxides are presumably present in the emission plume as well. Consequently, the ~~amount of iodine between~~ emitted mass of iodine (3.9 to 10.8 t~~derived here from the IO alone needs to be considered~~) can be regarded as a lower limit ~~. The amount of iodine derived from the Kasatochi eruption~~ for the iodine content in the Kasatochi emission plume because this range is derived directly from the IO observations. Detailed chemical modelling would be needed to derive the total amount of reactive iodine in the volcanic plume from the observed IO column amounts by taking into account the other iodine species and all known chemical reactions that are taking place in the hot exhaust of the individual volcano. Such a modelling exercise is however out of scope of the current study. In addition to the presence of other iodine species, iodine oxides may polymerize into particles, while there is no evidence that bromine oxides do under atmospheric conditions. This might lead to an underestimation of the iodine to bromine ratio if only gas phase species are considered.

The emitted mass of iodine inferred for the Kasatochi eruption in August 2008 is of the same order of magnitude ~~determined by measurements at degassing volcanosfor one year~~as previously determined for the annually integrated flux for degassing volcanos, e.g. 10 t/yr of iodine at Mt. Etna, Italy, (Aiuppa et al., 2005) or 12 t/yr at Satsuma-Iwojima, Japan (Snyder and Fehn, 2002). This is in line with observations for bromine, where for one given volcano the Br flux from an individual eruption can be of the same order of magnitude as the annual Br flux from degassing (Aiuppa et al., 2005). The temporal evolution of the integrated amounts is discussed in ~~See~~Sect. 4.

3.4 Spatial distributions of IO, BrO and SO_2

In order to investigate the spatial plume structure more closely, Fig. 5 gives an expanded view of the volcanic plume. The retrieved column amounts of IO (left) and BrO (center) are shown together with those of SO_2 (right) for the days August ~~09~~ 9, 2008 (top) and August 11, 2008 (bottom). SO_2 column amounts are derived in the spectral window between 312.5 and 327 nm using an iterative retrieval approach (Richter, 2009).

Previous satellite studies ~~have observed that~~ reported that often BrO is enhanced around the plume center (Hörmann et al., 2013). For the two depicted cases, the IO column amount is also lower in the plume center than in some areas around the center. In general, the IO and BrO plumes have similar spatial extent and shape. It is however interesting to note, that maximum IO and BrO column amounts are not observed in the same satellite pixels, and that the details of the spatial patterns differ. On August ~~09,~~ 9, 2008, largest BrO enhancements are detected in the West and East of the plume, while IO is also enhanced there but even more in the South of the plume. On August 11, 2008, BrO maxima are seen in the West, and IO maxima are split into two regions in the North and South of the volcanic plume.

The IO and BrO ~~data from~~ vertical column amounts that are observed within a rectangular latitude-longitude box ~~enclosing~~ which encloses the entire volcanic plume ~~has been investigated individually for each~~ are investigated for each individual day between August ~~08 and 12.~~ 8 and 12, 2008. The correlation coefficient between IO and BrO considering the data from the respective area lies between $R = 0.62$ and $R = 0.84$ on the days from August ~~09 to 12.~~ 9 to 12, 2008. On the first day, August ~~08~~8, the correlation is lower at $R = 0.42$. These results with relatively large and positive values of R indicate that iodine and bromine compounds are emitted together into the volcanic plume, but also that there are factors influencing the temporal evolution of the two gases differently as R is clearly below unity ($R < 0.85$~~. The chemical pathways of iodine and bromine within the plume are probably not independent from each other. Formation and loss processes may interfere with each other. Although the rate coefficients for the reactions of I and Br with are similar, the smaller expected concentrations of I than Br imply that the time constant for IO production is slower than that for BrO. As a consequence, large amounts of Br that react with , thereby strongly reducing the abundance, may prevent the build-up of IO resulting in spatially separated maximum values for the two halogen oxides. The reactions between IO and BrO, as well as self reactions of IO impact on the spatial distributions and maximum amounts. Furthermore, the time of emission of the precursor substances may differ to some degree. Iodine and bromine have different solubility in volcanic fluids (Aiuppa et al., 2009). As a consequence, degassing from the magma may take place at different pressure, i.e. at different depth and time, for the two halogen species.~~).

The IO and BrO distributions are again similar to those of SO_2, but even larger differences occur than between the distributions of the two halogen compounds. For SO_2, no occurrence of lower values in the plume center is observed. On some days, such as the example day August 11, SO_2 is at maximum in the plume center. On day August ~~09~~9, two SO_2 maxima are seen, one part is crossing the plume center, and one part is situated more to the Southern edge of the plume. ~~In general, the comparison between the trace gas spatial distributions is interesting because it yields potentially information on the eruption process and chronology. Details of the plume composition and evolution need to be analysed in the future by chemical transport modeling to provide better insight into the complex reactions taking place within the plume.~~ The three different trace gases observed by satellite hence show several individual aspects in their spatial distribution within the volcanic plume.

4 Discussion

Comparing the integrated numbers of IO and BrO molecules in the volcanic plume, one important and interesting point is that the amount of iodine is only about one order of magnitude smaller than that of bromine. For the individual days ~~August 09~~ from August 9 to 12, 2008, the ratio for the integrated number of BrO to IO molecules lies between 6.7 and 10.0~~(~~, and amounts to 4.2 on August ~~08). The corresponding ratio for the mass of~~ 8, 2008. The corresponding mass ratio for BrO to IO ~~lies~~ ranges between 4.0 and 6.7~~(~~, and amounts to 2.8 on ~~day August 08),~~ August 8, 2008, using data from Fig. 4.

Figure 6 shows a scatterplot between IO and BrO column amounts from the individual satellite observations. Data from ~~four days August 09~~ the four day period August 9 to 12, 2008, is included in the comparison. As in the correlation analysis ~~mentioned in See~~described in Sect.3.4, for each day those measurements are used that fall into a rectangular area enclosing the volcanic plume. The slope for all data of IO vs. BrO columns is 0.09 with a correlation coefficient of 0.74. This observation is consistent with findings by Aiuppa et al. (2009) who estimate a one order of magnitude difference between the volcanic abundances of the two halogen species iodine and bromine. In addition, Pyle and Mather (2009) estimate the annual fluxes of volcanic HBr and HI to be on the order of 5-15 Gg/year for HBr and 0.5-2 Gg/year for HI, respectively. The uncertainties in emission fluxes given by the latter study are rather large, but the results ~~agree on the difference of one order of magnitude between the two halogens~~for the halogen flux ratios agree with the present satellite observations within their error bars.

The interesting point is that the seawater abundance yields a ratio of Br/I of 15,000, i.e. a four orders of magnitude difference between I and Br. ~~This implies that the~~ By considering singly the IO and BrO observations, the iodine vs. bromine ~~ratio in the volcanic plume is~~ number ratio is thus enhanced by about three orders of magnitude ~~judging~~ in the volcanic plume as compared to sea water. Modelling of the halogen chemistry within the volcanic plume would be required to calculate the iodine and bromine amounts from the IO and BrO ~~observations. While other~~ column observations. These estimates are performed under the given restrictions, and the present observations of volcanic emissions of IO shall encourage including the chemistry of iodine and iodine oxides in volcanic halogen chemistry modelling in the future. Other studies have shown that while the Cl vs. Br ratio for volcanic condensates is in agreement with the seawater ratio of around 650 (Gerlach, 2004; Aiuppa et al., 2005), the ratio of Cl vs. I is about two orders of magnitude lower in volcanic plumes than in seawater (Honda et al., 1966; Honda, 1970; Snyder and Fehn, 2002; Aiuppa et al., 2005). Consequently, an enhancement of iodine species takes place in the processes which determine the release of halogens from volcanic activity.

Explanations for the observed enhancement of iodine in volcanic emissions relative to seawater are connected to the magma composition of the specific volcano. As Kasatochi is an oceanic arc volcano, marine sediments which are carried into the Earth mantle at the subduction zone, directly influence the composition of the volcanic material. Marine sediments in turn are enriched in iodine compounds from organic material (Muramatsu and Wedepohl, 1998). In addition, volcanic emissions are influenced by the composition of the melts and fluids in the volcanic chamber. ~~Hydrothermal experiments have been~~ Results of hydrothermal experiments were used to analyse the compositions of hydrous fluids and silicate melts with respect to the different halogens (Bureau et al., 2000). It was found that the partition coefficient between fluid and melt is clearly larger for iodine than for bromine and chlorine. The partitioning into the fluid phase is therefore stronger for iodine than for bromine which is again stronger as for chlorine. Consequently, volcanic emissions to the atmosphere are expected to be enhanced in iodine relative to the other halogens.

~~The~~

Of interest is also to study the temporal evolution of the observed IO and BrO ~~amounts in the plumeis of interest~~column amounts within the plume. The observations on the first day after the eruption, however, may be influenced by dust and clouds accompanying the eruption especially close to the volcano (Theys et al., 2009). Consequently, trace gas amounts could be larger than quantified by the spectroscopic observations. Comparison of the temporal behaviour of IO and BrO shows that their evolution is similar with maximum integral amounts occurring one to three days after the eruption ~~.~~ (cf. Fig. 4). BrO reaches its highest values (around 5×10^{29} molecules) earlier than IO. ~~Different~~ The different chemical pathways and time constants for IO and BrO production and destruction ~~will~~ also influence the temporal variation ~~in the ratios~~of the I/Br ratio. However, the temporal changes between August ~~09~~ 9 and 12, 2008, are close to the limit of being significant. Considering only the 1σ standard deviation of IO on the order of 2.5×10^{12} $\mathrm{molec/cm^2}$, the uncertainty on the integrated IO molecule number within the volcanic plume lies between 0.8 and 1.2 $\times10^{28}$, using the plume areas from August ~~09~~ 9 and 11, respectively. As a result, details in the temporal evolution need to be interpreted with care. Overall, it is interesting to note that the ratio of observed IO and BrO (Fig. 4) shows little change during the aging of the plume within the five analysed days. This observation may imply that higher iodine oxides which are formed more rapidly at larger IO concentrations (cf. estimation of IO mixing ratios below) are photochemically labile inside the volcanic plume. Thereby the IO may persist in the plume for a longer time period than what would be expected from the atmospheric lifetime of IO. The evolution of iodine species in the volcanic plume may be further affected by particle formation and heterogeneous reactions. Murphy and Thomson (2000) measured enhanced iodine content in aerosols in the upper troposphere and lower stratosphere (UTLS) region. This finding has two further implications. Particles may serve as a sink for iodine reducing the availability of reactive iodine, and on the other hand they may provide pathways for heterogeneous reactions from which reactive iodine compounds may be released again.

The spatial distributions of IO, BrO and SO_2 are described in Sect. 3.4, and some differences between the three species are observed. The chemical pathways of iodine and bromine within the plume are probably not independent from each other. Formation and loss processes may interfere with each other. Although the rate coefficients for the reactions of I and Br with O_3 are similar, the smaller expected concentrations of I than Br imply that the time constant for IO production is larger than that for BrO. As a consequence, large amounts of Br that react with O_3, thereby strongly reducing the O_3 abundance, may prevent the build-up of IO resulting in spatially separated maximum values for the two halogen oxides. The reactions between IO and BrO, as well as self reactions of IO also impact on the spatial distributions and maximum amounts. Furthermore, the time of emission of the precursor substances may differ to some degree. Iodine and bromine have different solubility in volcanic fluids (Aiuppa et al., 2009). For the two halogen species, degassing from the magma may therefore take place at different pressures, i.e. at different depth of the volcanic abyss. In addition, some clear differences between the spatial distributions of the halogen oxides and SO_2 are found. In general, the comparison between the trace gas spatial distributions is interesting because it potentially yields information on the eruption process and chronology. Details of the plume composition and evolution need to be analysed in the future by chemical transport modelling to provide better insight into the complex reactions taking place within the plume.

For an estimate of the impact of volcanic iodine on atmospheric chemistry, the volume mixing ratio (vmr) is a more relevant quantity than the column amount. For a rough estimate, the vertical plume extent derived by Theys et al. (2009) is used. They determine the major part of the plume to reside between 8 and 12 km altitude. The retrieved integrated number of IO molecules of ~~around~~ about 5×10^{28} molecules ~~from days~~ for August 10 and 11, 2008, is used as lower limit of the emitted iodine amount. ~~The lateral plume extent on these days lies around~~ On both days the plume extends horizontally over $5 \times 10^5\,\mathrm{km}^2$. Spreading the observed IO homogeneously within the 4 km thick layer and over the entire plume extent, the average vmr would be around 3 pptv at 10 km altitude using US standard atmosphere pressure and temperature values. Certainly, local vmr values will exceed this average ~~number~~ vmr due to an inhomogeneous distribution within the plume. ~~An iodine abundance~~ Iodine mixing ratios of 3 pptv ~~strongly impacts, e.g., on the ozone levels (Bösch et al., 2003; Saiz-Lopez et al., 2015a) and constitutes~~ may have a strong impact on ozone concentrations (Bösch et al., 2003; Saiz-Lopez et al., 2015a) and constitute a large perturbation of stratospheric iodine, which is measured and estimated to be on the sub-pptv level.

Iodine from volcanic eruptions has several possible implications for atmospheric composition. The ~~Kasatochi plume altitude reaches~~ upper part of the Kasatochi plume may have reached into the lower stratosphere. Consequently, the ~~satellite observations of large amounts of iodine after the Kasatochi eruption indicate ,~~ presented satellite-based observations of iodine monoxide indicate that volcanic eruptions may ~~lead to a substantial input of iodine to the stratosphere as well as the upper troposphere lower stratosphere (UTLS) region , depending on the eruption altitude and plume rise~~have an impact on the iodine concentrations at least regionally in the upper troposphere and lower stratosphere.

The above estimated IO vmr of 3 pptv in the Kasatochi plume will be diluted with time. Spreading the released trace gas amount over the area of the entire globe decreases the vmr at the given altitude by three orders of magnitude as compared to the plume area. Consequently, strong implications for ozone depletion through iodine from a single volcanic eruption are probably mainly regional and restricted in time. Primarily, the lower stratosphere or UTLS region is affected. However, the region impacted by the emitted iodine may be dislocated from the erupting volcano due to the quickly moving volcanic plume covering distances of typically around several hundred km per day.

Due to the larger chain length for the removal of $\mathrm{O_3}$ by $\mathrm{BrO_x}$ and $\mathrm{IO_x}$ than by $\mathrm{ClO_x}$, loss of $\mathrm{O_3}$ in the stratosphere can be significantly impacted by the BrO and IO in addition to ClO released from volcanic eruptions. In this case the lower stratosphere ~~will be~~ may become most affected. This could impact on ozone hole chemistry when volcanic eruptions enter the polar vortices, an issue recently raised by Solomon et al. (2016).

Background iodine amounts between 0.1 and 0.4 pptv in the free troposphere as observed recently (Puentedura et al., 2012; Dix et al., 2013) are possibly also influenced by volcanic activity. Following a volcanic eruption, the iodine amount will directly influence the local and regional chemistry by reducing the ozone levels. The impact of the ability of volcanic IO to form aerosol condensation nuclei requires further study. In addition, volcanic plumes may be subject to long-range transport and therefore lead to effects also at larger distances.

The Kasatochi eruption was in some respect special as it was a major eruption, the plume altitude was relatively large and also bromine amounts were larger than for other investigated volcanic plumes (Hörmann et al., 2013). IO has not yet been detected for any other eruptions investigated, at least not at the Kasatochi levels. Scaling with the observed bromine amounts, iodine levels for the other eruptions could just be below or around the detection limit of current space based instruments. Future satellite instruments with finer spatial resolution and improved signal-to-noise ratio may allow the observation and detailed investigation of iodine species in volcanic plumes more frequently.

It is interesting to speculate on the amount of halogens emitted to the atmosphere from past major eruptions which have severely impacted on atmospheric composition prior to halogen observations from space. For the Pinatubo eruption in 1991, for example, a total mass of about 20 Tg of SO_2 was emitted. The eruption injected gases and aerosols up to 25-30 km altitude, i.e. around the maximum stratospheric ozone mixing ratio. In relative terms, the IO vmr will be increased at these high altitudes due to much lower air density as compared to the Kasatochi estimates. Assuming a similar magma composition as that for Kasatochi, i.e. similar halogen to sulphur ratios, an amount of around 100 t of IO as well as 1 kt of BrO could have been emitted into the stratosphere from Pinatubo with corresponding impact on stratospheric chemistry over extended horizontal distances and periods. A detailed assessment again requires better knowledge and studies of the loss of iodine and bromine in the stratospheric aerosol.

5 Summary and Conclusions

~~For several days following~~ Following the major eruption of the Kasatochi volcano in August 2008, iodine monoxide ~~was~~ is observed by satellite ~~measurements in the emitted volcanic plume~~ in the volcanic plume for several days. This is the first experimental evidence of IO from a volcanic eruption. The satellite sensors SCIAMACHY and GOME-2A both detect slant column amounts of IO above 4×10^{13} molec/cm^2 in the volcanic plume for several days following the Kasatochi eruption. Maximum vertical columns above $2\times10^{13}\,\mathrm{molec/cm^2}$ are derived. The presented observations also represent the first reported retrievals of IO from measurements of the GOME-2A instrument. In comparison to tropospheric IO observations in polar and mid-latitudinal regions, the observed column amounts are large, reducing the uncertainties and facilitating analysis of individual measurements. The IO data in the plume shows good fitting quality with fitting errors around 6% for SCIAMACHY and below 15% for GOME-2A retrievals.

Overall, the IO enhancements coincide in space with previously published BrO and SO_2 observations. While the plumes of IO, BrO and SO_2 are roughly found in the same area with similar shape, the maximum amounts of the individual species, however, do not always coincide. Differences between IO and BrO are smaller than those between the halogens and SO_2. The emission chronology as well as chemical conversions are presumably individual for the three compounds and could probably lead to the observed differences in spatial distributions.

Correlating all observations of IO and BrO between August 9 to 12, 2008, yields a slope of 0.09, i.e. IO amounts are about one order of magnitude smaller than those of BrO. ~~This means~~ Judging from the IO and BrO column amounts alone, this volcanic ratio indicates a three order of magnitude difference with respect to the seawater ratio between iodine and bromine in agreement with previous filter measurements of volcanic samples at arc volcanos. For this relative enhancement of iodine two reasons play a role. Iodine shows a stronger preference than bromine to partition into volcanic ~~fluids than volcanic melts~~ fluid than melt in the volcanic chamber ~~below~~ located underneath the volcano. This relative partitioning between fluid and melt determines the gas phase composition from an eruption. In addition, iodine enriched marine sediments are carried into the Earth's mantle in the subduction zone and directly influence the composition of the magma.

An integration of the observed IO amount within the emission plume results in a large mass of around 10 t (4 to 12 t) of IO emitted from the volcano. ~~Comparing these numbers to the results of~~ By comparing the integrated numbers of IO and BrO molecules found within the volcanic plume, the BrO~~, the ratio for BrOto IO molecules lies~~ /IO number ratio ranges between 6.7 and 10.0, while the ~~ratio for the mass of BrOto IO~~ BrO/IO mass ratio lies between 4.0 and 6.7. Together with the knowledge that the Kasatochi BrO plume reached predominantly the altitude between 8 and 12 km, it can be concluded that a substantial input of iodine to the lower stratosphere, UTLS and free troposphere has taken place following the Kasatochi eruption. If the IO amount is homogeneously spread over the plume area and within the main 4 km thick vertical layer, a vmr of 3 pptv at an altitude of 10 km results. The local vmr can be ~~much~~ even higher due to inhomogeneous distribution in the volcanic plume. ~~An iodine vmr~~ Iodine volume mixing ratios of around 3 ~~pptv has~~ pptv may have substantial impact on the atmospheric composition, e.g., through regionally reducing the ozone ~~levels~~concentrations.

The investigation of past and future volcanic eruptions with respect to their IO content and impact on tropospheric and stratospheric chemistry is subject to further work and in future will be facilitated ~~in the future~~ by improved satellite instrumentation.

6 Data availability

Satellite trace gas column data from SCIAMACHY and GOME-2A observations can be obtained on request from the authors.

Competing interests. The authors declare that they have no conflict of interest.

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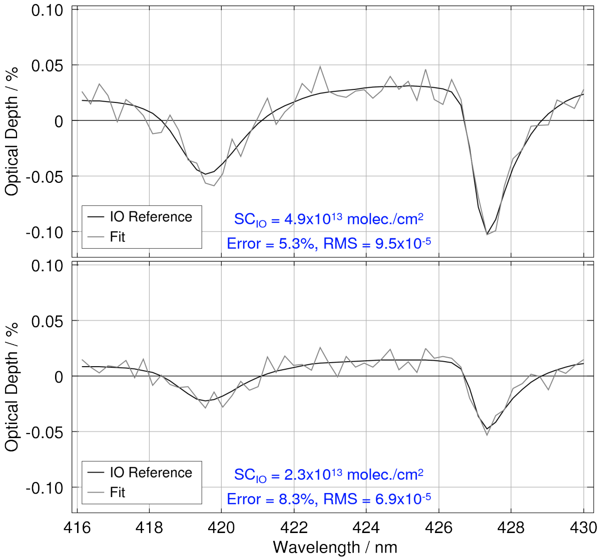

Figure 1. Example fitting results from SCIAMACHY on day August 11, 2008, with two different IO slant column amounts recorded at 55.34°N, 220.21°E (top) and 54.90°N, 215.92°E (bottom). The fit (grey) shows the measurement optical depth after all other features except for the IO absorption (black) have been subtracted. The optical depth RMS values are 9.5 and 6.9 $\times 10^{-5}$, respectively.

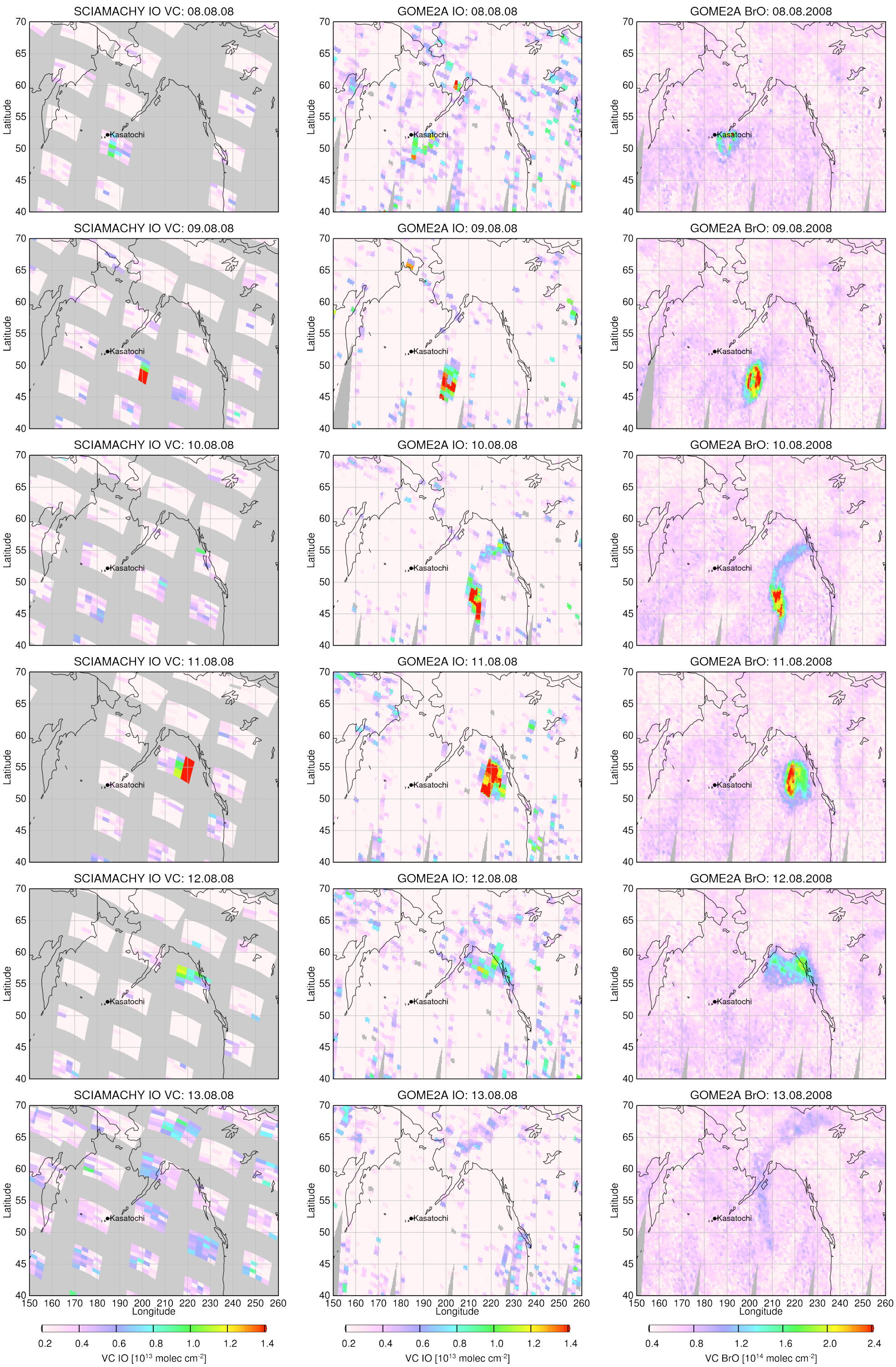

Figure 2. Retrievals of IO from SCIAMACHY (left) and GOME-2A (middle) together with observations of BrO from GOME-2A (right) for 6 days following the eruption of Kasatochi volcano on August ~~08~~8, 2008. Regions without data coverage are shaded in grey.

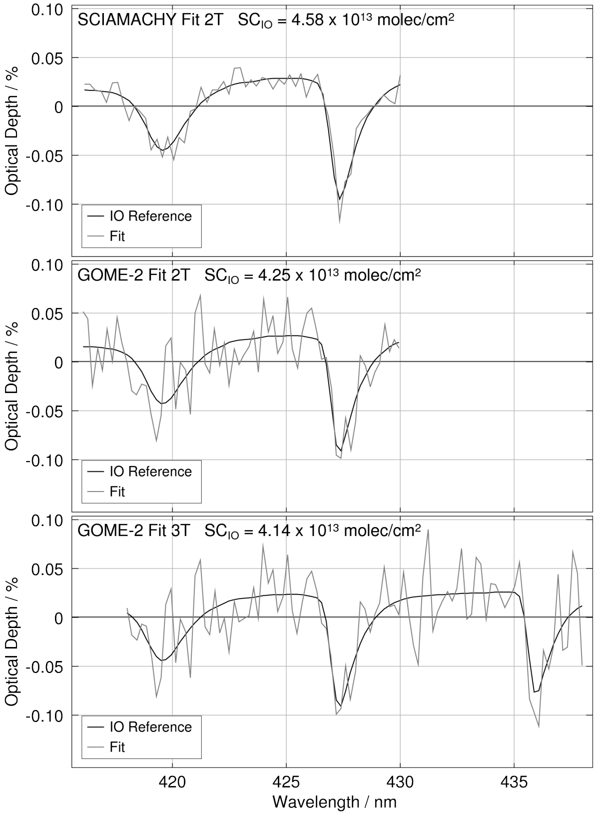

Figure 3. Spectral fitting results from day August 11, 2008, for a collocation between SCIAMACHY (top) and GOME-2A around 55°N and 220°E. For GOME-2A, the results from two different fitting windows are shown, using the SCIAMACHY standard IO fitting window (center) and using a larger spectral window covering three spectral absorption bands of IO (bottom).

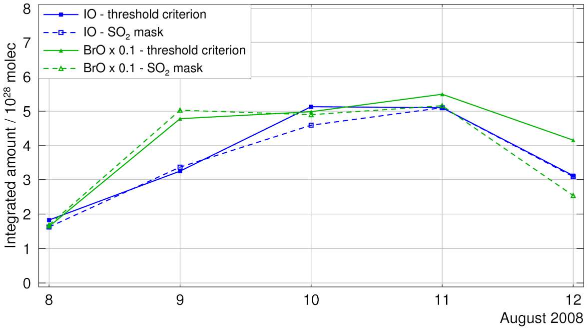

Figure 4. Time series of integrated IO (blue) and BrO (green) amounts. BrO data is scaled by a factor of 0.1. For both trace gases, two methods for the plume definition are applied, the threshold criterion and the SO$_2$ mask.

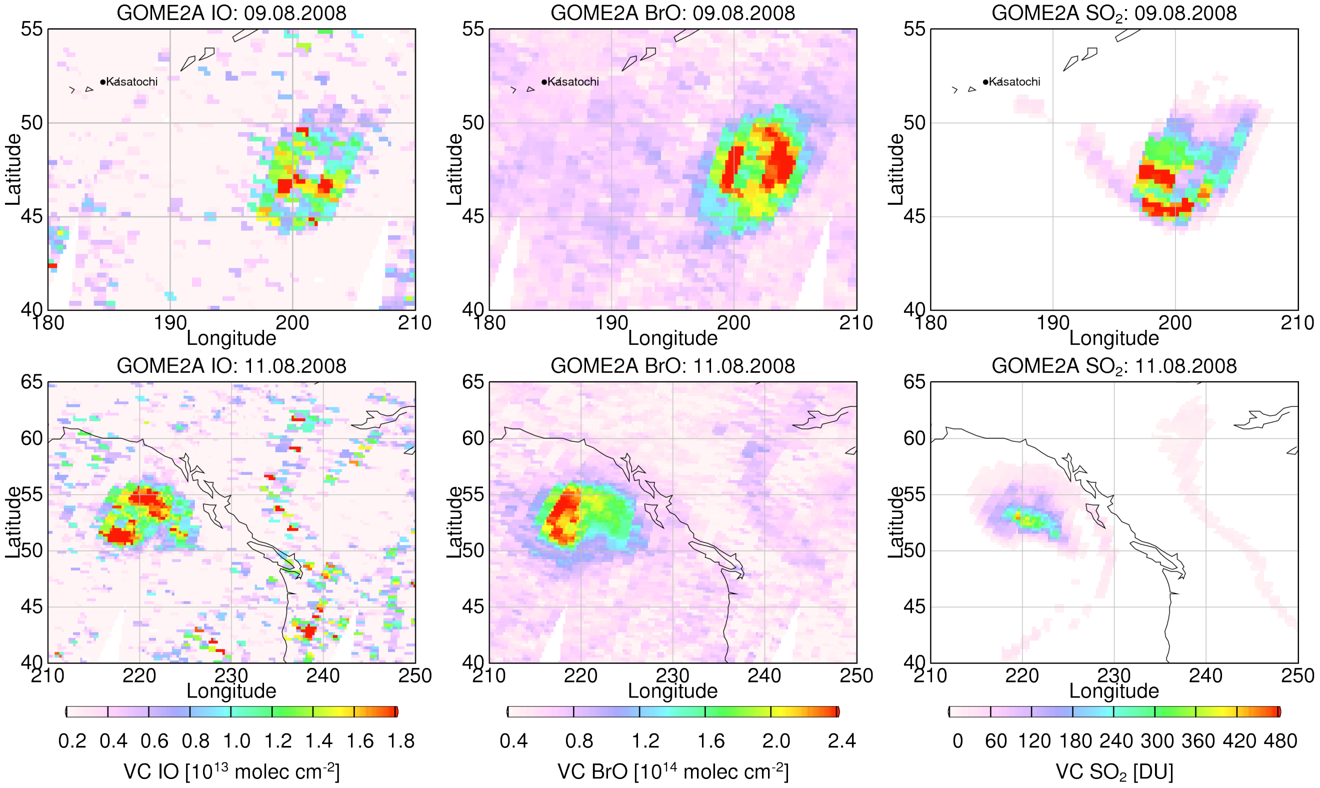

Figure 5. Close-up of the volcanic plumes of IO (left), BrO (center) and SO$_2$ (right) on the days August ~~09~~ 9 (top) and August 11 (bottom)~~.~~ , 2008. While the plume extent and shape are similar, differences in the spatial distribution patterns are visible.

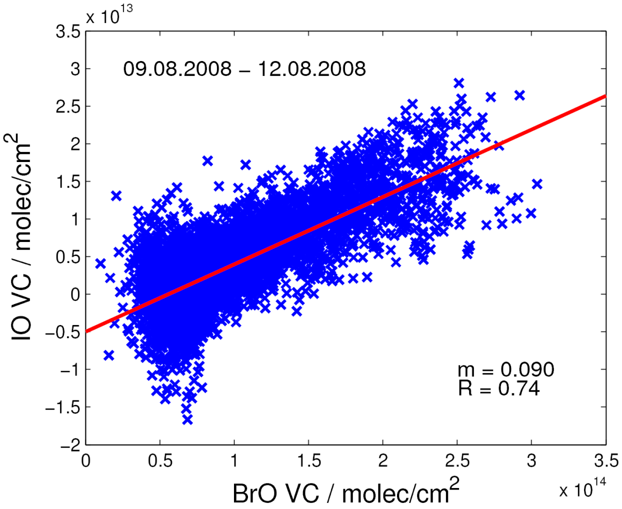

Figure 6. Scatterplot of IO vs. BrO column amounts. Data from the four days from August ~~09~~ 9 to 12, 2008, is included.