Review for manuscript Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-619, 2016 by Schönhardt et al.,

The present paper reports on iodine oxide (or its precursors) emitted from the volcano Kasatochi past the August 07, 2008 eruption. The detection of IO is performed in back-reflected skylight received by the SCIAMACHY instrument on ENVISAT and the GOME-2 instrument on MetOp-A using the well-known DOAS technique. From the analysed data semi-quantitative information on the total amount of emitted iodine is inferred and compared with the volcanic emissions of bromine and sulfate dioxide.
The study reports on robust and valuable observations, but the interpretation of the data needs some clarifications. Also the manuscript's English and presentation style deserves some major wrap-up.

1. Major comments

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?), mid-latitude and high latitude UT/LS.

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.

2. Minor comments

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).

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.

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.

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….

More example:

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

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

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.

More examples:

- Page 4, line 19: The comparably large IO columns are connected -→ The comparably large IO column *amounts* are *detected with*
- Page 5, line 10: The DOAS analysis yields the trace gas slant column values→ The DOAS analysis yields (differential) slant column amounts…
- Page 5, line 10: In order to convert these numbers …..→ In order to convert the slant column amounts…..
- Page 6, line 29: 3.3 Analysis of IO and BrO amounts →: 3.3 Analysis of 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
- 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.
- 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.
- Page 8, line 21: … retrieved amounts of … instead of …retrieved column amounts ….

3.3 A wrong comparative!

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…

- 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 magnitude*s* lower in volcanic plumes than in seawater.

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, …

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).

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
- Page 4, line 31: ……which is assumed to have small column amounts of IO..-> which is likely to contain small column amounts of IO
- Page 5: The header of Table 1 need to appear on top of the table.
- 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 °.
- 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.
- 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.
- 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.
- 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 …
- 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.
- 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.

- 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
- 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 ….
- 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…
- Page 7, line 22: ….. but due to the latter observation ….-> … but due to the latter finding
- 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.
- 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…
- 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 pressure*s*, i.e. at different depth of the volcanic abyss (erase …and time).
- Page 9 line 1 to 16: Move to the discussion section.
- 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?
- Page 9, line 23: Data from four days August 09 to 12…-> Data from the period August 09 to 12, 2008….
- 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.
- 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 magnitude*s* in volcanic plumes 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.
- 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.-> 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.
- 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….
- 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

- 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….
- 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).
- Page 10, line 2: In this case the lower stratosphere will be most affected -> In this case the lower stratosphere may become most affected.
- 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…
- 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.
- Page 12, line 22: ……..and will be facilitated in the future…-> and in future will be facilitated

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