

Interactive comment on “Simultaneous satellite observations of IO and BrO over Antarctica” by A. Schönhardt et al.

A. Schönhardt et al.

schoenhardt@iup.physik.uni-bremen.de

Received and published: 1 June 2012

Referring to the Interactive Comment of Anonymous Referee #1 from 13 February 2012

We are grateful to Referee #1 for the review of our manuscript and the helpful comments. In the following, all comments by the Referee are addressed in the same sequence they were published in the Referee's review. The questions are answered and the requests have been used to improve the manuscript and we hope to have fully answered the Referee's questions.

The Referee's comments are printed in italic font, our answers and explanations

C16644

are printed in usual black font as well as text parts from the original version of the manuscript. New text passages for the revised version of the article are written in blue colour. First, the "Main points" made by Referee #1 are addressed in Part 1. The "Minor points" are treated in Part 2.

Part 1. Answers to the Main points of Referee #1

Comment 1

Given that the IO is very likely close to the surface, it would be useful to provide the reader with some sense of the concentrations of IO that are probably being observed. Comparison with the long-path DOAS measurements of Saiz-Lopez et al would provide a useful benchmark. It is the concentrations that matter for understanding the atmospheric significance.

Answer to Comment 1

The Referee mentions an important point. For chemical reactions, the trace gas concentration is the determining quantity. The satellite observations in the first place yield the slant column amounts. They need to be converted to vertical columns using the air mass factor (AMF), and the vertical columns are converted to concentrations or volume mixing ratios using the altitude profile of the respective gas. The altitude profile in addition influences the AMF value, and in this way has a two-fold importance.

The altitude profile of IO is not well known so far, and differences between different locations are to be expected. However, the knowledge of the profile shape is essential. Assuming the IO to be close to the surface which is in agreement with most previous

C16645

studies and assumptions (Saiz-Lopez et al., 2008; Frieß et al., 2010), estimations for the IO mixing ratios in the boundary layer can be derived. In latest studies, however, wide spread and substantial free tropospheric abundance of IO has been reported in tropical regions (Volkamer et al., 2012; Saiz-Lopez et al., 2012). Free tropospheric or even stratospheric abundances of IO may or may not be relevant for Antarctic scenes. This is so far an open issue. Therefore, it is important to keep in mind this uncertainty owing to the fundamental assumptions.

The conversions from vertical columns to mixing ratios and especially the comparison to the long-path DOAS measurements of Saiz-Lopez et al. (2007), have been discussed in (Schönhardt et al., 2008) considering the IO to be situated in the lowest 1 km or 100 m. We agree with the referee, that this relation should be mentioned in the current manuscript as well. In Section 3 the manuscript says that "Over widespread areas the vertical column lies between 1.0×10^{12} molec cm⁻² and 1.5×10^{12} molec cm⁻²". This statement is based on the IO six year average. A vertical column value of 1.0 or 1.5×10^{12} molec cm⁻² corresponds to a concentration of 1.0 or 1.5×10^8 molec cm⁻³ within a 100 m layer and a mixing ratio of 3.7 or 5.6×10^{-12} , i.e. 3.7 or 5.6 pptv, at 273 K. These values are of the same order of magnitude as observed by Saiz-Lopez et al. (2007) close to the surface by long-path DOAS observations in the years 2004/2005 and by Atkinson et al. (2012) observed by ship-borne MAX-DOAS in early 2009 when assuming a 200 m boundary layer.

Considering a boundary layer box profile, the mixing ratio of IO will change by approximately one order of magnitude when assuming a 1 km instead of a 100 m thick layer for the case of a bright surface where the AMF hardly depends on the profile shape. The boundary layer in Antarctica can easily be as shallow as 100 m. In any case, the altitude profile will retain its strong influence in this conversion procedures, which is even more the case above dark surfaces, as in addition the AMF depends on the profile more than it is the case above ice and snow.

C16646

Changes to the manuscript

- The following paragraph has been included in the manuscript in Section 3
For the understanding of the IO influence on chemical composition, the amounts in terms of concentrations or mixing ratios are relevant. Starting from column amounts, the computed mixing ratio is strongly dependent on the assumed altitude profile, which is not well known. Assuming the IO to be close to the surface which is in agreement with several previous studies and assumptions (Saiz-Lopez et al., 2008; Frieß et al., 2010), estimations for the boundary layer IO mixing ratios can be derived. In latest studies, however, wide spread and substantial free tropospheric abundances of IO have been reported in tropical regions (Volkamer et al., 2012; Saiz-Lopez et al., 2012). If free tropospheric or even stratospheric abundances of IO are relevant for Antarctic scenes is so far an open issue.

The conversion from vertical columns to mixing ratios and the comparison to long-path DOAS measurements of IO mixing ratios by Saiz-Lopez et al. (2007) in Antarctica, have been previously discussed in (Schönhardt et al., 2008). A vertical column value of 1.0 or 1.5×10^{12} molec cm⁻² corresponds to a concentration of 1.0 or 1.5×10^8 molec cm⁻³ within a 100 m layer and a mixing ratio of 3.7 or 5.6×10^{-12} , i.e. 3.7 or 5.6 pptv, at 273 K. These values are of the same order of magnitude as observed by Saiz-Lopez et al. (2007) close to the surface by long-path DOAS observations in the years 2004/05 and by Atkinson et al. (2012) using ship-borne multi-axis DOAS in early 2009 when assuming a 200 m boundary layer. Iodine chemistry with IO amounts on the ppt level may have noticeable influence on atmospheric composition in Polar Regions, especially on O₃ levels and HO₂/OH and NO₂/NO ratios (Saiz-Lopez et al., 2007) as well as particle formation (Atkinson et al., 2012) and potentially also enhanced mercury oxidation via Br (Saiz-Lopez et al., 2008).

C16647

Considering a boundary layer box profile, the computed mixing ratio of IO will change approximately by one order of magnitude when assuming a 1 km instead of a 100 m thick layer for the case of a bright surface where the AMF hardly depends on the profile shape. The boundary layer in Antarctica can easily be as shallow as 100 m. In any case, the altitude profile will retain its strong influence in the conversion steps, which is even more the case above dark surfaces.

Comment 2

One conclusion of the paper is that the role of biology on the underside of sea-ice in producing gas-phase iodine needs now to be studied in situ. That implies that these levels of IO matter. But this paper does not really explain why, or simply assumes that it is self-evident. Ozone depletion is mentioned in the introduction; however, presumably ozone is not substantially destroyed within this boundary layer, or IO and BrO would not be formed. The satellite provides the unique opportunity to see what difference these IO levels make on a regional-to-continental scale. A few sentences indicating how this might be done, in combination with modelling, would be helpful.

Answer to Comment 2

As has been discussed in reply to Comment 1, the computation of IO concentrations from satellite observations depends on the altitude profile. Therefore, also the estimated IO impact on atmospheric composition will strongly depend on this and is currently not well established. The determination of the iodine impact can only be done if certain assumptions are made and can only be specified more precisely if further measurements enlarge our knowledge and understanding of the open aspects.

C16648

The important point is, that under reasonable assumptions the satellite IO observations would be consistent with a large, widespread and non negligible impact of iodine chemistry on ozone levels and particle formation. However, due to the various assumptions that have to be made in the retrieval and can currently not be verified, the satellite data do not yet provide strong constraints on the range of possible surface IO mixing ratios. Dedicated studies will be needed to investigate this further.

Considering the IO in a box profile of 100 m or 1 km as before, will lead to mixing ratios on the order of several ppt or somewhat below one ppt, respectively. These values are average values over long time and the spatial extent of a satellite pixel. On a shorter time and smaller spatial scale much larger IO abundances may be present, which is relevant in non-linear iodine chemistry and particle formation. In this sense, the satellite measurements yield a lower limit of the expected effects.

Saiz-Lopez et al. (2007) and Calvert and Lindberg (2004) have provided insight into the potential impact iodine chemistry may have on ozone depletion in the polar boundary layer by use of ground-based measurements and modelling studies. The immediate effect of iodine on ozone levels appears to be strongly influenced by meteorology (Saiz-Lopez et al., 2007). However, up to now insitu measurements of simultaneous iodine and ozone measurements are sparse. The presence of halogens is nevertheless regarded necessary for the explanation of ozone depletion events. One especially important aspect of iodine except for its direct ozone depletion potential is the enhancing effect on O₃ loss by bromine chemistry. While Calvert and Lindberg (2004) use relatively large amounts of iodine precursors in their model calculations, they showed that the combination of iodine and bromine reactions in a polar troposphere is much more efficient in depleting O₃ than iodine or bromine chemistry alone. Saiz-Lopez et al. (2007) have found that the depletion rate of polar tropospheric O₃ increases approximately by a factor of four when a few ppt of iodine (in agreement with their observations) are added to the present bromine loading.

C16649

In the presence of a few ppt of IO, ozone is not necessarily completely removed, but the levels adjust to a lower value (not necessarily locally if advection and/or entrainment from above is strong). As typical boundary layer O₃ levels are about 3–4 orders of magnitude larger than IO levels, small amounts of IO should be retained also during low ozone phases.

Furthermore, IO is an important precursor for particle formation. Concentrating on the Polar Regions, Atkinson et al. (2012) have observed particle formation as well as particle growth during a recent campaign period in the Weddell Sea area. The particle formation was attributed to active iodine chemistry. As IO levels simultaneously observed by Atkinson et al. (2012) during the cruise are in agreement with satellite IO observations, the widespread satellite IO results suggest potential impact of iodine mediated particle formation on a fairly large spatial scale. The rate of particle formation, however, depends crucially on the number density (as opposed to the total column) of the nucleation precursor IO.

In order to further use the satellite information for estimations of the iodine influence on levels of O₃, OH, particles and other crucial components, on a regional or continental scale, information (or otherwise assumptions) on the small scale spatial and temporal variation and on the vertical profile is necessary. Ideally, ground-based as well as aircraft measurements would be performed in several different representative locations and times to investigate these aspects. Building on such information from reference points and model computations, the satellite observations provide the opportunity to upscale the expected IO influence from the local measurements to a regional-to-continental scale.

C16650

Changes to the manuscript

- Additional sentence in Section 3 (see also answer to Comment 1)
iodine chemistry with IO amounts on the ppt level may have noticeable influence on atmospheric composition in Polar Regions, especially on O₃ levels and HO₂/OH and NO₂/NO ratios (Saiz-Lopez et al., 2007) as well as particle formation (Atkinson et al., 2012) and potentially also enhanced mercury oxidation via Br (Saiz-Lopez et al., 2008).
- Changes to the last paragraph in Section 8
In addition, for an improved understanding of the importance of atmospheric iodine, combined field, satellite and modelling studies would be helpful. Under reasonable assumptions, e.g. on the IO vertical distribution, the presented satellite IO observations would be consistent with a few ppt IO in the polar boundary layer and therefore a widespread and non negligible impact of iodine chemistry on atmospheric composition. These IO levels would indicate a noticeable influence on Antarctic ozone as well as OH amounts and particle formation. However, due to the various assumptions that have to be made in the retrieval and can currently not be verified, the satellite data do not yet provide strong constraints on the range of possible surface IO mixing ratios. Dedicated studies investigating this further would include ground-based and aircraft measurements of the temporal and spatial variation and especially of the vertical distribution of iodine species at several representative locations. Model computations based on the input from these reference points may then be extended to further areas by also using satellite IO observations in an upscaling procedure to a regional-to-continental scale, and in this way aim at an improved determination of iodine impact on the atmosphere. The satellite observations of IO over several years, presented in this manuscript, provide valuable insight into the larger scale distribution of IO and its spatial and temporal variation.

C16651

Comment 3

The discussion on page 9 about averaging the monthly data from 6 years is fine to get the seasonal trends. However, there are year-to-year differences (e.g. between 2006 and 2009) which are quite significant. Are there any indications of why, for instance any linkage to sea ice coverage?

Answer to Comment 3

This is a good question, and the precise reason for the variation is not yet clear. While the IO spatial pattern is similar in all analysed years, the overall magnitude changes as discussed in Section 4. An instrumental effect causing a drift in the absolute IO amount might play a role. The pattern has a similar spatial shape and the level shift is small, on the order of 5×10^{-5} in optical depth. The difference between IO columns in the years 2006 and 2009 has little spatial structure.

From comparisons of sea ice concentration variations over the years, it can be concluded that a direct link between the overall magnitude of the IO signal and sea ice coverage is not present. The influence would not be a linear dependency as the overall sea ice cover does not change by the same factor as the IO signal between the years 2006 and 2009 shown in Figure 3. If the connection between sea ice and IO is determined by biological activity, the relation would have opposing aspects. The sea ice is needed in the first place as a habitat for the algae species enabling iodine emissions, while a thick and closed ice cover may suppress emissions of gaseous iodine. The actual emission flux is in any case dependent on other factors like temperatures of water, sea ice and boundary layer, as well as the status of the biosphere, nutrient support and others. In further studies, the year-to-year variation and potential reasons will need to be investigated in more detail.

C16652

Changes to the manuscript

- Additional sentence in Section 4 in the revised version
[In further studies, the year to year variation and potential reasons will need to be investigated in more detail.](#)

Part 2. Addressing the "Minor points" from Referee #1

Minor point 1: page 3, lines 11/12

one of the co-authors (Gomez Martin) published a recent paper in Z. Phys. Chem. which made significant progress in understanding how iodine oxide particles form and grow in the marine environment. This paper should be cited here.

The reference to the paper (Saunders et al., 2010) coauthored by J. C. Gómez Martín has been added here.

Minor point 2: page 9, line 16

This is confusing and should be rephrased "Due to many of the IO measurements being close to the detection limit ..."

C16653

Changes to the manuscript

- Original version:
Due to the comparably small amounts of IO close to the detection limit of the instrument (Schönhardt et al., 2008), it is necessary to average IO results over several weeks to months to create maps with sufficient data quality.
- Revised version of the manuscript:
Due to the comparably small atmospheric amounts of IO, many of the IO measurements are close to the detection limit of the instrument (Schönhardt et al., 2008), making it necessary to average the IO results over several weeks to months to create maps with sufficient data quality.

Minor point 3: page 13, line 25

"...offer a good..."

The article "a" has been added here.

Minor point 4: page 14, line 22

The Saiz-Lopez et al (2008) paper showed that snow recycling was required in their model of IO in coastal Antarctica, and so should be referenced here.

Reference to the paper by (Saiz-Lopez et al., 2008) has been included.

C16654

Minor point 5: page 14, lines 26

The discussion of acid anhydrides needs some more details (and references?).

The respective sentence has been rephrased and some further information has been added.

Changes to the manuscript

- Original version:
The formation of hygroscopic iodine containing acid anhydrides, as a result of IO reactions, which act as condensation nuclei for new particle formation is likely to be an important part of this mechanism.
- Revised version:
As a result of IO reactions, iodine oxide compounds are formed which contain iodine acid anhydrides, such as I_2O_3 , I_2O_4 , or I_2O_5 , the latter being the anhydride of iodic acid HIO_3 and strongly hygroscopic (Jimenez et al., 2003). Iodine oxides may act as starting point for new particle formation (Jimenez et al., 2003; Burkholder et al., 2004; Saunders et al., 2010). The initial formation of the acid anhydrides is therefore likely to be an important step in any transport and recycling mechanism.

Minor point 6: page 15, line 21

"positively linked" implies some causality. You should consider a phrase like "closely correlated".

C16655

This is a good suggestion, as we did not intend to imply causality here. The wording has been changed in the revised version as suggested.

Minor point 7: page 15, lines 22-24

*This sentence is confusing and should be omitted. The correlation (or lack thereof) between IO and chl-*a* has not been established globally because there are so few IO measurements, almost all in coastal locations.*

Changes to the manuscript

- Original version:
Globally however, high chlorophyll-*a* concentrations do not necessarily simply correlate with high IO, so chlorophyll-*a* may be seen as an indication for IO appearance but not as a proxy.
- Revised version:
Globally however, the relation between IO and Chl-*a* has not yet been established based on ground-based measurements, because of the sparsity of IO measurements, most of them being taken in coastal locations. Initial investigations based on satellite observations indicate an ambiguous picture, some regions showing a positive relation between Chl-*a* concentrations and IO amounts and some without such a relation (Schönhardt et al., 2012). Chlorophyll-*a* may not necessarily be a useful proxy for IO appearance.

C16656

Minor point 8: page 16, line 11

Define what is meant by "sea ice concentration".

Changes to the manuscript

- The following changes have been included in Section 7.3 in the revised version:
In order to relate the IO appearance to sea ice cover, observations of sea ice concentrations are used. [...] Based on the brightness temperatures measured with the AMSR-E 89 GHz channel, the ice concentration data are a result of the ARTIST Sea Ice (ASI) algorithm (Kaleschke et al., 2001; Spreen et al., 2008). The observed field of view may contain regions with open ocean as well as sea ice covered areas. The sea ice concentration value is defined as the relative area (in percentage) of water covered by sea ice.

Minor point 9: page 18, line 27

no comma

The comma has been deleted.

C16657

Minor point 10

In several places, the abbreviation "cp." is used for "compare". It should be "cf."

The abbreviations have been corrected to "cf." in the revised version.

References

- Atkinson, H. M., Huang, R.-J., Chance, R., Roscoe, H. K., Hughes, C., Davison, B., Schönhardt, A., Mahajan, A. S., Saiz-Lopez, A., Hoffmann, T., and Liss, P. S.: Iodine emissions from the sea ice of the Weddell Sea, *Atmospheric Chemistry and Physics Discussions*, Vol. 12, No. 5, 11595–11639, <http://www.atmos-chem-phys-discuss.net/12/11595/2012/doi:10.5194/acpd-12-11595-2012>, 2012.
- Burkholder, J. B. and Curtius, J. and Ravishankara, A. R. and Lovejoy, E. R.: Laboratory studies of the homogeneous nucleation of iodine oxides, *Atmos. Chem. Phys.*, 4, 19–34, doi:10.5194/acp-4-19-2004, 2004.
- Calvert, J. G., and Lindberg, S. E.: Potential influence of iodine-containing compounds on the chemistry of the troposphere in the polar spring. I. Ozone depletion, *Atmospheric Environment*, 38, 5087–5104, doi:10.1016/j.atmosenv.2004.05.049, 2004.
- Frieß, U., Deutschmann, T., Gilfedder, B. S., Weller, R., and Platt, U.: Iodine monoxide in the Antarctic snowpack, *Atmos. Chem. Phys.*, 10, 2439–2456, <http://dx.doi.org/10.5194/acp-10-2439-2010>doi:10.5194/acp-10-2439-2010, 2010.
- Jimenez, J. L., Bahreini, R., Cocker III, D. R., Zhuang, H., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H., O'Dowd, C. D., and Hoffmann, T.: New particle formation from photooxidation of diiodomethane (CH₂I₂), *J. Geophys. Res.*, 108, D10, 4318, doi:10.1029/2002JD002452, 2003.
- Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J., and Plane, J. M. C.: Extensive halogen-mediated ozone de-

C16658

- struction over the tropical Atlantic Ocean, *Nature*, 453, 1232–1235, <http://dx.doi.org/10.1038/nature07035>doi:10.1038/nature07035, 2008.
- Saiz-Lopez, A., Mahajan, A. S., Salmon, R. A., Bauguitte, S. J.-B., Jones, A. E., Roscoe, H. K., and Plane, J. M. C.: Boundary layer halogens in coastal Antarctica, *Science*, 317, 348, <http://dx.doi.org/10.1126/science.1141408>doi:10.1126/science.1141408, 2007.
- Saiz-Lopez, A., Plane, J. M. C., Mahajan, A. S., Anderson, P. S., Bauguitte, S. J.-B., Jones, A. E., Roscoe, H. K., Salmon, R. A., Bloss, W. J., Lee, J. D., and Heard, D. E.: On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for O₃, HO_x, NO_x and the Hg lifetime, *Atmos. Chem. Phys.*, 8, 887–900, <http://dx.doi.org/10.5194/acp-8-887-2008>doi:10.5194/acp-8-887-2008, 2008.
- Saiz-Lopez, A., Ordoñez, C., Gomez Martin, J. C., Lamarque, J.-F., and Kinnison, D.E.: Global modelling of upper tropospheric-lower stratospheric iodine: budget and implications for ozone, *Geophysical Research Abstracts*, Vol. 14, EGU2012-8580, EGU General Assembly, 2012.
- Saunders, R.W., Kumar, R., Gómez Martín, J.C., Mahajan, A.S., Murray, B.J., and Plane, J.M.C.: Studies of the formation and growth of aerosol from molecular iodine precursor, *Z. Phys. Chem.*, 224, 1095–1117, doi:10.1524/zpch.2010.6143, 2010.
- Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H. K., and Burrows, J. P.: Observations of iodine monoxide columns from satellite, *Atmos. Chem. Phys.*, 8, 637–653, <http://dx.doi.org/10.5194/acp-8-637-2008>doi:10.5194/acp-8-637-2008, 2008.
- Schönhardt, A., Richter, A., and Burrows, J. P.: Iodine Monoxide and the relations to sea ice and biological activity, *Proc. of ESA, SOLAS & EGU Joint Conference "Earth Observation for Ocean-Atmosphere Interactions Science"* Frascati, Italy, 29 November - 2 December 2011, ESA SP-703, March 2012.
- Volkamer, R., Coburn, S., Dix, B., Sinreich, R., Lechner, M., Atlas, E., Guenther, A., Duhl, T., Sommariva, R., von Glasow, R., Myriokefalitakis, S., and Kanakidou, M.: Controls from a widespread surface ocean organic micro layer on atmospheric oxidative capacity, *Geophysical Research Abstracts*, Vol. 14, EGU2012-6761-1, EGU General Assembly, 2012.

C16659