

Interactive comment on “Iodine monoxide in the Antarctic snowpack” by U. Frieß et al.

Anonymous Referee #2

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General Comments

MAX-DOAS measurements of IO at the Antarctic Neumayer Station are presented. One special aspect of these measurements is the involvement of negative elevation angles, viewing into the snow besides the instrument which is situated at an altitude of 7m above the snow. From a total of seven viewing angles (2 below the horizon, 4 above and the zenith direction), the authors deduce vertical column information for three different layers, i.e. the atmosphere above the instrument, the 7m layer below the instrument, and a third layer within the snowpack, by applying radiative transfer considerations. From the measurement results, the authors infer that a large fraction of the IO column is situated inside the snowpack instead of in the air above. The presented data set and the data analysis are valuable and the new findings are interesting for the field of halogen chemistry in Polar Regions. The manuscript is largely well written and comprehensive.

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The discussed results constitute a new concept which has implications for the local chemistry and nucleation processes of iodine particles. It would be valuable to add some ideas and conclusions to the manuscript on the consequences and the impact of high IO concentrations within the snowpack (e.g., on local chemistry, particle nucleation, etc. what the authors consider relevant).

Some specific comments and recommendations for improvements are listed below and should be addressed by the authors. After according revisions of the manuscript, I recommend publication in ACP.

Main comments

The total column of IO is subdivided into 3 different column parts, above and below the instrument and within the snowpack. For the retrievals, a total of 7 different viewing angles are used. Although on p.25377 it is stated that “The retrieval of three partial VCDs v_a , v_b and v_s from MAX-DOAS measurements at 7 viewing directions, represents a well constrained problem”, this is only true if the 7 measurements are sufficiently independent from each other. However, as the authors state (e.g. on p.25372, l.18-20) and as it is common for DOAS measurements, the different viewing directions are not independent. The degree of dependency or common information changes also with the conditions, and can be calculated from the averaging kernels. I am sure the authors have assessed this problem. Are you sure that you can distinguish 3 pieces of independent information from the measurements? How is this determined/ensured?

Some open questions remain when considering the influence of blowing snow (or other aerosol in the lower layers?) on the retrieval. The influence of blowing snow on the optimal estimation retrieval is discussed on p.25379, and it is concluded that a layer of blowing snow would influence the retrieval, and the “model runs were able to reproduce the measurements as well, yielding around 10ppt of IO in the blowing snow layer”. p.25386, l.20-25: Here, the blowing snow is needed to explain the stronger scatter in

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data for the VCD below the instrument. Therefore, days with considerable amounts of blowing snow definitely exist and are apparently retained in the results for the atmospheric layers. As discussed on p.25379, however, this blowing snow would also mean that the light path through any IO above the snow would be strongly enhanced, increasing the SCD there. How can the retrieval for IO in the snowpack without taking into account the blowing snow be sustained in the view of the fact that blowing snow is obviously present (on enough days to cause the scatter in the middle layer) and that this would alternatively allow results with around 10ppt IO above the snow instead of in the snowpack? How do the results look like, if the snow pack, a layer with high aerosol load (e.g. blowing snow) and the entire atmosphere above (i.e. again 3 layers) are considered? Otherwise, were days with blowing snow clearly identified and excluded from the results for the snowpack, but not for the atmosphere? Is the larger scatter in the data for the layer above the snow maybe caused by a different process? I know that the authors have already defended their idea of high IO in the snow pack in the discussions here (response to the Interactive Comment), but there still seems to be this second possibility to explain the data. I don't see this as a problem for their interpretations, but maybe the influence of the blowing snow should be retained in the discussion and not ruled out too quickly. Otherwise, maybe this judgement needs to be better supported in the manuscript. In connection to the discussion on blowing snow: The idea arises if other aerosols in the lowest layers would strongly affect the retrieval of IO which do not depend on wind speeds. However, in the response of the authors to the Interactive Comment here, they have stated that aerosol levels are far too low in Antarctica. Maybe this should be added (with reference) to the manuscript in order to meet doubts of future readers.

p. 25364, I.4: There are earlier articles discussing the IO+BrO cross-reaction. e.g. Solomon et al., 1994, and Vogt et al., 1999.

p. 25364, I.9 ff: Here, the paper of Gómez-Martín et al. 2009, should be cited. This I see was also suggested by Referee#1. Especially as the authors mention the impact

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of the branching ratios, the yield found by Gómez-Martín et al. of close to unity for the reaction $OIO \rightarrow I + O_2$ should be cited in this respect. Even more suggestions for citations are already given in the Interactive Comment by J.Gómez-Martín, as well as in the answer by the authors.

p. 25378, II.16-21: The two step retrieval algorithm could be described in more detail. How (and why) does this improve the accuracy of the retrieval? Does the accuracy also improve if the (then additional) assumption on clear sky conditions is not perfectly fulfilled? Is this a new procedure here or can the authors provide a suitable reference?

p.25380, I.20-24: At this stage, it is not understandable, why an IO concentration of 20ppb is discussed without further concern and a level of 100ppb is considered unrealistically high. Both values are far beyond the concentrations measured before, so this judgement seems inappropriate if it is left without comment. Possibly, the authors have in mind the quantity from the later discussed analysis of around 95ppb of total iodine from the snow pit samples which is, however, interpreted as being "probably the absolute minimum amount of iodine that could be released from the snow pack", p.25383, I.3-4. Please just clarify.

p.25381, Section 5: The entire section does not feature a single reference. Please provide references for the included steps, like the measurement methods, appropriate sample storage and the assessment of the accuracy by the "standard reference material". Although ion chromatography and mass spectrometry are in principle well known procedures, specific applications/methods/instruments differ, and in general applied measurement techniques should be cited to guide the reader to an information source, just like it is done for the DOAS method also. Please give the explanations of the abbreviations BCR-611 (I.21) and SMOW (I.27).

p.25384, I.6-7: The strong diurnal variation and its form are surprising. This issue has been raised in the Interactive Comment already and I would like to see some more comments on this in the final manuscript. The same holds for the discussion of the

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seasonal variation. Potential disagreements (which in part are ruled out by the authors in the response to the Interactive Comment) should nevertheless be mentioned and shortly explained in the manuscript as many readers will know the former studies and wonder why they are not mentioned at this point.

p.25387, l.7: Referee#1 already criticized the term “source for iodine” for the snowpack, a comment which I would support in order to avoid misunderstandings with the “basic” source, e.g. biogenic iodine or other which is not yet fully understood. In connection to this: what is the conception of the pathways of iodine? Would the IO remain as gaseous iodine mainly within the snowpack without much IO escaping or does efficient IO transport occur to the atmosphere above (which would qualify the snow pack more as a source than if this does not happen)? Can the high IO concentration in the snow pack in that case still remain constant throughout the summer as found here?

In addition, a general conclusion or ideas would be desirable on the implications deduced from these completely new and interesting suggestion, e.g. on the chemistry and composition of the Polar Boundary Layer. What do these new findings change in the picture of halogen chemistry in the Antarctic?

p.25387, l.18: The statement that “IO amounts above the snowpack (...) are comparatively small”, is in principle correct but makes a wrong impression. They are only small in comparison to the huge amounts deduced for the snowpack, but not compared to previously found amounts. Even if the IO between snow and instrument is distributed evenly over the 7m height, the concentrations are large. Maybe rephrase or add a relation.

Smaller comments

p. 25364, l.16: To my knowledge, IO has been detected in the Arctic (e.g. Wittrock et al, 2000), although not much has been published on this and IO levels are very low and as stated correctly not comparable to the amounts seen on the Southern Hemisphere.

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p.25367, l.13: The term “DOAS” has been defined already in Sec.1.

p.25368, l.5: I don't think “scattering cross sections” is the right term here, as the dimension of k_r and k_m is “per m” as chosen here. Wouldn't “scattering coefficient” be the appropriate term?

p.25368, l.8: With “off-axis geometry” the authors refer to all directions except for the zenith. However, as “off-axis” is not a fixed term (e.g. it has a very different meaning in general optics and might not be known to readers in the present context), it would be helpful if this term would be defined.

p.25369, l.6: Instead of “root min square” the authors surely mean “root mean square”. In connection to this, on p.25370 RMS values are given, and it remains unclear, if Equation (4) on page 25369 lacks a division by the number of wavelength pixels or if this is just included in the RMS calculation. However, then the RMS is not equal to χ as stated on p.25369, l.6, but to χ/\sqrt{K} , if K is the number of included wavelength pixels. Please clarify.

p.25374, l.7: The unit of the given concentration should read molec/cm³ instead of molec/cm².

p.25378 l.8: As bold letters are used for vectors and matrices, please write the MxM size of the matrix **S** in normal letters.

p.25381, l.18: Sentence not well written. Probably the authors mean that replicate measurements showed generally less than 10% deviation?

p.25382, l.19: The sentence stops before being finished.

p.25382, l.21: As Fig.9 does not compare Neumayer measurements to mid latitudes, this statement cannot be “seen in Fig.9”. Please just give a typical range of iodine concentrations for mid latitudes or rephrase.

p.25382, l.25-26: The fact that hardly any iodine is found in the snow pit samples for

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the summer period is interpreted as “pointing to efficient and significant iodine release from the snowpack”. Would it be alternatively (in principle) possible, that in summer just no iodine is deposited, instead of first deposited and again released?

Data analysis on p.25385 and Fig.11: The upper panel for the IO mixing height above the snow in Fig.11 brings up a question. The assumption, that the concentration remains constant across the snow/air interface seems to be reasonable. However, the assumption that the concentration remains constant above the snow enabling the calculation of an IO layer height seems problematic when looking at Fig.11. Whenever the concentration in the snowpack goes down (e.g. on each day shortly after noon), the layer height suddenly rises strongly. Does this indicate that the assumption is not correct? Speaking of orders of magnitude, the overall analysis would probably not change much, but maybe it should be stated that the IO concentration is most probably not constant above the snow? What is the main purpose of the calculation and discussion of the layer height in this context? (Is it mainly to confirm with layer heights found for NO_x in Greenland?)

Corrections in the figures:

Fig.3: As θ is used in the text for the SZA, please change the ϕ to θ in the left figure.

Fig.4: I do not agree with the general statement, that the highest dSCDs are found in the negative elevation angles. During several periods of the day, the 2° direction sees the highest IO dSCDs (e.g. in the morning and at noon). I do agree of course, that the negative angles contain large amounts of IO, and in some cases, they are the highest, but neither are they overall the highest (these are found for the 2° around 6:00 in the morning) nor at most times. Please rephrase more carefully.

Technical Corrections

p.25364, I.20: Include the word “in” or what you mean in front of “coastal” in “reactive iodine coastal areas”.

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p.25365, I.4: typo - second “form” should read “from”

p.25365, II.16-18: The sentence is incomplete, something missing/too much either in the beginning and/or between “measurements” and “the retrieval”.

p.25367, I.17: Probably, an “i” is missing after “trace gas”.

p.25372, I.23: typo - “scatted” should read “scattered”.

p.25375, I.21: Please insert articles, especially for “asymmetry parameter”, also for “single scattering albedo”.

p.25377, I.2 and 25: Please use consistent plural form of sastruga, which is usually sastrugi, or (somewhat less common) also sastrugis. I wonder if a footnote should shortly explain this term anyway as it is not so commonly known.

p.25382, I.10: Please delete the extra word “it”.

p.25385, I.4-5: Please write “The … VCDs … are …” or “The … VCD … is”, singular or plural.

p.25388, I.7: Change the second “(3)” to (4).

References:

Gómez Martín, J.C., Ashworth, S.H., Mahajan, A.S., and Plane, J.C.M.: Photochemistry of OIO: Laboratory study and atmospheric implications, Geophys. Res. Lett., 36, L09 802, doi:10.1029/2009GL037642, 2009.

Solomon, S., Garcia, R.R., and Ravishankara, A.R.: On the role of iodine in ozone depletion, J. Geophys. Res. 99, 20491-20499, 1994

Vogt, R., R. Sander, R. von Glasow, and P.J. Crutzen: Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study, J. Atmos. Chem., 32, 375–395, 1999.

Wittrock, F., Müller, R., Richter, A., Bovensmann, H., and Burrows, J.P.: Measurements

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of iodine monoxide (IO) above Spitsbergen, *Geophys. Res. Lett.*, 27, 1471–1474, 2000.

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