**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Iodine monoxide in the Antarctic snowpack" *by* U. Frieß et al.

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We appreciate the detailed comments on our manuscript by J. C. Gomez-Martin (in the following referred to as G.M.). In particular we are happy to hear that G.M. regards the topic of our work to fall within the scope of ACP and the results presented to be new and atmospherically relevant.

Unfortunately, there are several misunderstandings and misquotes of our manuscript:

1) G.M. claims that we conclude that the main source of iodine in the Antarctic coastal boundary layer is the snowpack rather than biological activity in the ocean. It is important to point out that we clearly support the hypothesis that iodine in Antarctica is of biological origin (see P 25363, L4). In particular, our measurements indicate that (a) accumulation processes lead to a strong enrichment of particulate iodine (which is most likely of biological origin) in the snowpack, in agreement with the early findings

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of Heumann et al. (1987), and that (b) most of the particulate iodine is converted to reactive iodine as soon as sunlight is available. The processes leading to this accumulation and the built-up of large IO amounts in the snow interstitial remain, however, unknown. Similar assumptions of snowpack being the source of halogen radicals have been made in model studies by Saiz-Lopez et al. (2008).

2) We certainly nowhere in our manuscript state that the sources iodine in the Antarctic snowpack are meteorites. Rather, we refer to early studies of iodine content in Antarctic meteorites and rock samples which indicate that atmospheric iodine reacts with their surfaces. This has been clearly stated in the introduction.

G.M. suggested to update the summary of iodine chemistry in the introduction. While a detailed review of the iodine chemistry is clearly beyond the scope of our manuscript, we agree with G.M. that a somewhat more detailed discussion might be beneficial. To our understanding, the question of OIO photolysis and in particular the product channels are controversial in the available literature. While Ashworth et al. (2002) concluded that $OIO + h\nu \rightarrow I + O_2$ is a major product channel and correspondingly the photolytic lifetime of OIO is short, Ingham et al. (2000) and Joseph et al. (2005) were unable to detect I-atoms in OIO photolysis and concluded that the above channel was negligible compared to $\rightarrow O + IO$. In the latter case the threshold wavelength would be shorter than the range where OIO absorbs and consequently OIO photolysis would be very slow (Joseph et al., 2005). A slow photolysis of OIO is supported by a series of measurements showing noticeable levels of OIO during daytime (Stutz et al., 2007). In contrast to that, Ashworth et al. (2002) and Gomez-Martin et al. (2009) came to the conclusion that $O_2 + I$ is a dominant channel in the photolysis of OIO which would make the photolytic lifetime of OIO very short (of the order of seconds). We agree with G.M that the photolysis of OIO leading to O+IO is not occurring in the atmosphere (and we did not intend to state this in our manuscript). Our wording might have been slightly unclear and we will change this in the final version of the manuscript.

The IO absorption cross section chosen for this study (Hönninger, 1999) is in good

agreement with other available IO cross sections. For example, a peak absorption cross section of the 3-0 transition around 436 nm of 2.71×10^{-17} cm^2 measured by Hönninger is in good agreement with a value of 2.83×10^{-17} cm^2 from Spietz (2005) (if convoluted to a spectral resolution of 0.45 nm used by Hönninger, 1999). We expect a temperature dependence of the IO cross section and thus the detected IO dSCDs. However, to our knowledge the temperature dependence of the IO absorption cross section has never been investigated and all data published so far is measured at room temperature.

We do not know why it should be "confusing" that we talk about SCDs. It is clearly stated in the manuscript (P. 25378, L16), how measured dSCDs are converted to absolute SCDs.

Concerning the vertical grid of the IO profile retrieval, it makes no sense to use finer layers in the lowermost 50 metres, since the vertical resolution of the retrieved profiles near the surface is several hundred metres as a result of the low information content of MAX-DOAS measurements (e.g., Frieß et al., 2006; Vigoroux et al., 2009; Theys et al., 2007). In particular, there is certainly no information on the vertical distribution in the lowermost 7 metres of the atmosphere between snow surface and instrument (this would only be the case if a significant fraction of the light would be scattered inside this layer). The value given at 3.5 m is the box airmass factor representative for the whole layer below the instrument.

Our radiative transfer calculations are monochromatic since we do not expect a significant wavelength dependence of the radiative transfer within the small wavelength window of the IO retrieval.

Concerning the comments on the profile retrieval, we refer to the discussion in the manuscript. First of all, we can assume that the box – AMFs simulated by McArtim are physically meaningful, since the radiative transfer model has been validated during intercomparison exercises (Hendrick et al., 2006) and the snowpack optical properties

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have been adapted from previous studies of the snowpack radiative transfer (King and Simpson, 2006; Lee-Taylor and Madronich, 2002). Owing to the very small aerosol load of the Antarctic atmosphere, the atmospheric radiative transfer can be simulated very accurately. This has been confirmed by comparison of modelled and measured dSCDs of the oxygen collision complex. As pointed out in the manuscript, there are of course substantial uncertainties regarding the snowpack radiative transfer due to the uncertainties in the optical properties, leading to uncertainties in the retrieved snowpack IO concentrations. It has been shown how different snowpack extinction coefficients and assumptions on the vertical profile inside the snowpack affect the retrieval (Figure 8). Compared to the uncertainties from these parameters, the impact of phase function and single scattering albedo of ice crystals on the radiative transfer inside the snowpack are expected to be small, and sensitivity studies regarding these parameters as suggested by G.M. are beyond the focus of our studies.

G.M. claims that there might be alternative physical interpretations of our measurements which might also explain our observations, but does not state what alternative explanation this might be. We have shown that the representation of the IO profile by three layers (box profile of 25 cm inside the snow pack, single layer below the instrument, 1 km thick box profile above the instrument) yields simulated IO SCDs which are in agreement with the measurements. Omitting either the snowpack or the layer above the instrument, we are not able to simulate the measurements. These findings lead to the conclusion that the measurements cannot be interpreted in a meaningful way except if large amounts of IO are located inside the snowpack. We come to the same conclusions if we retrieve the IO profile on the full vertical grid. The more simple representation using a reduced vertical grid with three layers only has been chosen because this approach yields similar partial VCDs, and no a priori profile is required if only three layers are retrieved.

There are two reasons why blowing snow affects the measured IO dSCDs and leads to more scattered measurements, even if the majority of IO is located inside the snow-

pack. First, there is also some IO in the atmosphere above the surface, causing a signal which is amplified by multiple scattering if blowing snow is present. Second, an additional scattering layer near the surface also affects the radiative transfer inside the snowpack since both incoming sunlight and outgoing diffuse radiations need to traverse the blowing snow layer. G.M.'s statement that "this implies that the model would in days with wind speed over 5 m/s better represent the real conditions by including the blowing snow layer, in apparent contradiction to the previous statement" is therefore incorrect.

We agree with G.M. that further validation of the MAX-DOAS method in the future would be useful. However, measurements of NO_2 and ozone at Neumayer, which have been suggested by G.M. for validation, are unsuitable for these purposes. Typical atmospheric and snowpack NO_2 mixing ratios of some 10 ppt at Neumayer (Jones et al., 2000) are far beyond the detection limit of our instrument, and a tropospheric NO_2 signal, which might be caused by local contamination, has never been observed during more than 10 years of measurements at the trace gas observatory of Neumayer station. So far, it has not been shown that boundary layer ozone can be retrieved by MAX-DOAS, mainly because only a small fraction of the ozone total column resides in the troposphere. We have compared modelled and measured O_4 dSCDs and have found good agreement, providing confidence that our radiative transfer modelling is performed in a realistic manner.

The direct comparison of our MAX-DOAS data, which were measured during the day (SZA $< 85°$), with previous measurements of IO in Antarctica is difficult due to several reasons:

1. IO SCDs estimated from the MAX-DOAS measurements of the present study and from our previous zenith-sky measurements at Neumayer (Frieß et al., 2001) are of the same order of magnitude (around $(2-10) \times 10^{13}$ molec/cm^2). In Frieß et al. (2001), the seasonal variation of the IO dSCD betweeen SZA = 80° and 92°

was presented, showing a decrease in summer. This is, however, no proof that there is less IO in summer. Using a fixed Fraunhofer reference spectrum (instead of a daily reference), it turned out later that this is feature is caused by a slower decrease of the IO SCD during twilight in summer than in autumn and spring. From our initial zenith-sky measurements at Neumayer, we were only able to speculate about the vertical profile of IO, and mixing ratios were estimated under the assumption of a constant IO concentration within the boundary layer. From our MAX-DOAS measurements, it turned out that this assumption is not valid.

2. From the longpath-DOAS measurements at Halley, daily averages of the IO mixing ratio are presented by Saiz-Lopez et al. (2007). These decrease as days become shorter since there is no IO during the night, and indeed Figure 2 of Saiz-Lopez et al. (2007) shows that IO concentrations are proportional to the solar irradiance. In contrast, our MAX-DOAS daily averages are representative only for daytime (SZA $< 85°$), leading to a much smaller seasonal variation. Furthermore, the MAX-DOAS data during early spring and late autumn are very sparse due to the short duration of solar illumination and unfavourable weather conditions, decreasing the reliability of our data for these periods.

3. IO amounts deduced from MAX-DOAS measurements at Neumayer are significantly higher than from satellite (Schönhardt et al., 2008). However, SCIA-MACHY measurements with their large footprint of 60 x 120 km show a narrow band of IO along the coast near Neumayer, indicating that there might be a large gradient in snowpack IO concentrations from the coast towards the interior of Antarctica.

References:

Ashworth, S. H.; Allan, B. J. Plane, J. M. C.: High resolution spectroscopy of the OIO radical: Implications for the ozone-depleting potential of iodine, Geophys. Res. Lett., 2002, 29, 1456

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Frieß, U.; Monks, P.; Remedios, J.; Rozanov, A.; Sinreich, R.; Wagner, T. Platt, U.: MAX-DOAS O_4 measurements: A new technique to derive information on atmospheric aerosols: 2. Modeling studies, J. Geophys. Res., 2006, 111, D14203

Gomez Martin, J. C.; Ashworth, S. H.; Mahajan, A. S. Plane, J. M. C.: Photochemistry of OIO: Laboratory study and atmospheric implications, Geophys. Res. Lett., 2009, 36, L09802

Hendrick, F.; Van Roozendael, M.; Kylling, A.; Petritoli, A.; Rozanov, A.; Sanghavi, S.; Schofield, R.; von Friedeburg, C.; Wagner, T.; Wittrock, F.; Fonteyn, D. De Maziere, M.: Intercomparison exercise between different radiative transfer models used for the interpretation of ground-based zenith-sky and multi-axis DOAS observations, Atmos. Chem. Phys., 2006, 6, 93-108

Ingham, T.; Cameron, M. Crowley, J. N.: Photodissociation of IO (355 nm) and OIO (532 nm): Quantum Yields for $O(^3P)$ and $I(^2P_J)$ Production, J. Phys. Chem., 2000, 104, 8001-8010

Jones, A. E.; Weller, R.; Wolff, E. W. Jacobi, H. W.: Speciation and Rate of Photochemical NO and NO_2 production in Antarctic snow, Geophys. Res. Lett., 2000, 27, 345–348

Joseph, D.; Ashworth, S. Plane, J.: The absorption cross-section and photochemistry of OIO, J. Photochem. Photob., 2005, 176, 68-77

King, M. D. Simpson, W. R.: Extinction of UV radiation in Arctic snow at Alert, Canada (82°N), J. Geophys. Res., 2001, 106, 12,499–12,507

Lee-Taylor, J. Madronich, S.: Calculation of actinic fluxes with a coupled atmosphere - snow radiative transfer model, J. Geophys. Res., 2002, 107, 4796

Schönhardt, A.; Richter, A.; Wittrock, F.; Kirk, H.; Oetjen, H.; Roscoe, H. K. Burrows, J. P.: Observations of iodine monoxide columns from satellite, Atmos. Chem. Phys., 2008, 8, 637-653

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Saiz-Lopez, A.; Mahajan, A.; Salmon, R.; Bauguitte, S.; Jones, A.; Roscoe, H. Plane, J.: Boundary layer halogens in coastal Antarctica, Science, 2007, 317, 348-351

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. Heard, D. E.: On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for O_3, HO_x, NO_x and the Hg lifetime, Atmos. Chem. Phys., 2008, 8, 887-900

Stutz, J.; Pikelnaya, O.; Hurlock, S. C.; Trick, S.; Pechtl, S. von Glasow, R. Daytime OIO in the Gulf of Maine, Geophys. Res. Lett., 2007, 34, L22816

Theys, N.; Van Roozendael, M.; Hendrick, F.; Fayt, C.; Hermans, C.; Baray, J.-L.; Goutail, F.; Pommereau, J.-P. De Mazière, M.: Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21° S, 56° E), Atmos. Chem. Phys., 2007, 7, 4733-4749

Vigouroux, C.; Hendrick, F.; Stavrakou, T.; Dils, B.; De Smedt, I.; Hermans, C.; Merlaud, A.; Scolas, F.; Senten, C.; Vanhaelewyn, G.; Fally, S.; Carleer, M.; Metzger, J.-M.; Müller, J.-F.; Van Roozendael, M. De Mazière, M.: Ground-based FTIR and MAX-DOAS observations of formaldehyde at Réunion Island and comparisons with satellite and model data, Atmos. Chem. Phys. Discuss., 2009, 9, 15891-15957

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 25361, 2009.

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