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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Iodine emissions from the sea ice of the Weddell Sea" *by* H. M. Atkinson et al.

Anonymous Referee #1

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General comments:

This manuscript presents a large amount of data on iodine and other species in the Weddell Sea environment in an attempt to explain the high abundance of IO radicals observed (both previously and in this study) in this region, which is so far not understood. The study represents the most comprehensive polar iodine study to date with measurements of a variety of inorganic and organic species in air, seawater and sea-ice, and an attempt to reconcile the observations using a 1D model. Whilst in this way it is a useful addition to our knowledge, it is not presented, structured and discussed in a sufficiently coherent way to really discover what possible mechanisms might be producing iodine in the Antarctic. One potentially new aspect of the work is the link of iodine to particle production (which would be the first outside kelp beds/coastal regions), how-

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ever there is barely any detail on the particle observations. Similarly, despite apparently the main hypothesis given for the presence of IO being the biological production of I2 within sea-ice, there is insufficient data to show one way or the other whether this is the case (and missed opportunities to show whether this region has unique features which could explain the high amounts of iodine observed). There are further unsubstantiated comments in the manuscript – and also statements that appear to be erroneous (see below for details).

I also am confused by some of the data – why doesn't the I2 mixing ratio (with an atmospheric lifetime of seconds) apparently show any diurnal cycle? The fact that the modelled I2 (required to reproduce measured IO concentrations) is far smaller than the observed I2 is another factor which raises questions about this dataset.

In the Introduction, the authors emphasize the hypothesis that diatoms in Southern Ocean sea ice are a source of atmospheric iodine oxides in Antarctica. There are however many other potential mechanisms for iodine release in polar environments including in particular atmospheric –ice interactions (with laboratory and some field evidence for a variety of mechanisms). The Introduction should refer to these and evidence (or not) for each of these mechanisms should be discussed in the Results.

Production of iodine within sea-ice: The first obvious point is that this study would have benefitted greatly from measurements of I2 (and "AIC") within the sea-ice and brine in order to test the main hypothesis.

However the important finding here is that significant quantities of halocarbons were seen near the surface of the sea-ice and associated with diatom communities – thus opening up the possibility that halocarbons and possibly other iodine species may be transported into the atmosphere (see section below) from sea-ice. There was however very little information regarding these diatoms – it would be very useful to see data on their amounts and vertical profiles within the sea-ice and an idea of the representativeness of such surface diatom communities. Most studies shows that the vast majority of

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Chl a- and diatoms in sea ice are found in the bottom 50 cm or so (e.g. Palmisano and Sullivan, 1983; McGrath and Sullivan 1985). Are the surface diatom communities in the pack ice of the Weddell Sea unique - and could this be the reason for the enhanced iodine abundance in this region? Perhaps there could be some discussion as to what benefits algal communities to grow at the surface (light abundance and spectral composition) compared to the increased salinites and decreased temperatures. How might sea-ice structure (e.g porosity) effect algal communities?

It is interesting that the maximum iodide/iodate ratio and the main Chl-a peak (both linked to biological activity) were (as is more usual) towards the bottom of the ice - thus quite different to the halocarbon profiles which peaked at the surface. This should be discussed.

Transport of iodine within sea-ice: In order to deduce how halocarbons/iodine could be transported vertically within the sea-ice, vertical profiles of bulk salinity and of brine volume throughout the sea-ice (and how these change temporally) should be shown. There was no discussion of the critical brine volume fraction within the sea-ice that governs the connectivity of the brine channels and thus whether gases produced within the brine/ice will be transported to the surface. Note that during the ANFLUX experiment (McPhee et al., 1996) conducted in the eastern Weddell Sea, sea-ice temperature profiles indicated that the upper 5 cm of the ice column remained impermeable. The current study was conducted in the summer months thus the critical brine volume fraction may have been reached – however what about the earlier spring period when high quantities of IO have been observed?

What are the aqueous lifetimes of I2 and HOI ? Would they really hang around from winter to spring in the brine waiting to be released to the atmosphere?

P 11613: “The low diffusivity of halogenated compounds through ice as opposed to through brine (Loose et al., 2011; Shaw et al., 2011)”

This statement is confusing– both Loose et al. and Shaw et al dealt with transport

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through brine channels in sea ice (also in the case of Loose et al., through partial ice cover). If you freeze sea-ice, you will get brine channels!

Transport of iodine out of brine/sea-ice to the atmosphere:

P 11611: "As either type of ice is very porous, the brine in the channels will be in contact with the atmosphere and thus halocarbon concentrations in the brine are the aqueous phase concentrations, allowing a standard flux calculation to be made using air concentrations from the same days, provided the same factors affect fluxes from a brine layer on the surface of sea ice as the surface microlayer on seawater."

This sentence should be rewritten – it is confusing and too long -and the term "standard flux calculation" needs to be explained. Further, I disagree with the calculation method. Apparently the halocarbon brine-air fluxes were calculated simply from the product of the brine concentrations and a sea-air gas transfer coefficient kw. The latter is presumably calculated from the usual empirical expressions e.g. Nightingale et al. 2000. However, such expressions are used in the case where wind-driven turbulence governs gas transport from seawater. I strongly question whether such empirical expressions derived for sea-air transfer will be directly transferable to sea-ice brine – to-air transport. Also, surely the density of brine channels per area of ice needs to be accounted for?

Specific comments: 11598 "I2 has been proposed as the most important precursor for marine new particle formation" - Insert "coastal" after "marine"

Section 2.1 Diatom rich ice was very porous – how was porosity measured?

Section 2.2 Were studies performed which demonstrated stability of "AIC" over a period of 6 months?

A purge rate of 95 ml min-1 is very high – were breakthrough tests done?

"Particles" were counted with a Grimm 5.401 and sized with a DMA – give more details including particle size range, flow rates, sampling efficiencies. Typical particle number-

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size scans could be given in Supp. Mat.

Section 3.3 Explain what “rationalised to salinity” means

11610 “If iodocarbons were the source of IO in the atmosphere, this might partially explain why IO and BrO are similar during enhancements in the Antarctic”.

Does not follow. Explain or remove.

11611 Explain what is meant by “very porous,” – give quantitative data, and compare with data of other more typical sea ice.

Figures: Fig 2. Would be helpful to show a scale. How close is “close to the surface”?

Fig 7. Caption should be “upper” and “lower” not “left” and “right”

Fig 9. Why is the surface iodide/iodate ratio not shown?

In summary, I conclude that at present this manuscript does not reach conclusions that sufficiently advance this area of research. However, I think there is the potential within this study to make such gains if the datasets are mined more thoroughly and results substantiated more clearly.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 11595, 2012.