

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

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General Response:

We thank the authors of the two short contributions for the thoughtfulness they have brought to their questions, which are serious and important. They are also complimentary about our work in general.

We regret the more negative responses of the anonymous referees. The second referee's assertion “this study confirms... without adding much.. ” is demeaning: we present the first measurements of I₂ and of AIC in the region and the first comprehensive measurements there of iodocarbons in air, in sea ice and in sea water. The first referee acknowledges this fact.

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The referees ask for extra measurements that cannot exist without remaking the cruise, which is of course out of the question. The referees also ask for more speculation, some of which we have provided, but more of which would be out of place (e.g. about what happens in spring when we have no measurements).

Below, we satisfy the substantive points raised by the referees within the confines of the existing data. If we had fully solved the problem of the mechanism for emission of iodine compounds in the Weddell Sea, our article would be for Nature.

Response to Anonymous Referee #2

This paper builds in a linear fashion on the discovery of the Weddell Sea as an iodine “hotspot” and the general polar monitoring efforts that have linked, in some way, iodine emissions to snowpack. These earlier papers all suggest that the level of the iodine emissions cannot be fully understood on the basis of our current knowledge and generally invoke processes such as heterogeneous, ice-promoted chemistry or biological processing (by marine algae and related) to “explain” matters. Hence the campaign described in this study essentially confirms what we already know, albeit with a full suite of analytical (both chemical and computational) techniques employed and increases our knowledge about iodine emissions in polar regions. The work does increase our data-base substantially on inorganic and organic levels of iodine in the Weddell Sea but appears to have missed a great opportunity in moving our understanding forward regarding “an explanation of the phenomenon” by not measuring other possibly important chemicals and biologicals in the campaign. (Again linearly, and in line with earlier thinking, ozone, “particles” and chlorophyll-a are monitored but the obtained results on these species do not appear to add much to the mechanism story).

Response: We assert that our comprehensive data set adds greatly to our knowledge about iodine compounds in the Weddell Sea. It was an unfunded campaign, planned on HMS Endurance, and nearly cancelled at the last minute when HMS Endurance

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came close to sinking. The revised campaign had to be cut to fit available berths on RRS Shackleton.

In essence the stated aim of this work (first sentence of the abstract), which is “. . .to elucidate the mechanism of the local enhancement and volatilization of iodine”, is not fulfilled by this work. The reason for this is because the monitoring campaign performed was not sufficiently wide-ranging.

Response: We have now replaced “to elucidate” by “to make progress in elucidating”. To characterise our set of measurements as “monitoring” when many were by advanced techniques such as GCMS and I₂-denuders is derisory. It is difficult to reconcile this clairvoyant referee’s description “not sufficiently wide-ranging” with that of Referee 1 “the most comprehensive .. to date”.

What should have been done then? Several original papers and reviews on “halogen activation” by ices and snow are now available. (ACPD 12 8677-8769 2012 is the latest summary). One of the key parameters clearly linked to the releases is acidity and this has been known for some time. (Nature 359 522-524 1992; J. Geophys Res 104 23719-23727 1999; Chem Rev 103-4783-4800 2003). Some of the chemistry itself may take place on the ice surfaces (QLL) or at triple junctions and the release of iodine to the atmosphere by freezing sea-salt components has been shown to take place. . .again with pH acting as a control (J Phys Chem A 112 1677-1682 2008). So why were pH and sulfate and nitrate ion concentrations not measured here for a selection of the samples. . .those taken back to the laboratory for iodide/iodate analysis for example and also for experiments in situ? Perhaps pH was measured but not reported here; if it was then the information would be useful to publish and show that the field community actively takes on board related findings in the laboratory. Laboratory/Modelling studies on halide ions show that they possess a surface affinity in water with heavier counterparts such as iodide becoming preferentially attracted to the interface. (Chem Rev 106 1259-1281 2006; J Phys Chem A 115 5895-5899 2011). This type of potential effect deserves a mention in this manuscript particularly as it may

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lead to an accelerated iodine release mechanism by surface reaction of iodide with an oxidant such as ozone.

Response: The referee demands a set of measurements that would be valuable if they had been made, but they were not. Our unfunded campaign did not have the luxury of these measurements.

Indeed, oxidants such as hydrogen peroxide and nitrous acid/nitrite ions in the ices may also promote any halogen and interhalogen release. . .as predicted from the lab studies performed. Were such species, and similar, measured and their concentrations ascertained? If they had been then again, coupled with the known laboratory studies, our understanding for the elusive chemical mechanism for iodine release might have been improved.

Response: The referee demands a set of measurements that would be valuable if they had been made, but they were not. Our unfunded campaign did not have the luxury of these measurements.

There appears to be a link under certain circumstances in the Arctic region between bromine, ozone and mercury levels. Iodine has also been suggested to impact the depletion of GEM. (Atmos. Environ., 38, 5105–5116, 2004) Were mercury, GEM and particulate levels measured here to try to ascertain in this fairly unique, known iodine “hotspot” whether a similar relationship might exist? Again I guess the answer is no but this is a prime example of why, to me, this campaign represents a lost opportunity. The paper outlines the potential biological sourcing of the (organo-) halogens from seaice micro- and macro-algae. (Although it is of note that hydrogen peroxide is key to the (bio)-chemistry, which represents another reason for monitoring it here. J Geophys Res 101 20899-20908 1996). The idea has, of course, been discussed before as stated in the paper but the measurements made in the current study tend to mitigate against the importance of iodocarbons. This information is useful to know but again I sense a simple revisiting of issues rather than checking on something novel in the

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biological domain.

Response: The notion that we should have measured mercury in the Antarctic, where levels are so low that there are very few measurements in the literature, is bizarre. Further, there are few measurements of iodine compounds together with mercury in the Arctic (where the measurements are more feasible) because the issues of mercury depletion in the Arctic are associated with production of bromine compounds rather than of iodine. Bromine is not the focus of our paper.

The exciting question remains from this work: "What is the missing iodine source?" The microbiological literature is not without its hints on this matter. . . .although not mentioned here. Hence bacteria such as *Rhizobium* spp make methyl iodide in the presence of iodide ions. (App Environ Microbiology 67 2718-2722, 2001). Furthermore a variety that can exist in the extreme cold does exist. PBAP (Primary Biological Aerosol Particles) such as bacteria, spores and pollen are relatively routinely measured these days by fluorescence-based techniques such as UV-APS and WIBS; such measurements would have added real novelty to this manuscript. (Particle counting/sizing was made by a Grimm/DMA here but not in the PBAP size range of bacteria/spore interest as far as I can see in Figure 10). Methyl iodide formed by this known source could be readily photolysed to make active iodine.

Response: Clearly the referee would have enjoyed it if we had speculated in much more detail about the source. We felt unable to do so with the available measurements: that must be for the future.

I do have an experimental concern about the iodide/iodate ion methodologies employed for analysis. Why was the method of Lucia and Campos not employed to evaluate these species? (Marine Chemistry 57 107-117 1997). The technique used involves only cathodic stripping voltammetry and the spectrometric technique for iodate (which is interfered with by the possible presence of nitrite ions) then need not be employed.

Response: We used the technique given in the paper because it is in widespread use

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at UEA.

In summary I believe that all of the "unmonitored" species and processes to which I refer to above should be discussed in any revised manuscript, if only to put the campaign into a wider chemical and biological context. The decision about a transfer to publication in ACP then must rest on whether or not the paper fits into the journal scope that is a focus on studies with general implications for atmospheric science rather than investigations that are primarily of local or technical interest. It could be argued that the Weddell Sea as an iodine "hotspot" was already known and that this study simply confirms that without adding much to our ideas about the actual mechanism of iodine release from the region.

Response: It is a travesty to suggest that because it had already been suggested that the Weddell Sea was an iodine hotspot, our measurements add little. We present the most comprehensive data set yet about iodine compounds in the Weddell Sea. We have made comprehensive measurements of iodocarbons, and shown that they are insufficient to explain the observed IO – a major step forward.

Specific comments on the manuscript:

1. A more complete description of the Grimm and the DMA experiments in relation to counting efficiencies and size ranges detected etc. is required.

Response: Yes, now done.

2. First sentence of section 2.3 is sparsely worded.

Response: Yes, we have now lengthened the sentence.

3. Section 3.3. What does the first phrase of the first sentence mean regarding liquid phase? (On the QLL, in microveins, "brine"?). Some of the inorganic ions will be in the solid ice: Workman and Reynolds effect.)

Response: We mean in any liquid phase, as stated. The proportion of ions of Na and

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Cl in solid ice is negligible at temperatures above -24°C , and the proportion of sulphate in sea water is small enough that sulphate precipitated in the ice can be neglected in the brine calculation.

4. Section 3.4. . . .odd phrase: “. . .which is has been. . .”!

Response: Yes, the typographical error “is” is now removed.

5. Section 4. First sentence: the references are not given in a way that is consistent with the rest of the manuscript.

Response: Yes, now corrected.

6. Section 4. What evidence is provided by this campaign for the actual existence of HOI in ice? If this species is really a likely precursor to I₂ formation then it needs to have been detected; otherwise the acidic HOBr/Br⁻/H₃O⁺ type mechanism proposed here and previously in ACPD (8 2953-2976 2008) remains unsubstantiated speculation and should be left out of the manuscript. The reaction between iodide ions and hydrogen peroxide could lead to HOI (and basic OH⁻ ions) but this possibility only confirms the importance of monitoring other species like H₂O₂ and pH if the HOI route is going to be seriously suggested as a real contender for inorganic iodine production in the Weddell Sea.

Response: We do not propose from this campaign that HOI exists in ice, we merely repeat the speculation of Saiz-Lopez and Boxe in a very concise way. This speculation is at least as well-founded as others that the referee would have us make (such as the lengthy discussion on bacteria and spores suggested above), so it should stay.

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