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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “A mechanism for biologically-induced iodine emissions from sea-ice” *by* A. Saiz-Lopez et al.

Anonymous Referee #1

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Saiz-Lopez and co-authors present a modelling study aiming to explain reactive gaseous iodine observations in the Antarctic atmosphere. Previous studies have struggled to explain the observed concentrations, which are at such a level as to be potentially important to the surface oxidant budget through ozone destruction and perturbation to the HOx and NOx ratios. The current work investigates plausible mechanisms of iodine release to the polar atmosphere through microalgal production and transport through sea-ice brine channels and a liquid layer (and any snowpack overlying the ice). The resulting mechanism is used to try to explain observed IO concentrations and is further postulated to lead to IBr release. It is important that the mechanisms of polar iodine production and release are explored and this paper provides a useful attempt to do so. The content is very much in the scope of ACP and is likely to provide a valuable

contribution to the field.

In common with most such papers playing "what if?" model games, it is clearly difficult for the authors to balance the confidence of the assertions with the available observational constraint. The modelled mechanisms are plausible, but there appears to be quite a bit more uncertainty in the hypothesised channels than would appear to be recognised. I'd recommend publication of the work if the manuscript better reflected the level of understanding of the processes under consideration. Whilst the model is a commendable effort to incorporate the variety of detailed steps in the process, the paper only presents a hypothetically plausible mechanism. It would be a disservice for future work to blindly employ such a modelling treatment as though it were the sole possible (or even a moderately well-constrained) explanation for the release.

I have no problem with any of the results from the model as it is constructed and the authors should be commended on construction of a hypothetical framework that is able to explain the flux of reactive iodine to the Antarctic atmosphere. They should also be commended on sensibly presenting the conclusions in light of the uncertainties presented in the paper. However they should consider the following in preparing a revised manuscript suitable for publication in ACP.

In the section describing the diffusion treatment which is used to establish the depth-dependent diffusion timescales there is a potent description of the difficulties associated with realistic and quantitative evaluation of the gaseous permeability rates in sea-ice. The first and second law diffusion treatment and the approximation employed in the second law solution in the model appears appropriate, however the lack of constraint on the diffusion coefficient and the strong dependence of the nature of the matrix on brine concentration and temperature will lead to tremendous uncertainties. Figure 3 chooses a single diffusion timescale. In some way, the likely range of impacts at the bounds of diffusion rate uncertainty should be tabulated or displayed, perhaps in the supplementary material (say plotting peak I_2 flux and IO concentration after *n* days vs assumed diffusion timescale).

The balance in the complexity of the gaseous and condensed-phase reactions in the "QLL" is probably appropriate at the level of knowledge of halogen chemistry. However, the omission of non-ideal reaction rates and the large dependence of Henry's Law coefficients on the extremely high electrolyte concentrations in brine (85 to 210 parts per thousand, leading to very high activity coefficients) will be problematic. The concentration effect of the aqueous reaction rates is considered as though ideal. Whilst there are no studies that account for these effects to my knowledge, the very likely first order effect that activity coefficients will have on the rates must be acknowledged. Furthermore, the likelihood of condensed phase photolytic reactions should also be acknowledged owing to the residence time in the near surface brine. These considerations were raised by the unsolicited comment and some strong statement is required. I am also in agreement that the layer is a liquid brine - not a QLL. This nomenclature should be corrected throughout the manuscript, but is not really important in the context of the study.

The microalgal source strength and variability is obviously wildly uncertain, but the values well justified within the bounds of the available measurements. How sensitive is the model to the initiation with 10^{-4} M iodide biological pre-concentration? Again, some presentation of the likely range of impacts on the assumption should be presented, if it is significant. Otherwise a simple statement is sufficient.

There are a couple of other queries that the authors should clarify relating to the assumptions in the model:

There is a statement on p10273 "the iodine content in the QLL, which is that in seawater". Can the authors explain the source of this assumption? Along with the algal iodine concentration at the bottom, this is the driver of the diffusion through the brine channels and I don't understand where the assumption comes from (or perhaps don't understand the model construction as described).

The photolysis rates are calculated offline using the photon flux calculated using the

Thompson 2-stream code. What is the surface albedo that is used in the calculation? Obviously the upwelling irradiance from the high surface albedo will be substantial over snow and ice covered surfaces, leading to considerable enhancement of the photolysis rates. How is the molecular absorption and Mie scattering from the aerosol of the upwelling irradiance treated in the 2-stream code? On this note, is the aerosol scattering consistent with the surface area $10^{-7} \mathrm{cm}^2 \mathrm{cm}^{-3}$ that is used for the gaseous mass transfer approximation? How sensitive are the model results to the answers to the above?

The deposition rate of HOI, HI and $\mathrm{IONO_2}$ is dependent on the atmospheric stability and the vertical resolution of transport in the atmosphere. The catalytic release of IBr will depend on this deposition rate. How sensitive is the IBr release rate to the treatment of deposition of HOI, HI and $\mathrm{IONO_2}$ and the uptake rates on the surface?

Once the above have been discussed in the appropriate sections of the manuscript, the "uncertainties and future work" section should reflect the answers.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 10257, 2015.