

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

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This paper pursues an interesting objective, in line with the previous ACPD paper by Saiz-Lopez and Boxe in 2008. Although the objective is worthwhile, the modeling strategy is debatable. First of all, I am always very surprised when snow or ice modelers model QLL chemistry as if the QLL was similar to liquid water. There are now many studies that show beyond doubt that this is just totally incorrect, and one may wonder whether publishing any paper that makes this false hypothesis is in the interest of the community. For example, (Kahan and Donaldson, 2008, 2007; Kahan et al., 2010; Wren and Donaldson, 2010; Wren et al., 2013) have shown that rate constants in liquid water and at the ice surface were quite different. **Of course, in the case of complex models with enough adjustable parameters, an apparent agreement can al-**

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ways be found. For example, Bock and Jacobi (2010) proposed a reaction mechanism for nitrate photochemistry in snow and adjusted five reaction or photolysis rate coefficients to reproduce nitrate and nitrite concentrations measured in photolyzed artificial snow. In a subsequent erratum, Jacobi (2011) adjusted in a novel manner these five rate constants since the bulk to QLL volume ratio used to convert measured bulk concentrations into modeled QLL concentrations was wrong in the original publication. In both cases, experimental data were reasonably well reproduced, despite a factor of ~ 30 between modeled QLL concentrations in the two versions of this work. This example demonstrates that a wrong hypothesis can seem adequate in a model with a sufficient number of adjustable parameters (Domine et al., 2013). With the help of other co-authors, I tried to detail the many reasons why the QLL is very different from liquid water and why rate coefficients measured for water simply cannot be used to model QLL chemistry (Domine et al., 2013), and I suggest that snow chemistry modelers consider the arguments given in that paper. **[modified on 09 Mar 2016, see EC]** With the helps of other co-authors, I tried to detail the many reasons why the QLL is very different from liquid water and why rate coefficients measured for water simply cannot be used to model QLL chemistry (Domine et al., 2013), and I suggest that snow chemistry modelers consider the arguments given in that paper.

However, fortunately for Saiz-Lopez, Boxe and Carpenter, in their system, there is no QLL, but a true liquid. What forms at the surface of sea ice is a brine, i.e. a true liquid, and they should not call it a QLL. Simple considerations of the phase diagram of sea ice (Petrich and Eicken, 2010; Weeks and Ackley, 1982) will convince the authors that they are indeed modeling a true liquid. Now, this does not mean that the liquid water rate constants apply, because of the very high salinity of the brine that forms at the surface of sea ice. Rather than the 35 psu of sea water, the brine salinity is around 100 psu (Perovich and Richter-Menge, 1994) and it is likely that this high salt concentration will modify reaction rate coefficients.

Regarding the thickness of this brine, it is highly variable. It cannot be inferred from

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thermodynamic considerations, and certainly not from the highly debatable concepts developed by (Conklin and Bales, 1993) (which by the way, was omitted by the authors from their reference list) because it is the result of mostly kinetic processes involving the ice growth rate and the brine expulsion rate. (Perovich and Richter-Menge, 1994) measured it to be around 1 to 2 mm thick. I also observed brine on the surface of sea ice (Domine et al., 2005), and although I did not publish any brine thickness values, I agree with the estimates of (Perovich and Richter-Menge, 1994) for young sea ice. However, as the ice ages, the thickness of the brine rapidly decreases, because the brine is eventually expelled down to the sea water. On older sea ice, the brine thickness is probably only a few tens of microns thick, perhaps even much less.

There are many other aspects of this model that could be questioned, such as transport properties and light fluxes, but I will limit myself to these chemical and thermodynamic aspects. In summary, the chemistry of the QLL cannot in any case be modeled using rate coefficients measured for liquid water. The medium modeled by the author is not a QLL anyway, but a true highly saline liquid. I question that rate coefficients of chemical reactions in a brine of 100 psu are similar to those of liquid water. The thickness of the brine cannot be derived from thermodynamic considerations. It is 1 to 2 mm thick on very young sea ice, and my personal observations suggest that it is much thinner on older ice, probably a few tens of microns or perhaps even much less.

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