Reply to review of Saiz-Lopez et al., Atmospheric Chemistry and Physics, 2015

We have revised the manuscript based upon the input of the reviewers. We appreciate the positive comments and useful suggestions of the reviewers. In this reply, we show the comments of the reviewer in bold, our reply directly following the reviewer comments and the changes made to the manuscript are highlighted in blue.

Comment by Dr. Florent Dominé

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.

Following Dr. Dominé's comment, we have amended using the terminology QLL (quasi-liquid layer) and used sea-ice brine layer throughout the entire manuscript to describe this particular mobile component of ice/snow matrices.

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, a correct agreement can always be found.

Takenaka et al (1992, 1996) and Grannas et al 2007 found accelerated reaction rates ranging from 40 to 10^5 for different reactions, involving different species. The fact of varying degrees of reaction rate enhancement (compared to aqueous phase reaction rates) is not surprising as each system being investigated should be treated as an individual entity. This therefore leads to a high degree of uncertainty in the system, although please note that in this study we are using the best knowledge available. This will now be made clearer in the revised manuscript.

In the abstract we have added: "While a lack of experimental and observational data adds uncertainty to the model predictions, nevertheless the results show that the levels of inorganic iodine (i.e., I_2 , IBr, ICl) released from sea-ice through this mechanism could account for the observed IO concentrations during this timeframe."

The text of this paragraph was taken from the short comment acpd-15-C2361-2015 by Dr. Dominé. The comment was modified on 9 March 2016. Please see the new version at: http://www.atmos-chem-phys-discuss.net/15/C2361/2015 We take Dr. Dominé's suggestion, and the arguments provided in his work in 2013, into consideration and we acknowledge that the component where chemical reactions take place in our modelled system is composed by a true liquid.

However, fortunalely 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 that 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.

Please note, as also highlighted by Referee 2, that the complexity of the gaseous and condensedphase reactions in brine included in this study is appropriate at the level of knowledge of halogen chemistry. The reason why we were not able to take into account the effect of salting out/in on the temperature and salinity dependence of the Henry's law constant for species within the model and that is due the fact that there are no experimental data on this matter for species of interest to polar atmospheric science. Apart from the experimentally-derived Henry's law constant relations used in models, which is then extrapolated to lower temperatures, there is no experimental data that has assessed the dependence of the Henry's law constant on the salinity content of an aqueous solution containing solutes of interest to this study. Actually, only a few experiments have been done this and assess the dependency of the Henry's law constants for organic molecules as a function of temperature and salinity: 1) Dacey et al 1984 (Henry's law constants for dimethylsulfide in freshwater and seawater); 2) Dewulf et al 1995 (Measurement of Henry's Law Constant as a Function of Temperature and Salinity for the Low Temperature Range); 3) Rice et al 1997 (Henry's law constants for pesticides measured as a function of temperature and salinity); and 4) Cetin et al 2006 (Determination of Henry's law constants of organochlorine pesticides in deionized water and saline water as a function of temperature). A few other studies only measured the temperature dependence of Henry's law constants for organic compounds (Staudinger and Roberts 2001; Sahsuvar et al 2003; Nirmalakhandan et al 1997; Gorgenyi et al 2002; Cetin and Odabasi 2005). Upon examining these publications, it is clear that species Henry's law constants are predominantly governed by temperature in the aqueous phase. This can be contextualized by the following example. Tropical ocean waters are warmer than polar ocean waters. Tropical ocean waters exhibit $[\Gamma] \approx 1 \times 10^{-7}$ M, where coastal Antarctic ocean waters exhibit $[\Gamma] \approx 10$ nm to 150 nm (seasonally dependent) (Chance et al 2010). Antarctic Weddell sea-ice exhibit $[I^-] \approx 10$ nM (mean value) while surrounding water exhibit $[I^-] \approx 61$ nM

(mean value) (Atkinson et al., 2012). So Antarctic ocean water can be a one-order of magnitude less (low-end) or approximately the same iodide concentration as tropical ocean water (high end). Salting out may be more impactful at temperatures below the freezing point of sea-ice – using Antarctic Weddell sea-ice as a reference – but still, the effect of high salinity 70-100 psu appears to not be so impactful upon the solubility of iodide given the small difference in iodide concentration of tropical ocean water and polar ocean ater. Nevertheless, in the revised version, we will incorporate additional sentence about the omission of non-ideal reaction rates and the large dependence of Henry's Law coefficients on the extremely high electrolyte concentrations in brine (Also pointed out by Ref. 1).

The following text has been added in line 390: "The dependence of the Henry's law constants on the salinity was not considered due to the lack of the experimental data."

Regarding the thickness of this brine, it is highly variable. It cannot be inferred from thermodynamic considerations, and certainly not from the highly debatable concepts developped 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 processed 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.

We thank you for referring us to those earlier studies. We agree that thermodynamics and ice kinetics are well-coupled to determining the dimensions of the sea-ice brine layer, and that the range of brine layer thickness is highly variable – as shown by several experimental and modeling techniques (Huthwelker et al., 2006). We have added a statement to acknowledge this variability into the text.

We have added the following text in line 365: "Still, we do acknowledge that the range of thickness of is highly variable as shown by several experimental and modeling studies (Huthwelker et al., 2006)."

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 personnal observations suggest that it is much thinner on older ice, probably a few tens of microns or perhaps even much less.

Experimental and theoretical calculations of the thickness of the brine layer are variable (Huthwelker et al., 2006). Considering thinner brine layer dimensions, would favor even greater enhanced reaction rates – smaller dimensions – more frequency of solute interactions. We note that the fluid phase of sea ice is composed of brine inclusions that range from 0.1 to 10 mm in length (Light et al., 2003). Our calculated brine layer thickness is in the range of the values reported in Light et al., 2003.

Referee 1

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.

We are grateful to the reviewer for the positive review and constructive comments.

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.

We thank the reviewer for this very constructive suggestion. Our manuscripts describes the transport of gases through brine channels (given the limited amount of published content in this field) and also acknowledge that $I_2(g)$ can also be directly emitted via open fractures/leads in seaice and polygnas. In comparison to the permeation of brine, there has been relatively little consideration given to the process of gas permeation through sea ice, but it is conceptually similar to gas diffusion through the unsaturated (vadose) zone in soils. From those empirical relationships, we can infer that sea ice permeability would range from about 10^{-7} to 10^{-4} cm² s⁻¹ in first-year sea ice with 1 to 5% gas porosity, based on the Penman-Millington Quirk soil gas diffusion model (Moldrup et al., 2004; Kawamoto et al., 2006). The few laboratory and field estimates that have been made of gas diffusion through sea ice fall within this range, exhibiting quite large differences in magnitude, depending on the specific gas.

We have added in several places across the manuscript (e.g. abstract, results and discussion and uncertainties and future work sections) sentences to highlight uncertainties in the model framework, e.g. in brine thickness (discussed above), in diffusion coefficients (below), in liquid rate coefficients, etc. Also, we have made clear (in uncertainties and future work section) that the

proposed modelling treatment is not the only possibility for the release of iodine in the polar environment.

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.

We thank the reviewer for the constructive comments.

In the section describing the diffusion treatment which is used to establish the depthdependent 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 I2 flux and IO concentration after n days vs assumed diffusion timescale).

Loose et al (2011), Callaghan et al (1999), Mercier et al (2005) show that the diffusion coefficients in Antarctic brine channels ranges from 10-9 cm2 s-1 to 10-5 cm2 s-1 (fast diffusion component), and the gas phase diffusion coefficients in Antarctic sea-ice range from 10-7 cm2 s-1 to 10-4 cm2 s-1. We, therefore, pick mid-point values (Table 1 in the manuscript) to reflect the range of diffusion coefficients. Table 1 clearly shows that, whether diffusion is occurring through brine channels or via gas-phase diffusion, the timescale will be fast. Table 1 illustrates the diffusion timescale dependence as a function of the diffusion length equation. If the diffusion coefficient is between 10^{-7} to 10^{-9} cm² s⁻¹, iodine production would have to occur very close to the surface to be relevant for polar springtime chemistry.

The following text has been added in line 510: "Note, Loose et al (2011), Callaghan et al (1999), Mercier et al (2005) show that the diffusion coefficients in Antarctic brine channels range from 10^{-9} cm² s⁻¹ to 10^{-5} cm² s⁻¹ (fast diffusion component), and the gas phase diffusion coefficients in Antarctic sea-ice range from 10^{-7} cm² s⁻¹ to 10^{-4} cm² s⁻¹. Table 1 clearly shows that, whether diffusion is occurring through brine channels or via gas-phase diffusion, the timescale will be fast. If the diffusion coefficient is between 10^{-7} to 10^{-9} cm² s⁻¹, iodine production would have to occur very close to the surface to be relevant for polar springtime chemistry."

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.

Taking heed to the reviewer's advice, we will acknowledge this potential (while uncharted territory) impact. We were not able to take into account the effect of salting out/in on the temperature and salinity dependence of the Henry's law constant for species within the model and that is due the fact that there are no experimental data on this matter for species of interest to polar atmospheric science. Apart from the experimentally-derived Henry's law constant relations used in models, which is then extrapolated to lower temperatures, there is no experimental data that has assessed the dependence of the Henry's law constant on the salinity content of an aqueous solution containing solutes of interest to this study. Actually, only a few experiments have been done this and assess the dependency of the Henry's law constants for organic molecules as a function of temperature and salinity: 1) Dacey et al 1984 (Henry's law constants for dimethylsulfide in freshwater and seawater); 2) Dewulf et al 1995 (Measurement of Henry's Law Constant as a Function of Temperature and Salinity for the Low Temperature Range); 3) Rice et al 1997 (Henry's law constants for pesticides measured as a function of temperature and salinity); and 4) Cetin et al 2006 (Determination of Henry's law constants of organochlorine pesticides in deionized water and saline water as a function of temperature). A few other studies only measured the temperature dependence of Henry's law constants for organic compounds (Staudinger and Roberts 2001; Sahsuvar et al 2003; Nirmalakhandan et al 1997; Gorgenvi et al 2002; Cetin and Odabasi 2005). Upon examining these publications, it is clear that species Henry's law constants are predominantly governed by temperature in the aqueous phase. This can be contextualized by the following example. Tropical ocean waters are warmer than polar ocean waters. Tropical ocean waters exhibit $[I^-] \approx 1 \times 10^{-7}$ M, where coastal Antarctic ocean waters exhibit $[\Gamma] \approx 10$ nm to 150 nm (seasonally dependent) (Chance et al 2010). Antarctic Weddell sea-ice exhibit $[I^-] \approx 10$ nM (mean value) while surrounding water exhibit $[I^-] \approx 61$ nM (mean value) (Atkinson et al., 2012). So Antarctic ocean water can be a one-order of magnitude less (low-end) or approximately the same iodide concentration as tropical ocean water (high end). Salting out may be more impactful at temperatures below the freezing point of sea-ice – using Antarctic Weddell sea-ice as a reference – but still, the effect of high salinity 70-100 psu appears to not be so impactful upon the solubility of iodide given the small difference in iodide concentration of tropical ocean water and polar ocean ater. Nevertheless, in the revised version, we will incorporate additional sentence about the omission of non-ideal reaction rates and the large dependence of Henry's Law coefficients on the extremely high electrolyte concentrations in brine.

The following text has been added in line 390: "The dependence of the Henry's law constants on the salinity was not considered due to the lack of the experimental data."

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.

Taking heed to the reviewer's advice, we will acknowledge the potential impact of photolytic reactions at the sea-ice surface in the brine layer. The potential impact of NO_3^-/H_2O_2 photochemistry (within the context of the lack of multi-solute experimental data) to produce OH is likely minimal as condensed phase halogen chemistry (although is pH dependent, which would be the only impact via the production of OH) as halogen reactions are not involved with reactions with OH – in the condensed phase

The following text has been added in the Uncertainties and Future work section, line 665:

"We also acknowledge that $NO_3^{-/}H_2O_2$ photochemistry produce OH (Anastasio et al., 2007; Dubowski et al., 2001; Chu and Anastasio, 2003) may alter the pH of the snowpack. Given that halogen chemistry is pH dependent; such photochemical reactions may be interrelated through this context with halogen chemistry, although currently there is a lack of multi-solute experimental data to adequately simulate this process. Still, O'Driscoll et al (2006) report the production of trihalides via iodide- and nitrite-doped ice matrices."

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.

We will change the QLL terminology to sea-ice brine layer in the manuscript.

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.

We have carried out some sensitivity tests that show the iodine release not to be significally sensitive to an initial pre-concentration of 10^{-3} M \leq [I-] $\leq 10^{-4}$ M.

The following text has been added in line 474: "We conducted sensitivity simulations, which indicate that the release of iodine is not significantly sensitive to a pre-concentration of 10^{-3} M \leq [I-] $\leq 10^{-4}$ M."

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 model is driven with initial conditions of algal iodine at the bottom of the sea-ice and seawater iodine at the top. As diffusion through the brine channels occurs in the simulation the iodine concentration in the sea-ice brine layer evolves accordingly. Overall, the results are quite insensitive to these initial conditions in the model.

The following text has been added in line 481: "The upward diffusion through the brine channels is driven by an iodine concentration gradient. This gradient arises from the concentration difference between the iodine emission point (e.g. algae colonies) and the iodine content in the BL, which is ~ 10^{-7} to 10^{-8} M (Chance et al., 2010; Atkinson et al., 2012). For example, the upper limit for the concentration gradient can be up to ~ 10^{-4} M between the BL ([Γ] ~ 10^{-7} M) and the iodine source in the algae colonies ([Γ] up to 10^{-3} M)."

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?

In the 2-stream code, the irradiance reaching the surface is computed after photon attenuation, by aerosol scattering and molecular absorption, through 50 1-km layers in the atmosphere as a function of solar zenith angle, location and time of year.

The following text has been added in line 397: "Photolysis rates are calculated off-line from reported absorption cross-sections and quantum yields using a 2-stream radiative transfer code (Thompson, 1984), where the irradiance reaching the surface is computed after photon attenuation, by aerosol scattering and molecular absorption, through fifty 1 km layers in the atmosphere. The model is run with surface albedo of 0.85, typical of measurements made with an actinic flux spectrometer at Halley Station (Jones et al., 2008). The aerosol profile used in the radiative transfer code is consistent with aerosol loadings and surface area typical of remote locations (i.e. 10^{-7} cm⁻³)."

The model is run with surface albedo of 0.85, typical of measurements made with an actinic flux spectrometer at Halley Station (Jones et al., ACP, 2008).

The following text has been added in line 401: "The model is run with surface albedo of 0.85, typical of measurements made with an actinic flux spectrometer at Halley Station (Jones et al., 2008). The aerosol profile used in the radiative transfer code is consistent with aerosol loadings and surface area typical of remote locations (i.e. 10^{-7} cm⁻³)."

On this note, is the aerosol scattering consistent with the surface area 10–7 cm2 cm–3 that is used for the gaseous mass transfer approximation? How sensitive are the model results to the answers to the above?

The aerosol profile used in the radiative transfer code is consistent with aerosol loadings and surface area typical of remote locations (i.e. 10^{-7} cm⁻³).

The following text has been added in line 401: "The model is run with surface albedo of 0.85, typical of measurements made with an actinic flux spectrometer at Halley Station (Jones et al., 2008). The aerosol profile used in the radiative transfer code is consistent with aerosol loadings and surface area typical of remote locations (i.e. 10^{-7} cm² cm⁻³)."

The deposition rate of HOI, HI and IONO2 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 IONO2 and the uptake rates on the surface?

Typical deposition velocities in the model are 0.5 cm s^{-1} , and we assume the surface is flat. There is not a strong dependence of IBr release upon the deposition velocities of HOI, HI and IONO₂ since most of the iodine present in the sea-ice brine layer comes from below via diffusion through the brine channels.

The following text has been added in line 425: "Typical deposition velocities in the model are 0.5 cm s-1, and we assume the surface is flat. There is now a strong dependence of IBr release upon the deposition velocities of HOI, HI and IONO₂ since most of the iodine present in the seaice brine layer comes from below via diffusion through the brine channels."

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

All have been incorporated in the appropriate sections of the text, as detailed above.

Referee 2

General Comments The manuscript describes a mechanism for the release of iodine from sea-ice into the atmosphere. The motivation are recent studies which have recognized sea ice as an important source of reactive iodine to the Antarctic boundary layer, essentially based on ground based and satellite measurements of iodine oxide over the Antarctic sea ice. The primary source of iodine in this environment is suggested to be micro-algae underneath the sea-ice and the diffusion of iodine species through sea-ice brine channels resulting in an accumulation in the quasi-liquid layer (QLL) on the surface of sea-ice. The authors suggest that iodine is released into the polar boundary layer via different possible pathways, e.g. directly emitted from the QLL or emitted to the atmosphere directly through fractures in the sea-ice pack. The authors develop a multiphase model and run model simulations to interpret observations of elevated iodine oxide concentrations and conclude from the results that the levels of inorganic iodine (molecular iodine and interhalogens) released from sea-ice through the suggested mechanism could account for the observed IO concentrations. In fact, the sources and mechanisms of the release of iodine over sea-ice covered areas are still unclear. Thus, the suggested mechanism is an important contribution to improve our understanding of the boundary layer chemistry of iodine. In my opinion the results of the multiphase modelling study not only can account for the observed IO concentrations, the reported results might stimulate further investigations to better understand the halogen chemistry, e.g. the measurement of interhalogens. The paper is well written and fits perfectly to the scope of ACP. I highly recommend publishing the manuscript in ACP, however, have some very minor comments on the manuscript.

We are grateful to the Referee for the positive review and comments

Minor comments:

Page 10261, line 9: I would suggest to list the ionic composition of seawater in a consistent way (i.e. not listing calcium sulphate individually and listing cations and anions one after the other).

This has been amended.

In lines 125-126: "(e.g., sodium, calcium, sulphate, magnesium, chloride, and potassium)."

Page 10266: The authors introduce "the rule of five" and refer to this expression several times. Since I assume that not all atmospheric chemists and physicists are familiar with this "rule" a general explanation in the beginning of this paragraph would be helpful for the reader.

This is thoroughly discussed in the text (Section 3.2 Transport through sea-ice), line 291.

Page 10268, line 20: "Frankenstein" instead of "Frankestein"

This has been amended.

Page 10281, first line: R. Sander ?

We are referring to Stanley Sander at NASA-JPL. This has been amended in the revised manuscript.