Response to reviewers' comments

ES Saltzman (Referee)

This is an interesting and useful contribution towards understanding the behavior of Br and I in the sea ice/ice sheet system. The study will contribute towards our understanding of the possible utility of ice sheet Br and I as paleoproxies.

We appreciate the referee's interest and helpful comments.

Some specific comments/questions:

1. The Conclusions section should do a better job of pulling together the Arctic and Antarctic results. The striking differences in behavior of I should be noted and explained. If the authors themselves don't have a clear explanation, that makes the paper more interesting and should be highlighted both here and in the Abstract. The sentence "In Antarctica, Bromine and Iodine seasonal cycles are clearly preserved..." gives the misleading (at least for I) impression that the atmospheric seasonality is preserved. That impression is strengthened by the following sentence, stating that "These results illustrate that halogen production events observed by satellites are successfully preserved in polar snow and ice."

We agree that it has not yet been established that atmospheric seasonality of Br and I are directly preserved in polar snow. Indeed the results presented here (as well as the work of Frieß et al., 2010) indicate that there is remobilization of iodine and possibly also bromine in Antarctic surface snow in the presence of sunlight. We still need to establish the extent to which this remobilization occurs and how greatly this may affect the reliability of Br and I as quantitative proxies. We have rewritten the relevant sections of the abstract, discussion and conclusions to better summarize our findings and to highlight current gaps in the application of halogen proxies for paleo sea ice reconstruction.

2. Is it of any possible importance that the Arctic measurements were done on firn, while the Antarctic measurements were on ice? Is it possible that the apparent iodine seasonality evolves over time in the firn?

From the submitted manuscript this could be considered a possible explanation for the differences observed between Arctic and Antarctic sites. Fortunately, we have recently become aware of the related findings of Frieß et al. (Atmos. Chem. Phys., 2010), which allow a comparison of iodine in Antarctic coastal surface snow and show clearly that winter iodine peaks in Law Dome ice are also present in Neumayer surface snow. Hence it appears that different processes are at work regarding the retention and/or production of iodine seasonality in Antarctic and Arctic snow.

3. If the seasonal mobility of Antarctic iodine involves emission to the atmosphere, then variations in wintertime atmospheric transport could influence the amplitude of the local signal in ice year to year. Perhaps that could influence the interpretation of the signal as a paleoproxy.

We agree with the referee that atmospheric transport will influence the presence of iodine at the deposition site and may lead to variability from year to year, although such effects must be considered for all of the aerosols and impurities that are found in polar snow and ice records. The best way to distinguish between transport variability and emission source strength would be to compare recent iodine and bromine fluxes with the satellite record of sea ice variability. In combination with such comparisons, chemical transport modelling is essential to accurately constraining the mass balance and seasonal variability of the studied halogens. These approaches are a priority for future work.

4. In this study, Br_enrichment is used to quantify the bromine signal and iodine concentration is used to describe the iodine signal. That is like comparing apples and oranges - one is a ratio and the other is a concentration. I can see the utility of Br_enrichment for detecting timing of seasonality, but not quantitative comparisons. For example, interannual variations in Br_enrichment could easily be influenced by changes in seasalt rather than reactive Br. Br_excess (Br_total minus Br_seasalt) is a better quantity to compare to bromine levels between various years or to compare bromine and iodine levels.

We agree with the referee that Br-enrichment is a sensitive indicator of seasonality, whereas nssBr is more suitable for evaluating trends in Br emission and/or production by processes such as Br explosion events. We have updated figures 3 and 5 to show both nssBr and Br enrichment, as well as explaining in the text how we have calculated these parameters.

For the purposes of evaluating seasonality, Br-enrichment and nssBr are both effective at demonstrating that seasonal cycles of Br are present in Law Dome ice and hence the specific indicator used does not change the conclusions arising from this work. With regard to the Arctic samples, again we see good correspondence between bromine enrichment and nssBr. To be consistent with earlier work, we have decided to retain our presentation and discussion of Br enrichment but have also added nssBr where relevant.

As regards the comparison of iodine and bromine results, we believe that our approach is valid because iodine and bromine are complementary and independent proxies. They are complementary because their emission is linked to the presence of sea ice and they are both involved in photolytic reactions involving ozone destruction. They are independent because they have completely different emission sources - bromine is emitted from the ocean as sea spray and iodine is emitted from marine biota and algal colonies present under sea ice.

5. If the authors feel there is a compelling reason to use Br-enrichment, they should explicitly define it is calculated, how Na was measured, and how analytical errors were propagated. Also, the Na data itself should also be presented so the reader can compute Br-excess if they wish.

The full datasets presented in the manuscript are being made available to the public via the PANGAEA web archive (doi:10.1594/PANGAEA.833942).

6. Element names (bromine, iodine) should not be capitalized unless abbreviated

The text has been modified accordingly.

Response to referee (A. Saiz-Lopez)

This manuscript presents a report on the seasonality of bromine and iodine enrichment in two Arctic and one Antarctic location. This work follows previous reports by the same authors on the use of halogen records to infer Antarctic sea ice extent over glacial and interglacial periods. The current work further supports and extends the use of halogen enrichment in ice and the observed annual and seasonal variability to obtain information about past sea ice dynamics and its effect on halogen deposition on snow and ice. This work proposes some interesting thoughts about the processes driving the observed seasonality in both bromine and iodine in Arctic and Antarctic ice records. The paper is well written and structured and thus I recommend publication in ACP.

I would be grateful if the authors can first address or comment in the revised manuscript the question at the end of the following paragraph:

One intriguing aspect of the observations reported here is the different seasonality in the bromine and iodine records. For instance, in the Law Dome data the peak in bromine is in the austral summer whereas for iodine is the austral winter. The authors suggest that for iodine one explanation can be that the IO recycling in the snowpack stops with the arrival of the polar night and then all the active gas phase iodine would be deposited during the winter and hence the winter peak in the iodine record. For bromine, satellite measurements have shown considerable levels of BrO (i.e. active bromine chemistry) in summer over the region of Law Dome, and in fact to some extent into the interior of the continent. As for iodine, to sustain these levels of BrO during the sunlit period an active recycling of bromine must also exist (e.g. on sea-salt aerosols and/or snow/ice surfaces). Such levels of reactive gas phase bromine are only sustained in the presence of sunlight since the recycling process on sea-salt/ice/snow needs of the uptake of oxidized bromine (e.g. BrONO2, HOBr, BrONO) which in the gas phase will only form via reactions with BrO and Br, both of which have a photochemical nature. Therefore, if gas phase bromine is present throughout the summer and its recycling, as for iodine, needs sunlight, when the polar night arrives all this bromine will presumably, as hypothesized for iodine, also be deposited and concentrated in the early winter snow strata. However, the bromine record does not show this. The question then is where does the bromine go in winter?

We agree with the referee that this is an interesting and somewhat perplexing problem. As explained below, it appears that we can reasonably explain the bromine pattern at Law Dome. Instead it is the record of iodine that we find to be intriguing and unexpected. We identify two phenomena that need to be considered to explain our observations of bromine and iodine in Antarctic ice: seasonality of emission and sensitivity to re-emission from surface snow. This is not a comprehensive explanation but rather a guide to future investigations.

Regarding the seasonality of emission, ground-based observations at Halley station (Saiz-Lopez et al., 2007) show similar patterns of boundary layer BrO and IO concentrations, with a large peak in early spring and a smaller peak in late autumn. This pattern matches well with our observations of bromine enrichment and nssBr in Law Dome ice. In contrast, the pattern of iodine concentrations in Law Dome ice is quite different. For iodine, the main processes of atmospheric emission are still to be resolved. For example, it is not yet established whether iodine is primarily emitted from the open ocean in organic (CH_3I, CH_2I_2, CH_2ICl) or inorganic (I_2, HOI) form. The importance of iodocarbons produced by plankton colonies located under sea ice is also still to be quantified. While it is not well known how iodine is transferred from the ocean to the sea ice surface, the similar atmospheric concentration patterns of iodine and bromine suggest that both halogens are similarly photolysed over the austral polar day. Despite similar patterns in the atmosphere, the different patterns of iodine and bromine in Antarctic ice suggest that post-depositional remobilization is more important for iodine than for bromine.

Considering the re-emission of iodine and bromine in surface snow exposed to sunlight, there is no indication of strong remobilization of bromine from summer snow strata. The autumn peak observed for Br (denoted by vertical grey bars in Figure 3) may be due to deposition of boundary layer Br at the end of the polar day and/or the early formation of fresh sea ice. We initially speculated that this process may be involved in the formation of the iodine winter peak, but it is not supported by the consistent presence of an iodine peak throughout the winter ice strata. Instead, it is clear from Figure 3 that the late-summer bromine peak ends exactly when iodine concentrations increase. The termination of polar day is quite consistent with the final deposition of bromine and the initiation of iodine retention in snow. Our results confirm that iodine is efficiently remobilized from the snow surface in the presence of sunlight, as proposed by Frieß et al. (2010). The annual cycles of iodine in Neumayer snow and Law Dome ice suggest that iodine is reliably retained in winter snow strata.

The seasonal variability of Antarctic bromine and iodine in the boundary layer and in snow deposition are now reasonably well characterised, but further study is required to accurately quantify the transfer of iodine from the ocean to the boundary layer, as well as the amount of atmospheric bromine retained in summer snow strata. Considering that satellite-based sensors require sunlight to detect halogens, a dedicated year-round observation campaign with active DOAS instruments and fortnightly aerosol sampling, combined with chemical transport modelling, will be required to advance the current state of knowledge regarding polar halogens.