

Interactive comment on “Halogen-based reconstruction of Russian Arctic sea ice area from the Akademii Nauk ice core (Severnaya Zemlya)” by A. Spolaor et al.

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Anonymous Referee #1 Received and published: 8 October 2015 Review of “Halogen-based reconstruction of Russian Arctic sea ice area from the Akademii Nauk ice core (Severnaya Zemlya)” by Spolaor et al.

General comments This manuscript describes halogen-records (bromine and iodine) in Akademii Nauk ice core taken in Severnaya Zemlya, and presents authentic and original scientific material that has relevant implications for halogen chemistry and sea-ice records. On the whole, the topic of the manuscript is relevant and suitable for the scope of the “The Cryosphere”. Nevertheless, there are several points which require

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significant and careful revision for publication. My questions and specific comments are listed as follows.

We thank the referee for suggesting that the paper is suitable for the scope of “The Cryosphere” and for the useful comments that help to improve the quality of the paper. Below we carefully reply to all points highlighted and modify the main text following the suggestions

1. Influence by surface melt and infiltration As stated in Section 2-1, surface melt and infiltration occurred in Akademii Nauk ice cap during summer. These processes are associated closely with ice core quality. Water-soluble species can move and infiltrate under the conditions with surface melt during summer. Additionally, bromine and iodine in surface snow can be liberated preferentially through photochemical reactions and phase change (melt/freeze) after deposition onto snow surface. To interpret ice core records, more and careful discussion about post depositional processes (photochemical reactions and phase change) and quality of ice core (summer melt and infiltration) are required.

In the main text we already explain the quality of the core and the possible effects of percolation due to melting and infiltration events. In any case, considering the comments from the referee, we added two sentences to clarify (line 161-163). The Akademii Nauk Ice core contains melt layers giving evidence for summer melt and infiltration. However the stable isotopic records clearly show seasonal variations that have been used for annual layer counting (Opel et al., 2013), suggesting that the general climate signal is preserved. Stable isotopes are the most stable climate proxy (Pohjola, Moore et al. 2002, Vega, Pohjola et al. 2015) which is a good indication that also the other parameters can be retained. Even though other ice core proxies may be affected more, the deep infiltration and redistribution will be obstructed by melt layer that occur quite frequently. The effect of post depositional processes on halogens has been already evaluated in a previous paper (Spolaor, Vallelonga et al. 2014) Seasonality of halogen deposition in polar snow and ice) and suggest that Bromine is stable and pre-

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serve after deposition while iodine can undergo some remobilization without affecting the annual climate signal. It must be noted that we are not using the raw data but the annual averages that aims to smooth the possible effects of percolation.

2. Trajectory analysis Backward trajectory was calculated in this study. Calculated periods were 3 days in spring and 6 days in summer. Because transported distance depends strongly on the calculated periods for trajectory analysis, the calculated periods are fixed usually. Considering high uncertainty of longer periods, the calculated periods should be fixed to several days. What mode did you use to analyse the trajectory (vertical motion or isentropic)?

The different lengths of the calculated summer and spring backward trajectory (BT) periods are given by the different processes and elements we are evaluating. During springtime Br is involved in the main reactions and processes. For Bromine and considering the relatively fast deposition velocity of gas phase bromine (HBr), it is likely that the enrichment of bromine is more regionally influenced than for iodine. There are no references directly available for this proposition but it is supported by the findings of (Simpson, Alvarez-Aviles et al. 2005). They detected Br enrichments in snow in Alaska up to 300 km inland and our approach was to calculate BTs for an area of 300 km around the island, however some long-range transport could influence the deposition. For iodine, considering the atmospheric lifetime of some organic iodine compounds (CH₃I) in the order of 2 – 6 days (Carpenter 2003, Simpson, Brown et al. 2015) and possible re-cycling processes that can occur, we extended our BT calculation to 6 days for the summer period. We used the vertical motion mode and added this to the manuscript as well as the reason for the different calculated periods. The text has been modified accordingly (line 196-199 and 203-206).

3. Classification of trajectory Air mass history by backward trajectory was classified into three groups in this study. What was the criteria to classify the trajectory into three groups? Variance of the trajectory in each group might be large. Therefore, static analysis is required to estimate the difference.

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We used the Total Spatial Variance as criteria for the number clusters. TSV suggests 2 – 6 clusters, depending on the calculated season. For comparison we calculated different numbers of clusters, but due to the fact that the investigated source regions are large (e.g. Kara Sea or Laptev Sea), an increase of the number of clusters resulted in most cases in a subdivision of the cluster coming from different parts of the same source region. This means, that a major part of the variance of the trajectories is within the large extent of the investigated areas. For simplification and better comparability between the different periods we decided to use only three clusters, to get an indicative estimation of the origin of the air masses. The text has been modified accordingly (line 203-206).

4. Comparison to Na⁺ and Cl⁻ In this study, authors focused on halogens and seaice. In my opinion, this topic is very interesting and important to understand sea-salt and halogen chemistry, and past sea-ice change. Although Na⁺ and Cl⁻ are major sea-salts, bromine and iodine were only discussed in this study. Comparison among Na⁺, Cl⁻, bromine, and iodine provides likely more and better knowledge about halogen chemistry and sea-ice change.

Sodium and chloride in AN ice core show a linear correlation of $R^2=0.86$ so we can easily use one as function of the other. Sodium is the well-established tracer for sea water aerosol. We added the raw sodium records in the figure 5. The manuscript is focusing mainly on Br and I. Sodium and Bromine concentrations show a similar linear trend of $R^2=0.65$). However, we are not looking on the total Br signal but the Bromine that is not produced directly from sea spray aerosol, its excess or enrichment. In addition, it has been proposed that the Na⁺ in a short temporal scale (annual to decal) is mainly influenced by meteorological transport and is not useful for sea ice interpretation (Levine, Yang et al. 2014). The bromine signal is very similar to Na but it is the presence of excess bromine that is very important and discussed. Comparing iodine and Na, the correlation decreases to $R^2=0.5$ suggesting that the sea spray component is less important for this halogen. In addition, when we calculate the excess

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of iodine using sodium as sea spray tracer we detect that only 1% seems coming directly from sea spray aerosol suggesting that other sources are the driver of I. For this reason the usage of Na or comparison with is not useful to the discussion of the results presented.

5. Bromine data Excess Br was plotted in Figures to understand connection between Br (explosion) and sea-ice. Because bromine can be supplied from gaseous bromines and particulate bromine onto surface snow, total-Br (or both) might be better than only exc-Br.

Bromine can have different sources as sea spray, particulate bromine, biological production etc. Our aim is to distinguish the excess fraction that can be caused by other sources than sea spray aerosol. One of these sources is the bromine explosion occurring on the sea ice surface and, considering the previous work, it seems be the dominant source compared to the others mentioned here. The usage of total bromine is misleading and not useful for our proposal. In any case the text has been improved in the section 4.1 (line 287 to 330).

6. Sources of bromine and iodine Short description about potential sources of bromine and iodine is helpful for readers. Please add source lists and discussion in text. Actually, bromide is supplied by transport of sea-salt particles from open sea and sea-ice (including frost flower), gaseous bromines released through heterogeneous reactions on sea-salt particles and sea-salts on snow/sea-ice, and others. Also, iodine (iodide and iodate) is derived from biological processes and sea-salts.

We added a few sentences in the text to clarify. In any case regarding bromine we can distinguish two main sources: the sea spray aerosol and the other reaction that produces the Br excess. While the first is directly connected with sea spray aerosol (and with Na concentration) the second group is a composition of different emission that can be divided in biological production, bromine explosion and sea ice, pollution and heterogeneous reaction. Quantifying the amounts of all these reactions is quite

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difficult however, considering the previous work published by the authors we consider and suggest that the excess is mainly caused by the bromine explosion above sea-ice. For iodine identifying the sources is a difficult task. However, the general idea is that iodine in polar regions can be produced and emitted mainly by biological activity through the sea ice cracks or polynas. Other reactions could affect the total iodine concentration but future development are necessary to assess their contributions. In any case the text has been improved in the section 4.1 and 4.2 (line 287 to 330 for Br and 332 to 381 for Iodine).

7. Typo: page 4411 Line 19: These so called called Thanks to the referee to note this. We modified accordingly. REFERENCES Carpenter, L. J. (2003). "Iodine in the Marine Boundary Layer," *Chem. Rev.* 103: 4953–4962. Levine, J. G., X. Yang, A. E. Jones and E. W. Wolff (2014). "Sea salt as an ice core proxy for past sea ice extent: A process-based model study." *Journal of Geophysical Research: Atmospheres* 119(9): 2013JD020925. Pohjola, V. A., J. C. Moore, E. Isaksson, T. Jauhiainen, R. S. W. Van de Wal, T. Martma, H. A. J. Meijer and R. Vaikmaa (2002). "Effect of periodic melting on geochemical and isotopic signals in an ice core from Lomonosovfonna, Svalbard." *J. Geophys. Res. Atmos.* 107: 1–14. Simpson, W. R., L. Alvarez-Aviles, T. A. Douglas, M. Sturm and F. Domine (2005). "Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime." *Geophys. Res. Lett.* 32(4): L04811. Simpson, W. R., S. S. Brown, A. Saiz-Lopez, J. A. Thornton and R. v. Glasow (2015). "Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts." *Chemical Reviews* 115(10): 4035-4062. Spolaor, A., J. Gabrieli, T. Martma, J. Kohler, M. B. Björnkman, E. Isaksson, C. Varin, P. Vallelonga, J. M. C. Plane and C. Barbante (2013). "Sea ice dynamics influence halogen deposition to Svalbard." *The Cryosphere* 7(5): 1645-1658. Spolaor, A., P. Vallelonga, J. Gabrieli, T. Martma, M. P. Björnkman, E. Isaksson, G. Cozzi, C. Turetta, H. A. Kjær, M. A. J. Curran, A. D. Moy, A. Schöllnhardt, A. M. Blechschmidt, J. P. Burrows, J. M. C. Plane and C. Barbante (2014). "Seasonality of halogen deposition in polar snow and ice." *Atmos. Chem. Phys.* 14: 9613-9622. Spolaor, A., P. Vallelonga, J. M. C. Plane,

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