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.

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 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 preserve 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 (CH3 I) 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.

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 cloride in AN ice core show a linear correlation of R2=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 R2=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 R2=0.5 suggesting that the sea spray component is less important for this halogen. In addition, when we calculate the excess 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 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 produce 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.

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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.

Anonymous Referee #2
Received and published: 14 October 2015
General Comments:

The submitted manuscript presents results demonstrating both the connection between ice-core Br(exc) and spring sea ice in the Laptev Sea and the connection between iodine concentration and summer sea ice area as found in the Akademii Nauk ice core record. In a well-written and concise manuscript, the authors do an excellent job of demonstrating the statistically significant correlations and explaining the significance of the findings. The manuscript is relevant and of interest to the readership of The Cryosphere and I recommend for publication after some minor revisions.

Specific Comments:

pg 4411, lines 20-22: Some studies have also found Br depleted in the snowpack relative to Cl or Na, while others have found constant concentrations. It is more complex than simply stating there is enrichment of Br due to the bromine explosion and this should be discussed.

We agree with the referee and we improve the text in the manuscript (line 103-108). We also agree with the referee that it is possible to detect areas where Br is depleted in the snow compared to Na or Cl. However in all the sites where we measured Br (e.g. NEEM, Svalbard, Severnaya Zemlya, Law Dome, Talos Dome) we always detect an excess of Br (during interglacial samples, the aim of the paper is not to investigate the glacial transition). Depleted samples have been found by the authors in Antarctic samples collected very close to the coast. A recent paper from (Pratt, Custard et al. 2013) suggests that the BrO are mainly produced in sea ice area and Tundra. However, consider the results obtain in Svalbard (Spolaor, Gabrieli et al. 2013) we don't consider tundra regions as the main source for the excess of Br in Severnaya Zemlya.

pg 4413, section 2.1: Changes of the bromine and iodine concentrations in the snowpack over time needs to be more fully discussed. What about processes/reactions that may change the concentrations post-deposition? Although there is some reference to the effect of movement due to meltwater percolation, is it possible to get an estimate on the expected error?

It is not possible to have a precise estimation of how much Br and I can be re-allocated in the ice core. These questions have been already discussed in a previous paper published by the authors. Briefly we determined that Br is stable after deposition as well as later in ice while iodine could be remobilized inside the annual snow layer due to photolitic activities but the general annual climate signal seems to be maintained (more details are provided in (Spolaor, Vallelonga et al. 2014) - Seasonality of halogens deposition in polar snow and ice). The text has been improved (line 161-163).

pg 4415, lines 4-6: Why was HYSPLIT run for a different number of days for spring (three) vs summer (six)?

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 (CH3 I) 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 196-1969 and 203-206).

pg 4416, line 17: To me, it looks like there is a greater minimum than 44% for the period 1996-2000

For the period 1996-2000 the minimum is given by the sum of the two back-trajectories calculated. Both BT suggest a source of the air masses from the east with respect to Severnaya Zemlya, and likely Laptev sea. The sum of both is 49%. However to be more precise we use a cluster of 5 BT that suggest a minimum of 44% for that period. To be consistent in the figure we still continue to use the three cluster mean BT.

pg 417, lines 6-8: States that "seasonal changes in Kara Sea ice area are comparable but smaller than those calculated for the Laptev Sea." This is because the Laptev Sea is a larger area than the Kara Sea. If you normalized by sea area, the changes would be more comparable.

We agree with the referee and we modify the sentence. The changes in Kara and Laptev seas are similar however the rate of production of seasonal sea ice is higher in Laptev Sea (line 247-249).

pg 4418, lines 10-11: The authors state that the results "confirm the finding that Br(exc) is correlated with Laptev and kara Sea ice." However, the findings of the spring sea ice showed only correlation with Laptev ice and not Kara spring ice. This differs from the finding of the summer ice results with the Polyakov anomalies.

Thanks to the referee to note this typesetting errors. There is no correlation between Kara Sea spring sea ice and Br exc. We corrected the sentence.

pg 4429, Table 1: Why was the Br(exc) not compared to the summer sea ice areas? Presumably this was due to negative Br(exc) values. However, it would be important to still present negative Br(exc) values and see how the trend varied with sea ice extent. Perhaps it would be better to use Br(enr) values for statistical correlations instead. If not, then a scaling of the Br(exc) would be required to take logarithms. - Although it is helpful to see the raw Br and Na concentrations in the supplement, it would be helpful to have a plot showing these trends in the manuscript as well.

From previous results we detect that the excess of Bromine is caused by the Bromine explosion. Bromine explosion happens in springtime, so if there is a connection it must be within spring seasonal sea ice. The correlation between Brexc and summer sea ice is still positive however we do not have any thorough explanation to connect summer sea ice and Br excess. Na and total Br concentrations show a very similar trend (R2=0.65) and the authors do not think it can help in the data interpretation. In any case we add the raw Na signal in Figure 5. The main finding and object of the paper is to describe the behaviour of Brexc and Iodine with regard to sea ice.
Regarding scaling the Br exc we agree with the reviewer. In fact, the statistical correlations reported in the paper are computed with the log-transformed Br(exc), as shown in Table 1. In order to avoid any source of misunderstanding, we have amended the text in a few places in order to

emphasize that we took the logarithm of Br(exc).

pg 4421, lines 10-11: Why would the Svalbard record have less clear seasonal variability and be more susceptible to influences of summer melting and iodine re-emission when the climate conditions are similar?

Though Svalbard and Severnaya Zemlya are almost at the same latitude the climate is not the same. We need to keep in mind that Svalbard archipelago is influenced by the warm ocean currents coming from south. In summer time in Svalbard temperatures can rise up to 15°C. In addition during winter time the Svalbard archipelago presents sea ice only in the north eastern side while Severnaya Zemlya is surrounded. In Svalbard rain events can be present also during winter and spring time, for e.g. in 2015 three rain events has occured between December and April. Severnaya Zemlya climate is not strongly affected by the warm ocean current coming from south. Just to have an indication the average annual temperature in Svalbard is around -6.5°C while in SZ is close to -15°C.

Technical Corrections:

pg 4431, Figure 2: It would be helpful to crop all of the back trajectory images to show the same geographical region (i.e. enlarge images to have the same boundaries).

Thanks for the suggestion however the aim of the figure is show from which areas the air mass are most likely be originate and we prefer to be focused on the length of the BT. Re-scaling can under-estimate the local source.

Be consistent in use of either paleoclimate and palaeoclimate (e.g., pg 4410, line 22 vs pg 4413, line 13)

Thanks to the referee to note this. We adopt paleoclimate.

pg 4412, line 23: missing "the" before "last 50 years" - pg 4418, line 12: missing "to" before "iodine"

Thanks to the referee to note this.

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