

## ***Interactive comment on “Sea ice dynamics influence halogen deposition to Svalbard” by A. Spolaor et al.***

**A. Spolaor et al.**

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Answer Referee 1

This paper presents an intriguing data set and is generally well written. It could have interest to members of the fields of sea ice biogeochemistry, atmospheric chemistry, and snow physical and chemical processes. The authors present a set of data spanning a \_eight year period for which they relate bromine and iodine concentrations in snow and firn to sea ice dynamics. Their methodology is sound overall but I have some comments about how they selected using the pan-Arctic sea ice coverage to present their findings. I also would urge them to investigate whether winds (blowing over open leads, water, or ice) could play a role in the signals they present. They likely have more chemical composition data to contribute to this story (ie the 28 trace elements

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they measured). The total lack of investigating wind fields, back trajectories, etc. is a weakness in the paper. Even a wind rose from an area nearby for each year would be worth presenting. I suspect this paper's results could yield intriguing discussions about how relationships between snow and the snow chemical archive can be used to “back calculate” sea ice presence, absence, and dynamics. But some more support from meteorological, sea ice, and chemical composition data would make it a far better paper.

We agree with the referee and have significantly improved the manuscript (section 3.2 and 3.3) by investigating air mass patterns and the change in sea ice extension for each Arctic region (New Figure 4, 5 and 7). We note that in the first version we used sea ice extension data from JAXA while for the revised version we use data from NSIDC since they produce also a regional sea ice extension. It must be noted that though both data set show similar trends, differences exist when we extract the seasonal and March-May sea ice extension (see the additional plots attached). Regarding the use of other measured trace elements, we preferred not to insert these data in the paper because both the source and the atmospheric dynamic of these elements are different from those of halogens, and will instead be considered in another manuscript which is currently in preparation.

Additional plots Legend: Calculation of the seasonal and March-May sea ice extension with the NSIDC (black line) and JAXA (red line) data series. Thought both time series show similar trend some differences are present.

Below are the detailed responses for each comment:

General comments keyed to the text: Line 29: “the” is not needed after “and” We applied the change

30: They mention a “shallow ice core” but in fact they were really drilling into firn, yes? The referee is right, the core did not extend to the close-off depth. We have changed shallow ice core into shallow firn core through the text.

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35-37: I am not aware that the bromine explosion is associated only with first year ice? This may be the case but I am not aware that it does not occur over multi-year ice and/or over some inland locations near the coasts. Linking it to first year ice (only) may not be appropriate.

Bromine explosions can occur in different locations. A recent paper published in Nature Geoscience (Pratt et al. 2013) suggests that bromine explosions can happen also in tundra snow but confirms that first year sea ice is a hot spot for gas phase bromine originating from bromine explosion, especially driven from the fresh snow on the surface. No field data are available but satellite measurements indicate some level of bromine explosion above multiyear sea ice (fast ice). Satellite data however suggest that bromine explosions are more consistent above first year sea ice. The sentence has been changed to more clearly reflect the current understanding of bromine explosion events. The sentence has been changed into: “. . . .explained by greater Br emissions during the Br explosion that have been observed to occur abundantly mainly above first year sea ice during the early springtime. . . .” 46: “spring and summer” ? “Spring-Summer” is not correct We changed the sentence accordingly 59: There are a lot more recent references than this 1995 paper to exhibit “recent observations”

We also refer to recent work by Parkinson et al. 2013 and Serreze et al 2003

62 and 63-65: there are references for these statements that are more valuable than web URLs.

We decided to use the web URLs because the data used for sea ice extension derive from a monitoring program. These have been changed in the following manner: the URL (<http://www.ijis.iarc.uaf.edu/en/index.htm>) into (data from Arctic Sea-Ice Monitor - IJIS at the [www.ijis.iarc.uaf.edu](http://www.ijis.iarc.uaf.edu)) the URL ([http://nsidc.org/data/seaiice\\_index](http://nsidc.org/data/seaiice_index)) into (data from National Snow and Ice Data Center, NSIDC, at [nsidc.org](http://nsidc.org))

67: exceeds Changed accordingly

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75: of Arctic and Changed accordingly

80: and most other locations where multiple references are presented: there seems to be no space between the “;” and the first letter of the next reference.

Changed accordingly

102-103: Results from many studies have shown that blowing snow over sea ice is another way to move ions around from ocean to land. See Simpson et al. JGR 2005. Have you explored the sulfate to sodium ratio on the samples to investigate the potential frost flower signal? Is whether it exists or not? Or is related to specific ice conditions? Many of the frost flower versus sea ice surface papers use this ratio as a tracer. Regardless it is not as simple as “sodium comes from two sources” What do iodide and bromide do in the dataset investigated?

We agree with the referee that it is incorrect to invoke two sources for sodium, as sodium can be influenced by several sources, including sea spray, dust deposition, frost flowers etc. We know that many papers use the sulphate to sodium ratio to identify the role of frost flowers in deposition; however, we do not have sulphate data, only total sulphur. The ratio we obtain is higher (on average 17.0) compared to the average Na/S value in seawater (11.9). However, other sulphur sources could be non-negligible (such as MSA, nss-S, and anthropogenic sulfate). It is likely that some aerosol originated from frost flowers but with our data we cannot discriminate specifically. Additionally, (Roscoe et al., 2011) suggest that frost flowers are very stable in the presence of wind. Our study is focusing on the ratio between bromine and sodium that does not suffer from fractionation in the frost flower phase, which means that the aerosol originating from frost flower does not disturb the bromine enrichment we detect. In addition a recent paper (Pratt et al. 2013) suggests that frost flowers are not a source for gas phase bromine, suggesting that no further fractionation after frost flower formation is possible or likely. Furthermore, we would direct the referee’s attention to a similar question posted by Referee 2: The idea of lofting aerosol from frost flowers has largely

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been discounted, see e.g. Roscoe et al., JGR, 2011. The paper suggested by the second referee strongly suggests that blowing wind above an area of sea ice with frost flowers does not cause aerosol production.

154: "Sample" Changed accordingly

164: due to sample processing Changed accordingly

167: snow pit samples or core samples or both?

The sentence has been changed from:

The decontaminated firn samples were sealed into UPW-rinsed PE bags, melted at room temperature in darkness and then aliquotted into LDPE vials. To evaluate the possibility of contamination due to the sample processing, artificial ice cores produced from UPW were handled and prepared in an identical manner to the samples. No external contamination was detected as a consequence of the core processing. Snow-pit samples were transported directly to Venice, then melted at room temperature under a class 100 laminar flow bench. For halogens analysis 10 mL of melted water was transferred to 12 mL acid-cleaned LDPE vials. Other aliquots were taken for determination of stable isotope ratios and concentrations of major and minor ions and trace elements. The snow pit and core samples has been double-packed in LDPE bags and transported to Venice, where the samples remained frozen until analysis.

Into:

The decontaminated firn samples were sealed into UPW-rinsed PE bags, melted at room temperature in darkness and then aliquotted into LDPE vials. To evaluate the possibility of contamination due to sample processing, artificial ice cores produced from UPW were handled and prepared in an identical manner to the samples. No external contamination was detected as a consequence of the core processing. Snow-pit samples were transported directly to Venice, then melted at room temperature under a class 100 laminar flow bench. For halogens analysis 10 mL of melted water was trans-

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ferred to 12 mL acid-cleaned LDPE vials. Other aliquots were taken for determination of stable isotope ratios and concentrations of major and minor ions and trace elements.

237-240: I do not buy it that the atmospheric iodine is associated with air flow over open water. What about locations where there was open water and nilas, centimeters thick, forms? This would be thin ice that could be closer to the Antarctic situation mentioned. This situation, close to the idea of "potential frost flowers" posed by Kaleschke and others in the mid-2000s, would create locations where iodine could be sourced through the ice rather than open water. Yet they were recently/formerly open water. Have you looked at MODIS images for the times represented in the data to see what the ice looked like in terms of leads? What does the ice typically look like upwind of the sampling location? Are there polynyas, areas of open rubble, areas of dynamic ice, and/or areas of landfast ice? This would also be related to the applicability of the "greater Arctic Ocean sea ice" extent as per processes occurring near the field sampling site.

Few papers specify the atmospheric source(s) of iodine in the Arctic region. There are many studies regarding iodine emission from the ocean but just a few, quite recent works, for the Arctic region. To answer this question we need to consider two aspects. The main source of iodine is the biological production from the ocean as Methyl-iodine, iodoform and other organic species. These species, once photolysed in the atmosphere, could react with ozone and other radicals to produce inorganic iodine compounds (e.g. IO). Mahajan et al. (2010) detected spikes in atmospheric IO concentrations mostly when the air masses move over open water, such as polynyas or open leads. A recent paper (Carpenter et al., 2013) showing that HOI and I<sub>2</sub> are emitted from sea-water following the uptake of O<sub>3</sub> could explain why open water would enhance atmospheric iodine. However, that mechanism requires high levels of iodide ions in the sea surface; measurements show that high levels are mainly associated with warm (tropical) oceans. (Pabi et al., 2008) thoroughly investigated primary production in the Arctic ocean, confirming that an increase of open water strongly influences the

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level of biological production. In particular they claim that “The higher rates of primary production in the Arctic in recent years are reflected in large and widespread positive primary production anomalies, particularly in 2005 and 2006, that correspond to strong positive open water anomalies”. We detect a similar increase of iodine concentration during the same period (Figure 3). (Zhou et al., 2013) show that the Arctic sea ice is mainly impermeable, meaning that the same process of sea ice algae release cannot be invoked as an explanation in this region. Our theory is that the change in the sea ice extension during spring time can explain iodine variation. Three-day back trajectory analysis shows that two main paths cross the sea ice region of the Greenland sea, Barents sea and the Arctic basin. However, changes in spring sea ice in the Arctic basin are minimal during this, making the first two reservoirs the main sources. Thought organic iodine species have a short atmospheric lifetime, CH<sub>3</sub>I could have an atmospheric life time from 2 to 6 days, thus the source region could be further away than the places shown by the 3-days back trajectory, including also Baffin Bay (see new Figure 4 with 6-day Back Trajectory calculations). In addition we cannot exclude that all Arctic regions could contribute. Our assumption is that iodine is mainly emitted from biological production in ice free sea water in the form of organic iodine. Following the referee's comments we improved paragraph 3.2 describing iodine and spring sea ice.

263-281: The above comments are related to this section. Please consider the previous answer

272: Greenland Sea Changed accordingly

275-276: I am not sure I follow this. Because the winds and ice dynamics are so complicated the authors decide to use the overall Arctic sea ice area? This is a severe weakness of the paper. They either have not looked at winds, imagery of ice dynamics and morphology, and back trajectories (which would be overlooking major drivers of weakness in the paper. Even a wind rose from an area nearby for each year would be worth presenting. I suspect this paper's results could yield intriguing discussions about how relationships between snow and the snow chemical archive can be used to

C947

“back calculate” sea ice presence, absence, and dynamics. But some more support from meteorological, sea ice, and chemical composition data would make it a far better paper.

The authors have investigated air mass dynamics and the decision to use the entire Arctic sea was made after a careful evaluation of the data. First of all the main back trajectory path is across the Greenland sea, Barents sea and Arctic Basin. Excluding the Bering and the Okhotsk seas the main variability of total Arctic sea ice extension during March-May is due to changes in the Barents Sea, Greenland sea and Baffin Bay, the three regions that most likely influence the iodine emissions (based on back trajectory calculations). However, considering the atmospheric lifetime of CH<sub>3</sub>I emitted, that are in the range between 2-6 days (Vogt et al.1999), we need to consider not only the variability of the sea ice regions close to Svalbard but also regions not directly close to the archipelago. Even the Bering sea and Hudson Bay could have some influence.

Regarding bromine, the literature suggests that bromine explosions could influence coastal deposition for a range of 300 km suggesting local influence (Simpson et al., 2005) from the sea ice region around Svalbard. Changes in total Arctic seasonal sea ice extension is mainly due to changes in the Arctic Ocean that covers around 30% and up to 60% of the basins close to Svalbard. However, we must stress that back trajectories do not show the source region but only three days back in time, so we cannot exclude that the massive bromine explosion that happens in the Canadian Arctic, Baffin bay and Hudson bay have no influence on the bromine deposition to Svalbard. In particular we measured the main bromine enrichment during 2008 in correspondence with the largest seasonal sea ice extension of the last 10 years especially in the Arctic basin. Our working theory is that local sources are most relevant, however we cannot exclude that other arctic regions, such as the Canadian Archipelago, could influence bromide enrichment. These issues are now discussed in the relevant paragraphs.

276: Did the Comiso paper look at the area of interest? If not then it may not be relevant. If so then state that.

C948

We made a mistake in that Comiso does not investigate sea ice variation in different sectors but with different resolutions divided the sea ice into 120° sectors and 30° sectors. We misunderstood that. The sentence has been changed accordingly. We evaluated single sectors and the evolution trend is not similar everywhere but, as explained in the previous response, the main changes appear to be due to the area around Svalbard.

279-281: good job acknowledging this.

288: why are frost flowers referenced here? It may be a diversion/confusion for people since they are not part of the conclusions of the work.

Changed accordingly

299: in the surface

Changed accordingly

298-303: Again I wonder about winds. Also the “bromine explosion” is but one piece in the halogen chemical reactions that occur during Polar springtime. The bromine explosion events are an intriguing process and may be part of the story here but they are also part of the more complicated and more spatially diverse ozone and mercury depletion events. Obviously, where bromine production can/does occur this provides a potential bromine source for the snow record. However, this only occurs in wintertime. How does the data account for years like 2006 and 2009 and 2010 when there is more bromine present in summer deposition than during the winter time of 2003-2005? To invoke sea ice as the source in late spring then how could some summer and fall deposition patterns have higher bromine values when bromine explosion (and sea ice) are not present? Same type of question but for iodine: where does the iodine come from during non sea ice conditions? If it is related to open sea water in the pack ice then why are the summer time deposition values not higher than winter? These aforementioned questions may be attributable to firn melting during the summer perhaps and smearing

C949

the winter time signal (?). Is there temperature data from the site or nearby to provide information on what summers experienced melt and to what degree did downward percolation affect the firn record? Can the information in Figure 2 on ice lens presence and size be used to provide insight into this? A statistical analysis of concentrations above, within, and below ice lenses may shed some insight?

The bromine explosion is a rapid gas-phase bromine emission from the first year sea ice surface. The reaction mechanism involves ozone and contributes to ozone depletion events. Satellite images clearly show that the Arctic, and especially the first year sea ice, are areas where bromine explosions frequently occur. The bromine explosion begins at the end of winter (March) and continues to the beginning of summer (first days of June). The graph (Figure 6) that the referee comments on does not show the bromine concentration but the enrichment compared with the Br/Na sea water ratio. The year 2008 features a spring with higher seasonal sea ice and we find greater bromine enrichment. Only for the first two years (2011 and 2010) are we able to distinguish seasonality in the bromine enrichment, though the results could be disturbed by percolation (see also the response to referee 3 regarding this). It is possible that for the previous years the percolation that occurred during the summer in the Holthedalfonna glacier could have smoothed the original seasonal signal making any seasonal interpretation quite difficult and uncertain. We can only consider that the signal we detect is likely the average of the year where only in the springtime is bromine enriched with respect to sea water values. Though the isotope signal is preserved and we are able to distinguish the seasonality we cannot exclude that percolation has not acted to smooth the halogen record observed. Iodine is produced by biological production from open sea water mainly during spring time. The retreat of the spring sea ice could affect iodine emission by increasing the area of ice-free ocean surface. Pabi et al 2008 detected a correlation between the decreasing sea ice area during spring time and increasing biological primary production. Unfortunately no data are available for the temperature at the site. There is a meteorological station at the bottom of the glacier but this data cannot be used since it is approximately 500 metres lower in altitude with

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a wind regime that is strongly influenced by katabatic winds from the upper part of the glacier. We have also evaluated the concentrations of halogens before and after ice lenses. The data do not show a statistical pattern, meaning that sometimes higher values were found above the ice lenses, sometimes below and at other times within the ice lense layers.

311-312: Is there data on precipitation or snow layer concentrations from this or other studies? Are cooler seasons associated with more or less snow precipitation events (?) and could this affect concentrations?

No other data of iodine and bromine in the Svalbard glacier are present in the literature. Investigations of the halogen concentrations in the aerosol phase show that spring time is the period associated with enhanced iodine and bromine activity. The deposition of bromine and iodine from their gas phases occur mainly by dry deposition and not by snow/wet deposition. Regarding snow precipitation seasonality and ice lens formation and redistribution of ions, we direct the referee to Pohjola et al. (2002) who found that some volatile and acidic ions were easily mobilised by melt layers, while other elements and water isotopes were largely unaffected.

325-328: same comments as before: it seems to easily explained away that the local ice and meteorological conditions are ignored. If you are going to do this I would recommend at least some Supporting Information showing the local conditions and how/where they are the same (ie are represented by) or different from the total Arctic sea ice areal extent.

We improved our back trajectory analyses which confirm that the halogen source regions are mainly from the sea ice area.

344 and onward: Looking at the "winter" time periods identified in Figure 2D and the peak sea ice information and I concentrations in Figure 3 I wonder why some years have their highest I concentrations in winter and some have their lowest I concentrations in winter. This would be in disagreement from the hypothesis that the I comes

C951

from open water during the sea ice time (winter). Lines 261-262 suggest that ozone could play a role but the ozone fluctuations are likely in late spring (when bromine explosions are likely and ozone depletion events likely) so is there any link there?

Iodine chemistry is biologically mediated and occurs in spring (March-May). Also Sturges et al (1988) give important information regarding iodine emissions. Iodine could play a part in the ozone depletion during spring but it likely only plays a minor role compared to bromine. While bromine explosions are present only during the March-May period, it is clearly demonstrated in the papers of Sturges et al (1988) and Toom-Sauntry et al. (2002) that iodine is emitted not only during the March-May periods but also during summer and early fall. Iodine seasonality is to an extent disturbed by this late emission. In addition the percolation that can happen in the Svalbard core could affect the iodine signal smoothing the seasonal signal.

367-368: given the short data series acknowledged is it appropriate to apply the various statistical treatments to the data? I pose this somewhat rhetorically but a N of 10 or so (ie the # of winter or summer periods) may not be sufficient and/or the distribution of the data may not be correct for the statistical analyses. Some acknowledgement of the applicability of the statistical analyses to the N and distribution of data should be provided. Could be a few sentences here and there.

We acknowledge this important issue as explained in the revised statistical paragraph (2.4) in the new manuscript version. Essentially, we have employed a measure of association which is appropriate for small size data series.

Given the short available data series, the presence of association between the annual averages of %Brenr and seasonal sea ice area, and between the iodine and March-May sea ice is evaluated with the Kendall  $\tau$  rank correlation coefficient. The reason to prefer Kendall  $\tau$  to the usual correlation index is twofold. First, Kendall  $\tau$  is unaffected by the assumption of linearity underlying correlation index. This is an important property for this work because with small sample sizes evaluation of linear

C952

relationships is questionable. Second, the p-value for evaluating the Kendall tau significance can be computed exactly at small sample sizes, while the p-value for correlation significance is based on normality or asymptotic theory and thus it is very imprecise for small sample sizes. However, given that only a short data-series was available for producing these statistical comparisons, we consider these findings to be preliminary and only indicative.

Figures: 2 the “medium lens” and “large ice layers” are the same sized closed symbol in the legend but are different sizes in the graph.

Changed accordingly

Figure 3: the blue circles for “spring sea ice extent” are blue squares of larger size in the actual Plot

Changed accordingly

Figure 4 (Figure 6 in the new manuscript version) Blue circles denoting Average extension of seasonal sea ice are larger in the plot than the legend.

Changed accordingly

#### USEFUL REFERENCES

Carpenter, L. J., MacDonald, S. M., Shaw, M. D., Kumar, R., Saunders, R. W., Parthipan, R., Wilson, J., and Plane, J. M. C.: Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine, *Nature Geosci*, 6, 108-111, 2013.

Pabi, S., van Dijken, G. L., and Arrigo, K. R.: Primary production in the Arctic Ocean, 1998-2006, *J. Geophys. Res.*, 113, C08005, 2008.

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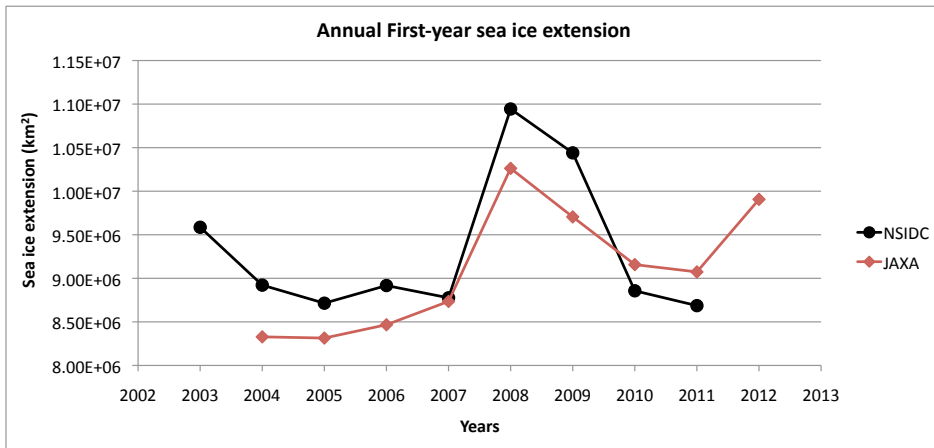
Simpson, W. R., Alvarez-Aviles, L., Douglas, T. A., Sturm, M., and Domine, F.: Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime, *Geophys. Res. Lett.*, 32, L04811, 10.1029/2004gl021748, 2005.

Zhou, J., Delille, B., Eicken, H., Vancoppenolle, M., Brabant, F., Carnat, G., Geilfus, N.-X., Papakyriakou, T., Heinesch, B., and Tison, J.-L.: Physical and biogeochemical properties in landfast sea ice (Barrow, Alaska): Insights on brine and gas dynamics across seasons, *Journal of Geophysical Research: Oceans*, n/a-n/a, 10.1002/jgrc.20232, 2013.

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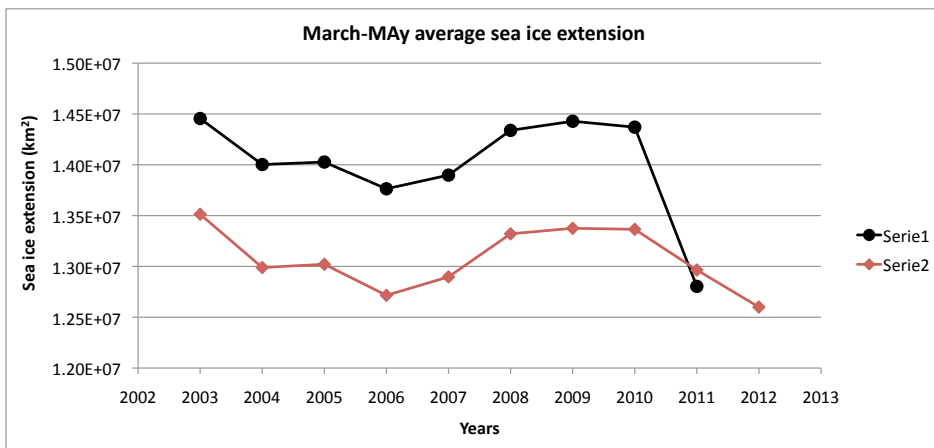
Interactive comment on *The Cryosphere Discuss.*, 7, 1075, 2013.

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**Fig. 1.** Calculation of the seasonal sea ice extension with the NSIDC (black line) and JAXA (red line) data series

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**Fig. 2.** Calculation of the March-May sea ice extension with the NSIDC (black line) and JAXA (red line) data series

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