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Sea ice dynamics influence halogen deposition to Svalbard

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Abstract

Sea ice is an important parameter in the climate system and its changes impact upon the polar albedo and the atmospheric and oceanic circulation. Iodine (I) and bromine (Br) have been measured in a shallow ice core drilled at the summit of the Holtedahlfonna glacier (Northwest Spitsbergen, Svalbard). Changing I concentrations can be linked to the spring maximum sea ice extension. Bromine enrichment, indexed to the Br/Na sea water mass ratio, appears to be influenced by changes in the seasonal sea ice area. I is emitted from marine biota and so the retreat of spring sea ice coincides with enlargement of the open ocean surface which enhances marine primary production and consequent I emission. The observed Br enrichment can be explained by greater Br emissions during the Br explosion that have been observed to occur above first year sea ice during the early springtime. In this work we present the first comparison between halogens in surface snow and Arctic sea ice extension. Although further investigation is required to characterize potential depositional and post-depositional processes, these preliminary findings suggest that I and Br can be linked to variability in the spring maximum sea ice extension and seasonal sea ice surface area.

1 Introduction

Sea ice is an important parameter of the Earth climate system as it affects global albedo and the net radiation balance of the Earth (Francis et al., 2009), as well as oceanic circulation (Holland et al., 2001). Autumn-winter sea ice formation causes an expulsion of salts into oceanic surface water with the result of producing denser surface water with respect to spring-summer surface waters, which are freshened by melting sea ice. Consequently, sea ice production alters surface Arctic Ocean stratification (Warren, 1983). Aagaard and Carmack (1989) proposed that the southward transport of sea ice through the surface circulation of the Arctic Sea could bring sea ice and fresh water to the deep water formation areas of the Labrador Sea and around the Greenlandic

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coasts. Additionally, sea ice forms an effective barrier between the atmosphere and the ocean surface, reducing the thermal and chemical exchange between these two compartments. Sea ice is also important for the polar biological community, from microalgae (Pabi et al., 2008) to the great mammals (Durner et al., 2009).

5 A synthesis of Arctic sea ice reconstructions has found a slight decline starting early in the 20th century (Polyak et al., 2010), with an overall retreat of both the summer and winter sea ice areas since the early 1980s. Recent satellite-based observations of sea ice have greatly improved our understanding of sea ice variability, in terms of temporal resolution (from daily to monthly) as well as surface area and thickness (Stern
10 et al., 1995). In particular, satellite measurements have definitively demonstrated the rapid increase in sea ice loss during the last decades and particularly during the last 10 yr (Stroeve et al., 2007). In this period the four lowest summer sea ice minima of the last 30 yr have been recorded (<http://www.ijis.iarc.uaf.edu/en/index.htm>) with the lowest sea ice extension recorded on 16 September 2012, with a surface area of 3.41 million km². The previous minimum was in 2007 with an extension of 4.17 million km²
15 (http://nsidc.org/data/seaice_index). Different model scenarios have been proposed to predict Arctic sea ice decline (Wang and Overland, 2012), however the most recent measurements have highlighted that the present sea ice decline exceed all predictions (Stroeve et al., 2007). Sea ice is one of the most sensitive components of the Earth
20 climate system (Kinnard et al., 2011), with models potentially underestimating all of the different aspects that contribute to sea ice variability (Rampal et al., 2011).

Accurate reconstruction of sea ice variability before the satellite era is important for understanding interactions between sea ice extension and both the forcings and effects of climatic changes. These results are also important for model calibration. Many different
25 approaches have been proposed to reconstruct sea ice variability. Marine sediment cores are widely used due to their capability to record the source of sediment and thus the pathways of the Arctic and sub-Arctic oceanic circulation (Darby, 2003). The occurrence of floating ice could be revealed by the presence of ice-rafted debris (Lisitzin, 2002), while sea ice-related paleo-productivity can be inferred from the sedimented

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remains of microscopic organisms and other biomarkers (Cronin et al., 2008). Recently, the determination of highly-branched isoprenoids (IP₂₅) in specific sea ice diatoms have been proposed to describe the past sea ice variability (Vare et al., 2009; Fahl and Stein, 2012). Coastal records also help to understand the past dynamics of sea ice, producing a clear signal both in coastal sediment and landforms (Polyak et al., 2010). In addition integration of various paleoclimate archives allows a broad reconstruction of past sea ice variability in the Arctic (Kinnard et al., 2011).

A weakness of the available reconstructions of paleo-sea ice dynamics is that they are characterized by poor temporal resolution. Many atmospheric conditions are recorded in ice core proxies, such as dust deposition, temperature, solar radiation and atmospheric gas concentration (Wolff et al., 2010) and so they are employed extensively for reconstructing past climate (Petit et al., 1999). The absence of reliable and specific proxies has limited their application to reconstructions of sea ice dynamics. Methanesulphonic acid (MSA) has been used to reconstruct sea ice variability (Abram et al., 2013) over the last few centuries at Law Dome in Antarctica (Curran et al., 2003) and from the Lomonosovfonna ice core from Svalbard (Isaksson et al., 2005). Although a positive correlation was found between MSA and sea ice for the Law Dome site, the Lomonosovfonna MSA record showed a negative correlation between sea ice extent and MSA concentration. It has been proposed that the reduced ice cover in the Barents Sea allowed a greater area for primary production as well as warmer water temperatures, thereby promoting DMS production (O'Dwyer et al., 2000). MSA is susceptible to post-depositional mobility and loss which renders it unsuitable for millennial-scale sea ice reconstruction (Smith et al., 2004). Sea salt sodium (ss-Na) has also been used to reconstruct past sea ice variations (Wolff et al., 2006). The sea ice surface is salt-enriched mainly because of the salt expelled in high salinity frost flowers and brine (Rankin et al., 2000) which can be lofted into the atmosphere and deposited on surface snow. However, despite the links between sodium and sea ice (Wolff et al., 2006), the contribution of open ocean sea-spray and wind transport must be taken into account (Petit et al., 1999). The sodium signal is therefore an integration of two

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different effects: sea spray aerosol and frost flower/brine production. There has been much recent progress in satellite-based measurements of trace gases in the atmosphere (Saiz-Lopez et al., 2007a). In particular, satellite images show that high levels of BrO and IO in the Antarctic atmosphere are located above seasonal or first-year sea ice (Schönhardt et al., 2012; Kaleschke et al., 2004). The increase of BrO concentration during the austral spring is likely due to the reaction of bromine with ozone which is one of the main mechanisms of ozone depletion events (ODEs) (Fan and Jacob, 1992) triggered by the injection of gas-phase bromine into the polar atmosphere during bromine explosions (Simpson et al., 2007). Simpson et al. (2007) and Kaleschke et al. (2004) revealed that the occurrence of bromine explosions are linked with the presence of first-year sea ice. These observations are also detected above Arctic sea ice where the atmospheric content of BrO is enhanced in spring time (Sihler et al., 2012).

Increased concentrations of iodine monoxide (IO), observed above Antarctic first year sea ice in the austral spring, have been related to production from algae growing under sea ice (Atkinson et al., 2012; Saiz-Lopez and Boxe, 2008). However, in the Arctic region, satellite measurements of IO do not show particularly high tropospheric concentrations during spring time (Schonhardt et al., 2008). On the other hand, recent Differential Optical Absorption Spectroscopy (DOAS) boundary layer IO measurements suggest an active iodine chemistry during spring time in the near surface atmospheric layer (< 100 m) associated with the formation of open leads or polynyas (Mahajan et al., 2010).

In this work we present iodine and bromine concentrations in a shallow firn core recovered in April 2012 from the Holtedahlfonna glacier in Svalbard. The core chronology, achieved by combined annual layer counting (ALC) and glaciological mass balance calculations, reveals that this record covers the last decade of snow deposition. Iodine and bromine were measured by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) under ultra-clean conditions. The results suggest that the variations in iodine concentration could be associated with changes in spring sea ice extension,

while bromine enrichment (relative to the Br/Na sea water mass ratio) is related to the variation of seasonal sea ice surface area.

2 Samples and methods

2.1 Firn and snow sampling

5 In April 2012, an 11 m long firn core was recovered from the summit of the Holtedahlfonna glacier (Spitsbergen, Svalbard, 79°09' N, 13°23' E, 1150 m.a.s.l.) using a 4'' aluminium auger powered by an electric drill. The sampling location is shown in Fig. 1. The core was drilled from the bottom of a 2.6 m snowpit, at the transition between the 2011 firn layer and the seasonal snowpack. The principal physical features of each firn core section (length, layering, dust horizons, ice lenses, crystallography) were recorded in the field. Stratigraphic snow samples were also collected, by inserting low density polyethylene (LDPE) vials perpendicularly into the snow-pit wall with a spatial resolution of ~ 5 cm down to a depth of 2.35 m. Considering that trace element concentrations in high altitude snow and ice samples are extremely low (ranging from ng g^{-1} to sub- $\mu\text{g g}^{-1}$), the samples were collected using the same stringent anti-contamination procedures developed for collecting snow and firn in Antarctica (Candelone et al., 1994). All sampling tools and LDPE bottles were pre-cleaned with diluted ultra-pure HNO_3 (Ultrapure grade, Romil, Cambridge, UK) and then rinsed several times with ultra-pure water (UPW, Purelab Ultra Analytic, Elga Lab Water, High Wycombe, UK). The scientists wore clean-room clothing and polyethylene (PE) gloves during the sampling. First, the surface of the snow-pit wall was removed with a PE scraper to avoid sampling any areas that may have been contaminated during the digging. The mass of each sample was 50 to 90 g, depending on the density of the sampled snow layer. The snowpack stratigraphy was recorded and physical parameters such as temperature, snow density, grain shape and size, hardness indexes (hand test and Swiss Rammesonde method)

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were measured. The form of the snow grains and their dimensions were established according to the International Association of Cryospheric Science classification.

2.2 Sample preparation

The firn core sections were processed in a class-100 laminar flow hood in the laboratory of the Italian research station in Ny-Ålesund. Core sections were cut to 5 cm resolution with a commercial hand saw that was carefully cleaned with methanol and UPW before and after each cutting operation. Processed samples were kept frozen in dark conditions to avoid any photo-activation of the halogens. The firn ice core samples were decontaminated according to a simplified chiselling procedure (Candelone et al., 1994), using a ceramic knife pre-cleaned with UPW. Three different knives were used to chisel away successive layers which may have been contaminated during drilling, handling, transport and storage. 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.

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2.3 Analytical methods

Concentrations of I and Br, as well as other 28 trace elements, were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS; Element2, ThermoFischer, Bremen, Germany) equipped with a cyclonic Peltier-cooled spray chamber (ESI, Omaha, US), following the methods of Gabrielli et al. (2005). The sample flow was maintained at 0.4 mL min^{-1} . Based on the method proposed by Bu et al. (2003) we developed an analytical procedure for the measurement of total Br and I in firn/ice samples. Particular attention was paid to maintaining a rigorous cleaning procedure between analyses as the measurement of these elements is sensitive to instrumental memory effects. A 24 h cleaning cycle was adopted before each analytical session to guarantee a stable background level. The 24 h cleaning cycle consisted of alternate flushing of ammonia solution 5 % (prepared from TraceSELECT® ammonium hydroxide solution, Sigma Aldrich, MO, US) for 3 min, followed by a UPW rinse lasting 30 s, and a 2 % HNO_3 wash (trace metal grade, Romil, Cambridge, UK) for 3 min. Between each analysis a single NH_4OH , UPW, HNO_3 , UPW cycle was sufficient to ensure that the background value is achieved (difference of $< 1\%$ compared to the initial background level). Iodine and Br were calibrated by external calibration using standards of 10 to 4000 pg g^{-1} . I and Br standards were prepared by diluting 1000 mg L^{-1} stock IC standard solutions (TraceCERT® purity grade, Sigma-Aldrich, MO, USA) in UPW. All calibration curves showed correlation coefficients greater than 0.99 ($\text{df} = 4$, $p = 0.05$). Detection limits, calculated as three times the standard deviation of the blank, were 5 and 50 pg g^{-1} for ^{127}I and ^{79}Br , respectively. Reproducibility was evaluated by repeating measurements of selected samples characterized by different concentration values (between 20 pg g^{-1} and 400 pg g^{-1} for I and between 400 and 600 pg g^{-1} for Br). The residual standard deviation (RSD) was low for both halogens and ranged between 1–2 % and 2–10 % for Br and I, respectively.

A Picarro L2120-i Isotopic Liquid Water Analyzer with High Precision Vaporizer A0211 was used to measure $\delta^{18}\text{O}$. The reproducibility of repeated measurements was

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better than $\pm 0.1\%$. Isotopic compositions measured are reported in the common delta units relative to standard VSMOW.

3 Results and discussion

3.1 Firn core chronology

5 Unlike the majority of the glaciers of Svalbard, the uppermost part of the Holtedahlfonna has a positive mass balance and hence preserves most of its annual snow deposition. Over the eight years, the net mass balance at the top of Holtedahlfonna glacier (1150 m a.s.l.) ranged from 640 to 1100 mm w.eq (average 760 ± 145 mm w.eq). The summer accumulation ranged from -38% (ablation) to $+4\%$ (accumulation) of the total, with an average value of -8% (Fig. 2b). Some melting and percolation is indicated by the presence of several ice lenses in the core (Fig. 2b) however it has been proposed that melt events have only a minor influence on the seasonal climatic signal determined from the $\delta^{18}\text{O}$ signal in Svalbard cores (Pohjola et al., 2002). This is also confirmed by our results, where a clear seasonality has been detected (Fig. 2c, d) despite the presence of melt layers. The core has been dated based on the seasonal variations of $\delta^{18}\text{O}$ as well as from annual mass balance calculations obtained from the difference between the winter accumulation and the summer melting. Mass balance estimates have been carried out through the measurement of several ablatometric stakes along the Holtedahlfonna glacier. The uppermost stake (#8) is located very close to the drilling site (about 40 m) and it provides precise and accurate accumulation data of the surrounding area. For this reason, mass balance measurements at stake 8 are used to support isotopic dating, especially when the $\delta^{18}\text{O}$ shows ambiguities (e.g. 2005 summer season, see Fig. 2). The shallow core and the snowpit cover the period from winter 2003 to spring 2012 (Fig. 2), with less than ± 1 yr uncertainty in the dating. Many factors can affect the accurate reconstruction of local temperatures based on the Holtedahlfonna $\delta^{18}\text{O}$ profile, hence we only use the $\delta^{18}\text{O}$ profile to evaluate annual deposition cycles.

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3.2 Iodine and spring sea ice

Iodine concentrations in Holtedahlfonna glacier samples ranged from below the detection limit (5 pg g^{-1}) to 249 pg g^{-1} (depth 68.9 cm w.eq), with most concentrations less than 118 pg g^{-1} . These values were compared to Na concentrations to ensure that marine salts did not significantly influence the I concentration at Holtedahlfonna glacier. The influence of sea salt deposition was calculated using Na as a conservative marine salt marker and considering a representative value of the seawater I/Na mass ratio of 5.9×10^{-5} (Turekian, 1968). On this basis, sea salt I was found to consistently account for less than 2 % of iodine concentrations.

Iodine can be emitted from the ocean in a number of ways. Firstly, via biological production and emission of a variety of organo-iodine compounds (Carpenter, 2003). Although CH_3I is the major organo-iodine species, it is photolysed relatively slowly in the atmosphere and thus is a less important source of active iodine radicals (I, IO, OIO) in the atmospheric boundary layer than photo-labile species such as CH_2I_2 and CH_2ICl . Secondly, by biological production of I_2 from macroalgae, which is important in coastal areas (Saiz-Lopez and Plane, 2004). Third, the uptake of O_3 at the ocean surface and its reaction with iodide (I) ions causes the emission of HOI and I_2 (Carpenter et al., 2013). It has been postulated that algae growing under the sea ice around Antarctica produce I_2 which percolates up through the ice and is then emitted to the atmosphere (Saiz-Lopez and Boxe, 2008; Atkinson et al., 2012). This source would account for the very high levels of IO radicals which have been observed in the coastal marine boundary layer of Antarctica (Saiz-Lopez et al., 2007b). In contrast, in the Arctic boundary layer the IO radical has proved to be difficult to detect, although recently small quantities were detected downwind of open leads or polynyas (Mahajan et al., 2010). It seems likely that the greater thickness of Arctic sea ice, compared to Antarctic sea ice, inhibits the upwelling of iodine through capillary channels in the ice (Saiz-Lopez and Boxe, 2008), and so atmospheric iodine in the Arctic is instead associated with air flow over ice-free ocean surfaces.

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The iodine profiles from Svalbard show two periods with high concentrations: between 2004–2006 and 2011–2012 the concentrations exceeded 50 pg g^{-1} (Fig. 3). These periods of maximum I concentration coincide with springtime (March to May) minima of Arctic sea ice extension. This negative correlation, which is highlighted using a logarithmic scale in Fig. 3, suggests that the average location of spring sea ice influences the iodine flux. Over the 9-yr observation period reported here, we note that a relatively small variation in spring sea ice extension (8%) corresponds to a much greater response in I concentration variability (1000%). Such a response is in accordance with the findings of Mahajan et al. (2010). If iodine was emitted in substantial quantities by algae blooming under the sea ice, a positive correlation between sea ice extension and I concentration should have been observed. Such an interpretation is supported by Differential Optical Absorption Spectroscopy (DOAS) measurements of atmospheric iodine in the Canadian Arctic that show that IO concentrations become detectable only in the presence of open sea water (Mahajan et al., 2010). No significant IO signal was recorded when air masses flowed above solid sea ice (Mahajan et al., 2010), implying that percolation of I through the sea ice is not a major IO emission mechanism in the Arctic.

Sturges and Barrie (1988) determined iodine and bromine concentrations in Canadian Arctic aerosol, demonstrating that I fluxes increased sharply during spring. This behaviour is likely associated with the phytoplankton bloom that occurs with the dawn of solar radiation in early spring (Pabi et al., 2008). The variation in biological primary productivity has also been investigated in relation to the presence of open ocean water in the Arctic (Pabi et al., 2008; Anderson and Kaltin, 2001). The reaction of deposited O_3 with I^- at the exposed ocean surface may also make a significant contribution during autumn.

Accurate estimation of the sea ice area influencing I deposition to Svalbard is difficult on account of the many factors to be considered, including air mass direction and speed, exchange with the free troposphere, and deposition of iodine compounds en route to the sampling site. The partitioning of iodine species between aerosol gas

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phase is a further uncertainty (Saiz-Lopez et al., 2012). Hisdal (Hisdal, 1998) showed a predominance of easterly and north-easterly winds in the northern part of the Svalbard archipelago during the spring time, with the majority of lower-altitude trajectories originating from the Arctic Ocean and Barents Sea (Rozwadowska et al., 2010; Eleftheriadis et al., 2009). On this basis it is possible to interpret I fluxes to Spitsbergen island as being primarily regulated by the extension and retreat of sea ice in the northern part of Svalbard and the Barents sea (Fig. 1b). The influence of sea ice in the Greenland sea should also be taken into account, based on the findings of Paatero et al. (2010) who deduced air mass pathways through the analysis of ^{210}Pb sources. Considering the variability of the air mass trajectories around the Svalbard islands and the other uncertainties listed above, we have decided to use the overall Arctic sea ice area as a metric to compare to our data. Comiso et al. (2002) have shown that the trends of different sectors of the Arctic approximate well to the overall trend of total Arctic sea ice. Despite aerosol studies demonstrating the seasonality of the iodine deposition (Sturges and Barrie, 1988), seasonal fluctuations were not clearly visible in our firn core profile (Fig. 3). We do not exclude the possibility that percolation of summer melt water as well as possible overlap of spring and autumn deposition peaks may have caused in situ smoothing of the I signal.

3.3 Bromine and seasonal sea ice

Bromine concentrations in Holtedahlfonna glacier samples ranged from 0.43 to 7.36 ng g^{-1} . As with Na, sea water is the primary emission source of atmospheric Br. Although the total Br concentration has a statistically significant positive correlation with Na ($r = 0.78$, p -value < 0.001), Br has an additional atmospheric production source which must be accounted for. Br_2 is produced by the uptake of HOBr on brine-covered (including frost flowers) first year sea ice (Kaleschke et al., 2004). Photolysis of Br_2 then produces Br atoms which react with HO_2 radicals to reform HOBr, thus setting up an efficient auto-catalytic cycle known as a bromine explosion (Simpson et al., 2007). Once in the gas phase, the major sink for bromine is HBr, formed by the reaction of Br atoms

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with HCHO. HBr can then be deposited as bromide ions in the snowpack. In order to evaluate the sensitivity of Br as a tracer of sea ice extension, it is necessary to remove the sea spray component by applying a correction based on the Br/Na mass ratio in sea water. We used a Br/Na value of 0.006 (Millero, 1974). The bromine enrichment percentage ($\%Br_{\text{enr}}$) was calculated using the formula $(([Br]_{\text{ice}}]/([Na]_{\text{ice}}] \cdot 0.006) \cdot 100) - 100$, where a value of $\%Br_{\text{enr}}$ equal to zero indicates an absence of Br enrichment compared to the Br/Na mass ratio. Hence, only positive $\%Br_{\text{enr}}$ values indicate production of Br as a result of the Br explosion.

The possibility of post-depositional processes affecting the Br concentration in surface snowpack was also considered. For instance, the uptake of species such as HOBr and HOI in the snowpack could recycle bromide ions to the gas phase as Br_2 and IBr, respectively. If these recycling processes were significant, then $\%Br_{\text{enr}}$ would be negative, representing an overall depletion of Br relative to the marine sea salt value.

As shown in Fig. 4, $\%Br_{\text{enr}}$ values are consistently positive, indicating that Br is not likely to have been significantly re-emitted from the Svalbard snowpack. The Holtedahlfonna glacier firn core record indicates that Br is almost always enriched beyond representative seawater values, in some cases up to 6 times (in 2008). Only a few samples are slightly depleted below seawater values. We find rather constant $\%Br_{\text{enr}}$ values of approximately 100 between 2003 and 2005, followed by a steady increase to a maximum of 350 in 2008 and then a return to values of approximately 100 between 2009 and 2012.

We observe that the trend of $\%Br_{\text{enr}}$ is consistent with less enrichment during cooler seasons and greater enrichment during warmer seasons (Fig. 4). Such an observation is in agreement with the findings of Sturges and Barrie (1988), who reported higher concentrations of Br in aerosol from March to May with a maximum in April. The consistent springtime enrichment of Br, beyond concentrations expected from solely marine salt inputs, suggests that the springtime peak of bromine explosion activity is the main source of Br deposited in Svalbard glaciers. Bromine is a particularly active element above seasonal sea ice during springtime. Satellite observations clearly show the

springtime increase of atmospheric BrO concentrated above first-year sea ice (Nghiem et al., 2012). Atmospheric BrO values have been observed to progressively increase from above older multiyear sea ice toward the seasonal sea ice margin (Richter et al., 1998; Sihler et al., 2012; Theys et al., 2011).

In Fig. 4, the %Br_{enr} is compared to the Arctic seasonal sea ice extension, where seasonal sea ice was calculated by subtracting the September (minimum) sea ice area from the March (maximum) sea ice area of the previous year (data from Japan Aerospace Exploration Agency, JAXA, via http://www.ijis.iarc.uaf.edu/en/home/seaice_extent.htm). For the most accurate assessment of %Br_{enr}, it would be ideal to evaluate the coverage of sea ice below the transport path of snow deposited at Svalbard. As was the case for I, such transport pathways are difficult to correctly evaluate, and hence we choose to consider the variability of total Arctic sea ice area rather than any particular region. The results obtained from the Holtedahlfonna glacier firn core show a positive relationship between seasonal sea ice area and %Br_{enr}. Both parameters increased after 2005 to a maximum in 2008, followed by lower values from 2009 to 2012. The similar trends of %Br_{enr} to those of seasonal sea ice area support our interpretation that absolute %Br_{enr} values are consistent with a sea ice-related source of Br production.

The role of biological Br emissions in the form of organic Br compounds was also evaluated. If biological emissions were to play an important role then a positive correlation would be expected between I and %Br_{enr}. In the data presented here, these two parameters show a statistically significant negative correlation of -0.32 (p -value < 0.001) suggesting that their fluxes are controlled by opposing sources and/or processes. We hypothesize that a decrease in seasonal sea ice causes a decrease in the area available to support the Br explosion. Simultaneously, decreased seasonal sea ice contributes to a reduced spring sea ice extent and hence increased I emission from the Arctic open water surface.

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3.4 Statistical evaluation

In addition to the simple correlations presented above, we have performed a statistical analysis of the relationship between seasonal sea ice area and %Br_{enr}, as well as between spring sea ice extent (average from March to May) and I concentration.

5 The statistical analysis first requires the segmentation of the $\delta^{18}\text{O}$ time series into sub-series' corresponding to each of the observation years from 2003 to 2011. In order to obtain this segmented series, we first applied a smoothing spline to the $\delta^{18}\text{O}$ time series and interpolated the series onto a regular grid. We then identified the turning points of the smoothed $\delta^{18}\text{O}$ series, with peaks corresponding to summer periods and troughs to winter periods. Turning-point identification was performed using Kendall information theory (Kendall, 1976) as implemented in the function "turnpoints" of the R (R Development Core Team, 2011) package "pastecs" (Ibanez et al., 2009). The peaks (summers) identified by this software are denoted in Fig. 2d as solid red triangles, while the troughs (winters) are denoted as solid blue inverted triangles. Accordingly, each calendar year corresponds to the period between consecutive blue triangles. During 2005, the algorithm automatically determined two peaks; however, when combined with Holthedalfonna mass balance data we attributed summer to the first peak. These invalid turning points are denoted by empty red and blue triangles in Fig. 2d.

10 The segmentation of the $\delta^{18}\text{O}$ time series was used to identify the %Br_{enr} and I data pertaining to the various observation years and hence allowed the calculation of annual average values of Br_{enr} and I. Given the short available data-series, the presence of association between the annual averages of %Br_{enr} and seasonal sea ice area is evaluated with the Kendall τ rank correlation coefficient. This choice is aimed at providing robust statistical evaluations that are unaffected by sample size and assumptions of linearity and normality. The Kendall τ rank correlation confirms the presence of a statistically significant association between the annual averages of %Br_{enr} and seasonal sea ice area ($\tau = 0.57$, p -value = 0.03). Vice versa, there is a statistically significant negative association between the annual averages of log(I) and the spring (March to

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May) sea ice ($\tau = -0.55$, p -value = 0.02). However, given that only a short data-series was available for producing these statistical comparisons, we consider these findings to be preliminary.

4 Conclusions and future development

I and Br profiles determined in a Holtedahlfonna glacier firn core demonstrate variability that can be statistically related to changes in sea ice extent and seasonal sea ice area during the past decade. The enrichment of Br in ice, relative to the sea salt proxy Na, can be attributed to the bromine explosion that occurs above seasonal sea ice during early spring. We suggest that the annual variation of %Br_{enr} is mainly influenced by the variation in the seasonal sea ice area. We find that the predominant Br enrichment occurs during spring and early summer, which coincides with the time period when the bromine explosion is most active. While Br is influenced by the variation of seasonal sea ice area, iodine is primarily emitted from open water and thus related to the changes in the spring sea ice extent. In particular, the retreat of spring (March to May) sea ice appears to be related to increased I concentrations, resulting from the increased biological productivity associated with open water and the reaction of O₃ with iodide ions in the sea surface layer. On the basis of this limited dataset, only tentative findings can be reported here. Further studies will be necessary to thoroughly understand and characterize the processes controlling I and Br transport and deposition in snow pack. The effect of snow melting and percolation should also be investigated, particularly considering the presence of summer melt layers such as those observed in the Holtedahlfonna glacier. The data presented here provide a provisional basis for linking I and Br to sea ice variability, which could lead eventually to reconstruction of past sea ice variations in the polar regions.

Acknowledgement. This work was supported by the Italian National Research Council (CNR), the Italian Ministry of Research through the PRIN project 2009 and by the EU Regional Development Foundation, project VeeOBS. The authors are grateful to Roberto Sparapani and Emiliano Liberatori (CNR) for logistical assistance, Heidi Sevestre and UNIS (The University Centre in Svalbard) for supporting the field operations, and Luisa Poto (University of Venice) for helpful discussions regarding marine biology.

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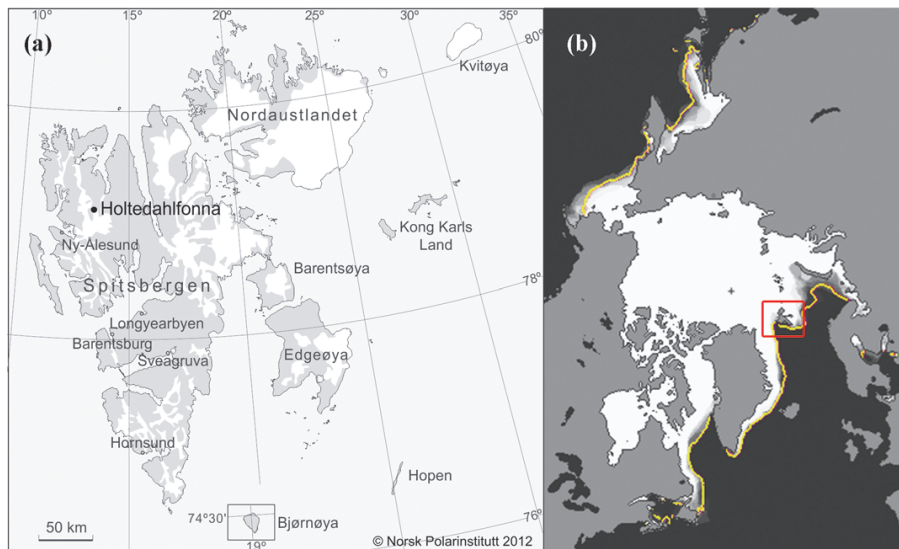


Fig. 1. (a) Map of the drilling site ($79^{\circ}09' \text{ N}$, $13^{\circ}23' \text{ E}$, 1150 m a.s.l.) at Holtedahlfonna glacier at Spitsbergen, Svalbard (courtesy of Norwegian Polar Institute). (b) Composite of ten years of observations of Arctic April sea ice extent (2002–2012). The white area represents the area always covered by sea ice in April. The black area represents the area of consistently open ocean surface in April. The grey graduations indicate the degree of alternation between open ocean and sea ice cover over the considered period. The yellow line is the average April sea ice extension since 1979 (images from <http://nsidc.org/arcticseaicenews/>). Red rectangle represent the Svalbard sampling location with respect to sea ice position.

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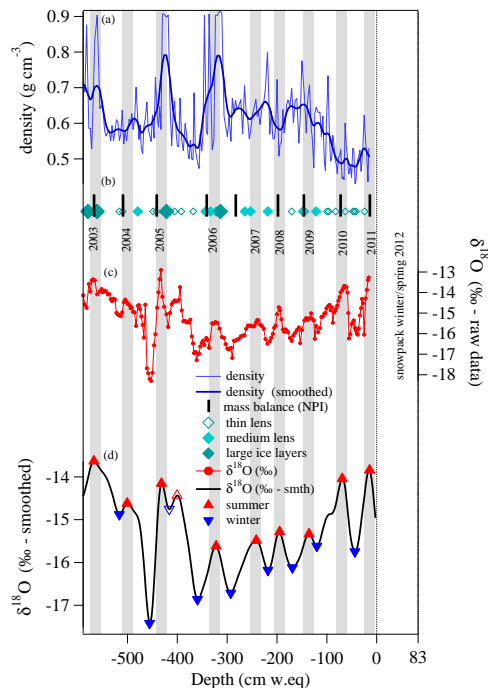


Fig. 2. $\delta^{18}\text{O}$ isotopic ratios **(b)** and density profiles **(a)** in the Holtedahlfonna firn core. Vertical black bars **(c)** indicate mass balance measurements carried out at 1150 m a.s.l in the Holtedahlfonna glacier summit, 40 m west of the drilling site. Diamonds **(c)** indicate the presence of ice lenses in the core; the increasing size of the diamond represents increasing thickness of the lenses. These are characterized as thin (< 20 mm), medium (20–100 mm) and large (> 100 mm). These data have been used to construct the core chronology, which covers 10 yr of deposition. Statistical assessment of the smoothed (smth) $\delta^{18}\text{O}$ profile turnpoints **(d)**. Solid red triangles indicate assigned summer peaks and solid blue triangles indicate assigned winter troughs. Empty red and blue triangles indicate spurious assignments of summer peaks and winter troughs. The grey bars indicate summer periods as inferred from the dataset.

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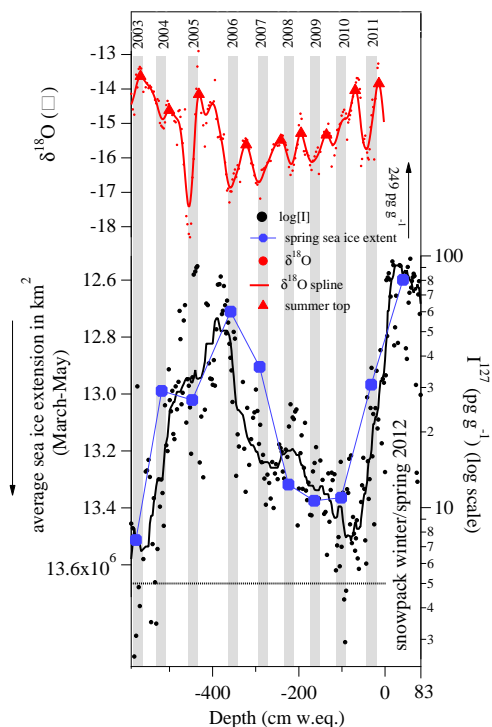


Fig. 3. Iodine concentrations in pg g^{-1} (black circles) compared with spring sea ice extent in km^2 (blue circles, reverse scale). Increased I concentrations in the firn core can be linked to decreased spring sea ice extension. The $\delta^{18}\text{O}$ (‰) profile is shown in red. The grey bars indicate spring-summer periods. The dotted line indicates the iodine detection limit (5 pg g^{-1}).

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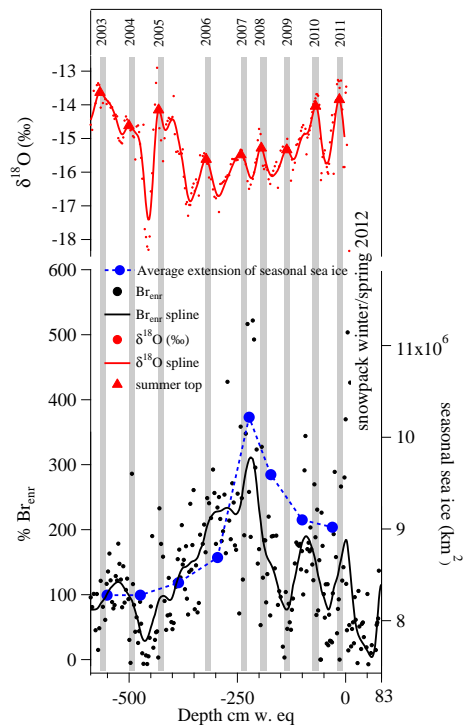


Fig. 4. Bromine enrichment ($\%Br_{\text{enr}}$, black circles) is compared to seasonal sea ice area (blue circles). Seasonal sea ice area was calculated as the difference between the March maxima of sea ice and the September sea ice minima of the previous year. Seasonal variability of $\%Br_{\text{enr}}$ is present in the upper part of the core. Bromine is enriched relative to seawater Na during the springtime, when the seasonal sea ice-produced Bromine explosion is most active. The grey bars indicate summer periods.

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