



Seasonality of
halogen deposition in
polar snow and ice

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Seasonality of halogen deposition in polar snow and ice

A. Spolaor^{1,2}, P. Vallelonga^{3,4}, J. Gabrieli², T. Martma⁵, M. P. Björkman^{6,*},
E. Isaksson⁶, G. Cozzi², C. Turetta², H. A. Kjær³, M. A. J. Curran^{7,8}, A. D. Moy^{7,8},
A. Schönhardt⁹, A.-M. Blechschmidt⁹, J. P. Burrows⁹, J. M. C. Plane¹⁰, and
C. Barbante^{1,2}

¹Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy

²Institute for the Dynamics of Environmental Processes – CNR, University of Venice, Dorsoduro 2137, 30123 Venice, Italy

³Centre for Ice and Climate, Niels Bohr Institute, Juliane Maries Vej 30, 2100 Copenhagen, Denmark

⁴Department of Imaging and Applied Physics, Curtin University of Technology, Kent St, Bentley WA 6102, Australia

⁵Institute of Geology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

⁶Norwegian Polar Institute, Fram Centre, Hjalmar Johansens gt. 14, 9296 Tromsø, Norway

⁷Department of the Environment, Australian Antarctic Division, Channel Highway, Kingston, Tasmania 7050, Australia

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⁸Antarctic Climate and Ecosystem Cooperative Research Centre, University of Tasmania, Private Bag 80, Hobart, Tasmania 7001, Australia

⁹Institute of Environmental Physics, University of Bremen, P.O. Box 330440, 28334 Bremen, Germany

¹⁰School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

* now at: Department of Earth Sciences, University of Gothenburg, Box 460, 405 30 Göteborg, Sweden

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Correspondence to: P. Vallelonga (ptravis@nbi.ku.dk)

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Abstract

The atmospheric chemistry of iodine and bromine in polar regions is of interest due to the key role of halogens in many atmospheric processes, particularly tropospheric ozone destruction. Bromine is emitted from the open ocean but is enriched above first-year sea ice during springtime bromine explosion events, whereas iodine is emitted from biological communities hosted by sea ice. It has been previously demonstrated that bromine and iodine are present in Antarctic ice over glacial-interglacial cycles. Here we investigate seasonal variability of bromine and iodine in polar snow and ice, to evaluate their emission, transport and deposition in Antarctica and the Arctic and better understand potential links to sea ice. We find that bromine enrichment (relative to sea salt content) and iodine concentrations in polar ice do vary seasonally in Arctic snow and Antarctic ice and we relate such variability to satellite-based observations of tropospheric halogen concentrations. Peaks of bromine enrichment in Arctic snow and Antarctic ice occur in spring and summer, when sunlight is present. Iodine concentrations are largest in winter Antarctic ice strata, contrary to contemporary observations of summer maxima in iodine emissions.

1 Introduction

Iodine (I) and bromine (Br) play important roles in atmospheric reactions and ozone destruction (Mahajan et al., 2010; Saiz-Lopez et al., 2007b; Simpson et al., 2007b; Solomon et al., 1994; Pratt et al., 2013; Saiz-Lopez and Plane, 2004). The ocean is the main Br reservoir but in the polar regions atmospheric concentrations are greatly enhanced by Br explosions, autocatalysing reaction chains that produce gas phase bromine (as BrO) while destroying boundary layer ozone in what has been referred to as ozone depletion events (ODEs) (Vogt et al., 1996; Pratt et al., 2013; Simpson et al., 2007a). Atmospheric BrO enhancements and ODEs occur during the polar spring (Frieß et al., 2004; Salawitch et al., 2010; Schönhardt et al., 2012) due to the presence

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of sunlight and, to a lesser extent, acid species (Vogt et al., 1996) and are primarily generated above first-year sea ice (Pratt et al., 2013; Begoin et al., 2010). At the end of the explosion cycle BrO is converted into HBr which is deposited and produces snow strata with Br enriched beyond the oceanic mass ratio of bromine to sodium (Br/Na) (Spolaor et al., 2013a; Spolaor et al., 2013b). In this way, Br and Na share a common oceanic reservoir and significant springtime Br enrichment can be observed due to the tropospheric enhancement of Br. The main source of atmospheric iodine is oceanic biogenic production (Chance et al., 2010; Saiz-Lopez et al., 2012; Wong, 1991; Atkinson et al., 2012), although the organic iodine compound (R-I) released into the atmosphere is rapidly oxidized to inorganic species in the presence of ozone and light (Vogt et al., 1999). Molecular iodine (I_2) and HOI are also produced abiotically by ozone deposition to the sea surface (MacDonald et al., 2013). In Antarctica iodine is mainly produced by sea ice algae and released to the free troposphere by permeation through porous first-year sea ice (Atkinson et al., 2012; Saiz-Lopez et al., 2007a). In the Arctic, iodine release is mainly associated with open-water leads and ice-free ocean areas because the sea ice is too thick for the permeation of iodine (Mahajan et al., 2010; Zhou et al., 2013).

Recent studies have highlighted the correspondence between halogen concentrations in polar snow and ice and sea ice extent. Sea ice presence is positively correlated with bromine enrichment relative to seawater salt ratios and negatively correlated with iodine concentrations over two glacial cycles in the Antarctic ice core record from Talos Dome (Spolaor et al., 2013b). The correlation with bromine enrichment suggested an increase of multi-year sea ice during glacial periods. The correlation with iodine suggested a doubling of seasonal sea ice extent during glacial periods. In the Arctic, bromine enrichment profiles in a Svalbard firn core are compatible with a decade of increasing seasonal sea ice extensions, defined as the annual change in sea ice cover from summer minimum to winter maximum (Spolaor et al., 2013a). The Arctic spring bloom of biological productivity is commonly associated with the maximum extent of ice-free ocean surface (Ardyna et al., 2013; Pabi et al., 2008), leading

to a negative correlation between atmospheric iodine concentrations and maximum (February–March) sea ice extension due to the biological source of iodine emission. Here, we extend these findings by investigating the seasonality of iodine concentration and bromine enrichment in one Antarctic (Law Dome) and two Arctic (Northwest Greenland Eemian Ice Core, NEEM, drilling site and Holtedahlfonna glacier, Svalbard) sites as shown in Fig. 1.

2 Methods

2.1 Samples

2.1.1 Law Dome, Antarctica

Law Dome ice core samples were obtained from the Law Dome summit (66°46' S, 112°48' E, 1370 m a.s.l.), a high-accumulation zone (0.70 m ice equivalent per year) which ensures that seasonal cycles are well preserved even at depth (Morgan et al., 1997). Law Dome is an ice dome located 100 km from the east Antarctic coast that is sensitive to the incursion of maritime cyclonic air masses crossing over sea ice. The Law Dome chronology has been developed by counting annual cycles of water isotopes and chemical impurities, constrained by volcanic deposition markers, allowing the two-metre long ice core section reported here (81.56 to 83.56 m) to be attributed to snow deposition from 1910 to 1914 AD with sub-annual uncertainty (Plummer et al., 2012). This section corresponds to the time of the 1911–1914 Australasian Antarctic Expedition, led by Sir Douglas Mawson, which conducted valuable observations of the Wilkes Land coastline at the time (Mawson, 1942). Law Dome ice core samples were obtained from the DSS0506 ice core. A 3 m long section of the ice core was cut into three 1000 mm × 35 mm × 35 mm rods that were sequentially melted and collected in PE vials cleaned in UPW. Aliquots were stored frozen and later sent to Venice for analysis.

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2.1.2 NEEM, Greenland

NEEM samples were obtained in July 2012 from a virgin snow pit site (77°25' N, 51°07' W) located approximately 3 km Southwest of the main NEEM ice core drilling site. The main NEEM drill site (77°27' N, 51°04' W, 2450 m.a.s.l.) features an annual mean temperature of -29°C and accumulation rate of 0.22 m ice equivalent per year (NEEM Community members, 2013). Samples were recovered using polystyrene coulter counter cuvettes driven into the wall of a 2 m snow pit cleaned using polycarbonate scrapers. Samples were sealed in PE bags and kept frozen until they were ready for analysis in Venice.

2.1.3 Holtedahlfonna, Svalbard

A 6 m firn core was drilled at Holtedahlfonna (HDF) ice dome (79°09' N, 13°23' E, 1150 m.a.s.l.) in 2013, allowing the investigation of aerosol deposition since 2004. Although Svalbard glaciers are often subject to summer melting, their high annual snow accumulation rates ensure that percolation ensuing from such surface melting does not invalidate the climate information contained in the records (Isaksson et al., 2005; O'Dwyer et al., 2000). The retention of multiyear variability in Svalbard snow has been recognized despite the loss of seasonal resolution of some reactive and volatile species (2002).

Holtedahlfonna firn cores were processed in a class-100 laminar flow hood in the laboratory of the Italian research station at Ny-Ålesund. Core sections were cut to 5 cm resolution with a commercial hand saw that was regularly cleaned with methanol and ultra-pure water (UPW, ELGA systems $18.2\text{ M}\Omega\text{ cm}^{-1}$). Processed samples were kept frozen in dark conditions to avoid any photo-activation of the halogens. The firn ice core samples were decontaminated using ceramic knives (Candelone et al., 1994) to avoid potential contamination from drilling, handling, transport and storage. Samples were sealed in UPW-rinsed polyethylene (PE) bags, melted at room temperature in darkness and then aliquotted into LDPE vials. Snow-pit samples were transported directly to

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Venice, then melted at room temperature under a class 100 laminar flow bench, with 10 mL of melted water used for each analysis.

2.2 Halogen determination in ice

Concentrations of I, Br and Na 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, USA) (Spolaor et al., 2013b; Gabrielli et al., 2005). The sample flow was maintained at 0.4 mL min^{-1} . 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.

The analytical system was cleaned for 24 h prior to each analysis session, consisting of alternating 3 min washes of 5 % ammonium solution (*TraceSELECT*[®] NH_4OH , Sigma Aldrich), then 2 % HNO_3 acid (trace metal grade, Romil, UK), with 30 s of UPW between reagents. Between each analysis a single cleaning cycle was run to maintain the background to within 1 % of the initial background level. Iodine and bromine were calibrated by external calibration using standards of 10 to 4000 pg g^{-1} . Iodine and bromine standards were prepared by diluting 1.000 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 ($df = 4$, $p = 0.05$).

2.3 Water isotope analyses

$\delta^{18}\text{O}$ values were measured using a Picarro L2120-i near-infrared Cavity Ring Down Spectrometer (IR-CRDS) with High Precision Vaporizer A0211 (Gkinis et al., 2010). The reproducibility of repeated measurements was better than $\pm 0.1\%$. Isotopic

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compositions measured are reported in the common delta units relative to Vienna Standard Mean Ocean Water (VSMOW) isotopic reference standard.

2.4 Satellite data

The SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric CHarographY) (Bovensmann et al., 1999) and GOME-2A (Global Ozone Monitoring Experiment-2A) (Callies et al., 2000) instruments are space borne UV-vis sensors in sun-synchronous orbits that view in nadir direction and detect the backscattered radiance from Earth as well as the solar irradiance. SCIAMACHY features additional IR channels as well as the limb viewing mode. For the present data analysis, only UV-vis measurements from nadir geometry are used. Spatial pixel size is 30 km × 60 km for SCIAMACHY and 40 km × 80 km for GOME-2A. For SCIAMACHY, the effective pixel size is up to 60 km × 240 km here due to the use of larger integration times in one of the spectral channels within the applied fitting window. SCIAMACHY ceased operation in early 2012; GOME-2A is presently in operation.

IO and BrO total slant column densities are retrieved from SCIAMACHY nadir data (416–430 nm fitting window, Schönhardt et al., 2008) and from GOME-2 data (336–347 nm fitting window (Begoïn et al., 2010)), respectively, using the Differential Optical Absorption Spectroscopy (DOAS) method (Platt, 1994). Due to the difficulty in detecting clouds over ice covered regions in satellite data, a cloud screening algorithm is not used here.

For improved signal-to-noise-ratio, an averaged Earthshine spectrum is used as reference background in the DOAS retrieval of IO. In contrast to BrO, no large amounts of IO have been reported for the stratosphere, therefore no stratospheric correction scheme has been applied.

Tropospheric vertical column densities of BrO are derived from total slant column densities using the stratospheric BrO climatology (2009) and tropopause heights from NCEP/NCAR Reanalysis 1 data (Kalnay et al., 1996) for separation of the tropospheric slant column. A tropospheric air mass factor is applied to derive tropospheric vertical

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columns assuming that all BrO is located and well mixed within the lowermost 400 m of the troposphere over ice with an albedo of 0.9. Outside ice and snow covered regions BrO amounts would therefore be underestimated. The method used here for deriving tropospheric BrO has been described in detail in the literature (Begoin et al., 2010).

Satellite time series data of the stations are produced at the coordinate of the respective ice core and snow pit and an area surrounding this with a radius of 500 km. Due to an interhemispheric bias in the satellite IO product, different reference regions are chosen for the two polar maps; 30–50° S and 150–170° W for the Southern Hemisphere, 60–70° N and 80–120° E for the Northern Hemisphere. Monthly averages are generated from datasets with at least 20 observations per day. The running mean is generated by averaging over 3 month periods, thereby producing a seasonal running mean.

3 Results and discussion

3.1 Satellite observations

Satellite measurements allow near-realtime quantification of atmospheric BrO and IO (Schönhardt et al., 2008; Begoin et al., 2010; Saiz-Lopez et al., 2007a). We have used GOME-2A and SCIAMACHY space-borne instruments to determine locations and atmospheric column amounts of BrO and IO, respectively, in the Arctic and Antarctic (Fig. 1). Both sensors operate in the UV and visible spectral regions and record the backscattered solar radiation, so halogen compound observations are unavailable for the Arctic (October–February) and Antarctic (April–July) winters. Satellite data cover 2009 to 2012, showing higher concentrations of both halogen species in Antarctica compared to the Arctic. BrO amounts were consistently largest over sea ice. In Antarctica, areas of largest amounts of IO coincide with those of BrO, though not generally at the same time. Arctic abundances of IO were close to the detection limit of the sensor and negative values were hence not uncommon. Satellite observations of BrO and

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IO in polar regions allow the identification of emission sources and seasonal patterns, which provide a context for interpreting any seasonality that may be found in snow and ice records of halogens.

3.2 Antarctic halogen seasonality

Iodine and bromine deposition in the coastal Antarctic Law Dome ice core exhibit clear seasonal variability over the 4-year sequence reported here. We interpret the deposition data with reference to modern satellite observations of Antarctic halogen compounds (Fig. 2). Annual cycles in water stable isotopes are clearly resolved and confirm the existence of sub-annual iodine and bromine variability (Fig. 3). Bromine enrichment in Law Dome ice increases in spring, coinciding with polar sunrise, with summer maxima and clear winter minima. Such seasonality is in overall agreement with recent satellite measurements of BrO concentrations above sea ice, with maximum concentrations during Austral spring. Within the available sampling resolution, there is some possibility of a time-lag between the August–September peak of atmospheric BrO (Fig. 2) and the November–February peak of bromine enrichment in Law Dome ice. If confirmed, such a lag would point to an influence of transport on the bromine enrichment in ice, potentially generated by repeating cycles of bromine emission and enrichment during the polar day (Spolaor et al., 2013b).

Iodine deposition in Law Dome shows abrupt seasonal variability, with the highest concentrations in the winter ice strata (Fig. 3). A winter peak in iodine is unexpected, considering the importance of sunlight for the activation of halogen chemistry. The SCIAMACHY sensor does not produce data during polar winter and is therefore unable to validate the winter peak of iodine observed in Law Dome ice. Year-round ground-based DOAS measurements of atmospheric IO at Halley station (Saiz-Lopez et al., 2007b) indicate that atmospheric IO and BrO concentrations are greatest in Austral spring (August to October) and below detection limit during Austral winter (May to August). We propose two potential mechanisms to account for a winter peak of iodine in Law Dome ice: summertime photochemical IO recycling in the snowpack that is

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halted during polar night, or remobilization of iodine in the firn/ice matrix from summer strata to winter strata. Summertime photochemical recycling of IO in the snowpack is required to account for observations of Antarctic boundary layer chemistry (Saiz-Lopez et al., 2008) and can explain the migration of IO from coastal emission sources to far inland Antarctica by repeated cycles of surface snowpack photoemission and deposition. Such recycling only occurs in the presence of sunlight, so IO would tend to be absent from spring/early summer snow strata and concentrated in autumn/early winter snow strata. Post-depositional migration within the firn/ice matrix is another potential explanation for iodine concentration maxima in winter ice strata and has been previously noted for methanesulphonic acid (MSA) and other reactive species. In a Law Dome ice core record, MSA was found to migrate from summer to autumn strata with minimal disturbance to seasonality, driven by gradients in sulfate and nitrate and stabilized in sea salt strata (Curran et al., 2002).

We consider the trends of iodine and bromine observed in Antarctic ice over the period 1910–1914 and the implications for reconstruction of sea ice variability. Such an approach has been previously applied to changes in seasonal sea ice extension over glacial/interglacial time scales (Spolaor et al., 2013b). Between 1910 and 1912 we observe Br enrichment in ice 6 to 7 times greater than seawater values, while maximum iodine concentrations were about 0.25 ngg^{-1} . In the following two years (1913–1914) Br enrichment is somewhat lower (3 to 5) while iodine concentrations decrease below 0.1 ngg^{-1} .

The reduced bromine enrichment peak observed for Austral summer 1912/13 (Fig. 3) suggests minimal summer sea ice extent for that year. This is supported by observations of the Australasian Antarctic Expedition, which recorded the Wilkes Land summer pack ice conditions for three consecutive years from 1911/12 to 1913/14. The Australasian Antarctic Expedition traversed the Antarctic coastline between 90° E and 150° E for three consecutive Austral summers, from 1911/12 to 1913/14. The collected expedition reports (Mawson, 1942) were published later and include ship logs and observations for all three seasons. The expedition traversed the sector relevant to Law

Dome (111–117° E, Fig. 4) from East to West, on 2 February 1912, 16 February 1913 and 11 January 1914. For the 111–117° E sector, the pack ice limits were observed at 65° S (1911/12) and 64.5° S (1913/14). For the summer of 1912/13, the expedition crossed the sector between 65° S and 64.5° S (Fig. 4) without sighting the pack ice limit. These observations are consistent with a reduced 1912/13 summer sea ice area and hence a reduced area of fresh snow for atmospheric bromine enrichment.

3.3 Arctic halogen seasonality

Iodine and bromine concentrations are reported for a 2 m deep snow pit sampled from the NEEM site in northwest Greenland, covering the period 2010–2012 (Fig. 5). Bromine enrichment values observed at NEEM are greater than at Law Dome, with summer peaks of Br enrichment. Compared to Law Dome, the greater Br enrichment values in NEEM ice are consistent with the location of NEEM being both downwind from Arctic Br production zones in the Arctic Sea and Hudson and Baffin Bays, as well as farther inland than Law Dome. NEEM iodine concentrations display annual variability with a summer peak that is consistent with satellite observations (Fig. 5). Arctic iodine emissions have been attributed to phytoplankton at the ice-free ocean surface (Spolaor et al., 2013a) and may be supported by the percolation of iodine via brine channels in sea ice when the sea ice temperature increases (Golden et al., 1998). The observed iodine deposition is consistent with a summer emission peak from the ice-free ocean surface. Although sea ice coverage is at a minimum during late summer, iodine release via brine percolation is also favoured by warmer temperatures, above a sea ice phase-transition threshold temperature of around -5°C . Increasing iodine concentrations coincide with decreases in summer sea ice extent (Fetterer et al., 2002, updated daily) from 2009 to 2012 (Fig. 5).

Halogen seasonality in the Arctic has also been evaluated from firn core samples collected from the Holtedahlfonna (HDF) glacier in Svalbard. In the HDF firn core iodine does not present a strong seasonality (Fig. 5) but does show an increasing trend from 2010 to 2012 consistent with the NEEM observations. Iodine concentrations in HDF

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during 2009 and 2010 are close to zero, in agreement with previous measurements in Svalbard snow (Spolaor et al., 2013a). Seasonal variability is retained for bromine enrichment (Fig. 5), with greater Br enrichment values in spring/summer strata and limited Br enrichment in winter strata. HDF Br enrichment values are consistently lower than those in NEEM, reflecting the proximity of HDF to the open ocean and hence less enrichment of atmospheric Br between emission and deposition.

4 Conclusions

We demonstrate that seasonality of Br and I is present in century-old Antarctic ice from Law Dome and in recent snow at NEEM (Greenland) and Holtedahlfonna (Svalbard). The data clearly show that products of bromine explosion events and iodine emissions are recorded in snow deposition and archived in ice. In Antarctica, Bromine and Iodine seasonal cycles are clearly preserved and possibly enhanced by repeated emission and enrichment in the presence of sunlight. These results illustrate that halogen production events observed by satellites are successfully preserved in polar snow and ice. Such observations clarify the sources and seasonality of polar halogen emission – vital parameters for the application of halogens in snow and ice to the investigation of past sea ice variability.

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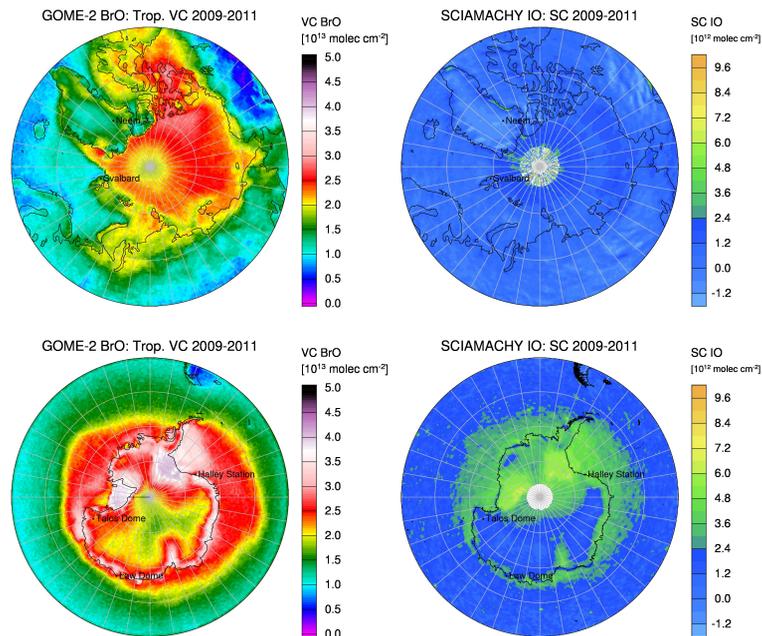


Fig. 1. Average atmospheric column amounts of BrO and IO in Antarctica and the Arctic between 2009 and 2011. Bromine and iodine concentrations are greatest above the Antarctic ice shelves and along the coast. In the Arctic, iodine concentrations are near the limit of detection by satellite. Sampling site locations are shown as well as other locations mentioned in the text.

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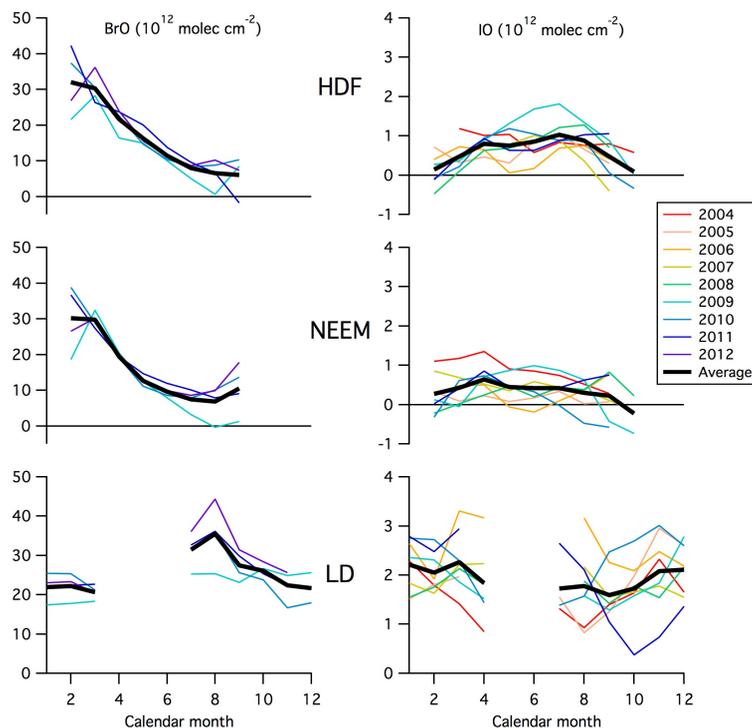


Fig. 2. Averaged monthly atmospheric column concentrations for BrO (left column) and IO (right column) for the sampling sites mentioned in the text. The lines show 3 month seasonal running means. Holtedahlfonna (HDF) is in Svalbard, NEEM is in Greenland and Law Dome (LD) is in Antarctica.

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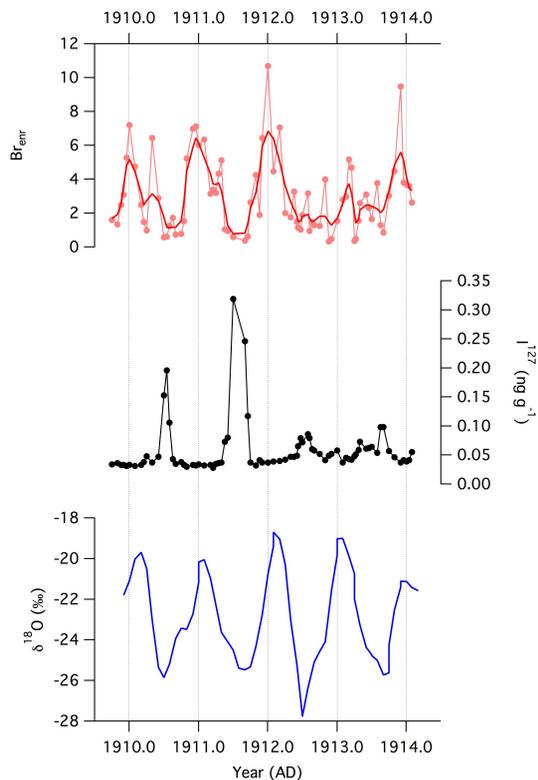


Fig. 3. Seasonal variability in bromine and iodine is archived in Antarctic ice. Bromine enrichment relative to seawater Br/Na mass values (red), iodine concentrations (black) and $\delta^{18}\text{O}$ isotope ratios (blue) in the Law Dome ice core, coastal East Antarctica.

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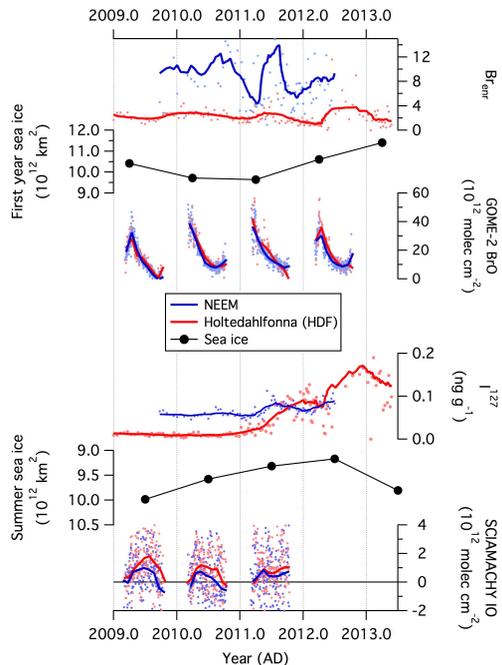


Fig. 5. Halogens in the Arctic atmosphere and surface snow compared to sea ice parameters from 2009 to 2013. For all data series, measurements corresponding to the NEEM site (North-west Greenland) are shown in blue, whereas measurements corresponding to Holtedahlfonna (HDF, Svalbard) are shown in red. The top half of the figure relates to bromine and the lower half to iodine. Bromine enrichment (Br_{enr} , calculated relative to seawater Br/Na mass values) and iodine concentrations determined in surface snow from NEEM and HDF are shown as individual data (points) and 15-point moving averages (lines). First year sea ice is defined as the difference between the March maximum and the preceding September minimum of Arctic sea ice extent. Summer sea ice (note reversed scale) is defined as the average sea ice extent between May and August. Daily (points) and monthly (lines) atmospheric column amounts of BrO and IO derived from satellite data are also shown for comparison.