Seasonality of halogen deposition in polar snow and ice

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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 emission is attributed to ~~emitted from~~ biological communities in the open ocean and 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 and iodine concentrations and Br enrichment (relative to sea salt content) ~~and iodine concentrations~~ in polar ice do vary seasonally in Arctic snow and Antarctic ice. Although seasonal ~~such~~ variability in halogen emission sources is recorded by satellite-based observations of tropospheric halogen concentrations, seasonal patterns observed in snowpack are likely also influenced by photolysis-driven processes. Peaks of bromine concentration and Br enrichment in Arctic snow and Antarctic ice occur in spring and summer, when sunlight is present. A secondary bromine peak, observed at the end of summer, is attributed to bromine deposition at the end of the polar day. Iodine concentrations are largest in winter Antarctic ice strata, contrary to contemporary observations of summer maxima in iodine emissions. These findings support previous observations of iodine peaks in winter snow strata attributed to the absence of sunlight-driven photolytic remobilization of iodine from surface snow. Further investigation is required to confirm these proposed mechanisms explaining observations of halogens in polar snow and ice, and to evaluate the extent to which halogens may be applied as sea ice proxies.

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 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) (Barrie et al., 1988; Vogt et al., 1996;

Simpson et al., 2007a; Pratt et al., 2013). Atmospheric BrO enhancements and ODEs occur during the polar spring (Richter et al., 1998; Frieß et al., 2004; Salawitch et al., 2010; Schönhardt et al., 2012). To obtain a bromine explosion, acidic conditions (Vogt et al., 1996) and cold temperatures provide conditions which amplify the chain length for the autocatalytic release of bromine (Kaleschke et al., 2004; Sander et al., 2006). These conditions are often found above first-year sea ice (Pratt et al., 2013; Begoin et al., 2010). The explosion cycle BrO is terminated by reaction of Br with formaldehyde, HCHO, to produce HBr, which is soluble and is likely deposited. This produces snow strata with Br enrichment that is greater than 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.

IO has been observed from space at high latitudes (Schönhardt et al., 2008; 2012). The main source of atmospheric iodine is currently considered to be oceanic biogenic production (Chance et al., 2010; Saiz-Lopez et al., 2012; Wong, 1991; Atkinson et al., 2012). 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 emission is attributed to the production of photolabile iodocarbons by sea ice phytoplankton and is released to the troposphere by permeation through porous first-year sea ice (Atkinson et al., 2012; Saiz-Lopez et al., 2007a). Frieß et al., (2010) observed that iodine was depleted in summer snowpack strata at coastal Neumayer station, and attributed summer concentrations of boundary layer iodine to photochemistry-induced remobilization of iodine from the snowpack. In the Arctic, iodine release is mainly associated with open-water leads and ice-free ocean areas. This is most likely because multi-year 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 extent, defined as the annual change in sea ice cover from summer minimum to winter maximum (Spolaor et al., 2013a). Despite the Arctic spring bloom of biological productivity occurring at the time of minimum ~~maximum extent of~~ ice-free ocean surface (Ardyna et al., 2013; Pabi et al., 2008), Spolaor et al., (2013a) found an anticorrelation between atmospheric iodine concentrations and maximum (February-March) sea ice extent ~~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 1000x35x35 mm sticks that were sequentially melted and collected in PE vials cleaned in UPW. Aliquots were stored frozen and later sent to Venice for analysis.

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 (Pohjola et al., 2002).

Holtedahlfonna firn cores were processed in a class-100 laminar flow hood at ~~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 MΩ/cm). 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 aliquotted into LDPE vials. Snow-pit samples were transported directly to Venice, ~~then~~ melted at room temperature under a class 100 laminar flow bench, ~~with and-~~10 mL of melted water was 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 minute washes of 5% ammonium solution (*Trace*SELECT® NH_4OH, Sigma Aldrich), then 2% HNO_3 acid (trace metal grade, Romil, UK), with 30 seconds 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).

Two measures of bromine have been calculated to evaluate the extent to which bromine has been concentrated in snow and ice by photochemical processes. Firstly, we have calculated non-sea salt bromine (nssBr) analogous to other parameters commonly calculated in glaciochemistry (eg, nssCa or $nssSO_4$). The formula used to determine nssBr is:

$$\mathrm{nssBr} = \mathrm{Br} - (\mathrm{Na} \times 0.006) \tag{1}$$

where Br is the total bromine concentration and Na is the measured sodium concentration. We use the Na/Br sea water ratio of 0.006 (Turekian, 1968). nssBr allows an evaluation of the total production of bromine that cannot be accounted for directly by sea salt, and is therefore useful for quantitative comparisons between different sites. We also calculate bromine enrichment (Br_{enr}) which is the ratio of total bromine to sea salt bromine. Bromine enrichment is calculated using the following equation:

$$\mathrm{Br_{enr}} = \frac{\mathrm{Br}}{(\mathrm{Na}\times 0.006)} \tag{2}$$

with the same definitions of Br and Na as for Equation 1. $\mathrm{Br_{enr}}$ emphasizes the seasonality of bromine enrichment processes such as the bromine explosion, but can be biased by locations with low sodium concentration. All bromine, iodine and sodium data reported here are publicly accessible at the PANGAEA online database (doi:10.1594/PANGAEA.833942).

2.3 Water isotope analyses

For Law Dome ice core samples, $\delta^{18}O$ was measured on subsamples of water (0.4 ml) that were equilibrated with CO_2 at 25°C with a VG Isoprep-18 equilibration bench. The oxygen isotope ratio of equilibrated CO_2 was measured on a VG Isogas SIRA mass spectrometer at the Central Science Laboratory - UTAS. The $\delta^{18}O$ values are expressed as per mil (‰) and relative to the Vienna Standard Mean Oceanic Water (V-SMOW) standard. The standard deviation (SD) of the $\delta^{18}O$ values for repeated measurements of laboratory reference water samples was less than 0.07 ‰.

For Greenland and Svalbard samples, $\delta^{18}O$ 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 ±0.1‰. Isotopic compositions measured are reported in the common delta units relative to Vienna Standard Mean Ocean Water (VSMOW) isotopic reference standard.

2.4 Satellite data

SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric CHartographY) (Burrows et al., 1995; Bovensmann et al., 1999), GOME (Burrows et al., 1999) and GOME-2A (Global Ozone Monitoring Experiment-2A) (Callies et al., 2000) 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 is a scaled-up version of GOME, featuring additional NIR and SWIR channels and capable of observing the top-of-atmosphere upwelling radiation in nadir, limb and occultation viewing modes. GOME, SCIAMACHY and GOME-2 were part of the ESA ERS-2, ESA Envisat and ESA/EUMETSAT Metop series of satellite platforms, respectively. These fly or flew in sun-synchronous orbits in descending node having respective equator-crossing times of 10:30, 10:00 and 09:30. For the present data analysis, SCIAMACHY and GOME-2A UV-vis measurements from nadir geometry are used. Spatial pixel size is 30x60km² for SCIAMACHY and 40x80km² for GOME-2A. For SCIAMACHY, the effective pixel size is up to 60x240km² 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 (Begoin 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 (Theys et al., 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 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 higher 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 retrieval. Satellite observations of BrO and IO in Polar Regions yield knowledge about emission sources and their seasonal variations. This can then be used in the interpretation of the seasonality 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). An autumn peak in bromine is also observed in Fig. 3, which we primarily attribute to the deposition of boundary-layer bromine at the end of the Austral day. In the absence of daylight, photochemical production of BrO ceases and any BrO present in the boundary layer is quickly scavenged. Peaks at the end of autumn are highlighted by grey bars in Fig. 3, and are in good agreement with a late-autumn peak in boundary-layer bromine observed using ground-based DOAS measurements at Halley Station (Saiz-Lopez et al., 2007b). An alternate explanation is that the late-Autumn BrO peak arises from the formation of fresh sea ice prior to the start of Austral night, which can act as a fresh source of marine salts for ODEs and ensuing bromine enrichment. More detailed observations are required to distinguish between these possible explanations.

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, because of the need for sunlight in the activation of halogen chemistry. The SCIAMACHY sensor does not produce data during polar winter and is therefore not useful for the validation of 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). Frieß et al., (2010) have observed a similar pattern of iodine seasonality in snowpack at coastal Neumayer station, attributing summer concentrations of boundary layer iodine to photochemistry-induced remobilization of iodine from the snowpack. The presence of identical seasonality in Neumayer surface snow and Law Dome ice confirms that the winter peaks of iodine are deposition-related and do not result from post-depositional remobilization. Our results confirm the findings of Frieß et al., (2010), that iodine is lost from Law Dome snow due to photochemical IO recycling in the snowpack that ceases 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. This explanation does not account for the absence of an IO peak in the ice record at the end of autumn (as is observed for BrO), nor does it explain how IO is deposited in Antarctic winter strata. Such questions can only be resolved by further investigation through sampling of Antarctic snow and aerosols as well as chemical transport modelling. ~~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, 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 ng g^{-1}. In the following two years (1913-1914) Br enrichment is somewhat lower (3 to 5) while iodine concentrations decrease below 0.1 ng g^{-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 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 ice 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 present ~~preserved~~ and possibly enhanced by repeated emission and enrichment in the presence of sunlight. The seasonal variability of bromine and iodine emission sources has been identified but further study is required to quantify accurately the amount of atmospheric bromine retained in summer snow strata, as well as the amount of iodine retained in winter snow strata. A dedicated year-round aerosol collection effort, combined with chemical transport modelling, offers the best likelihood of advancing the current state of knowledge regarding polar halogens.

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Figures

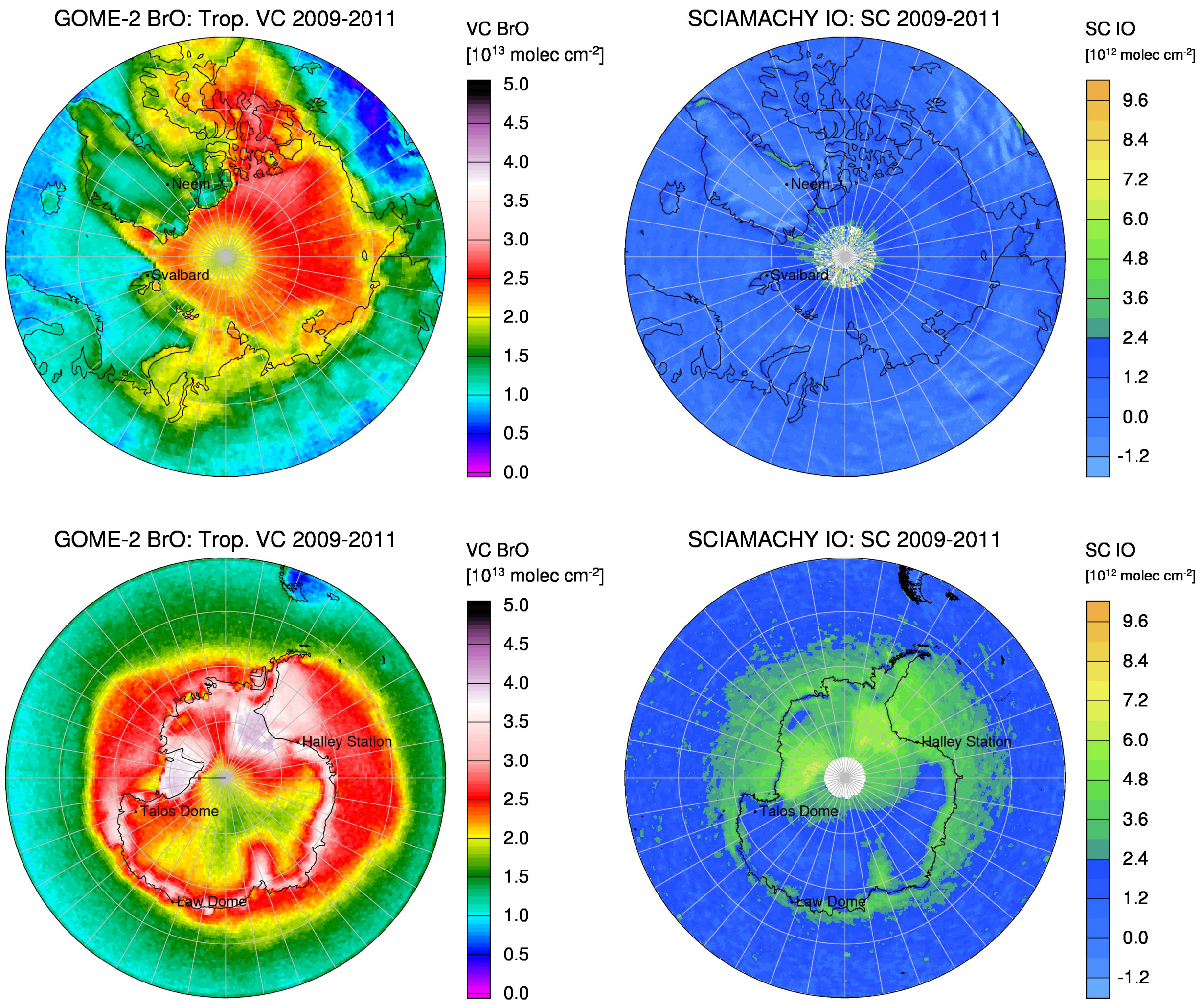

Figure 1. Average atmospheric column amounts of BrO and IO in Antarctica and the Arctic between 2009 and 2011. Bromine and iodine concentrations are greatest above the Antarctic ice shelves and along the coast. In the Arctic, iodine concentrations are near the limit of detection by satellite. Sampling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

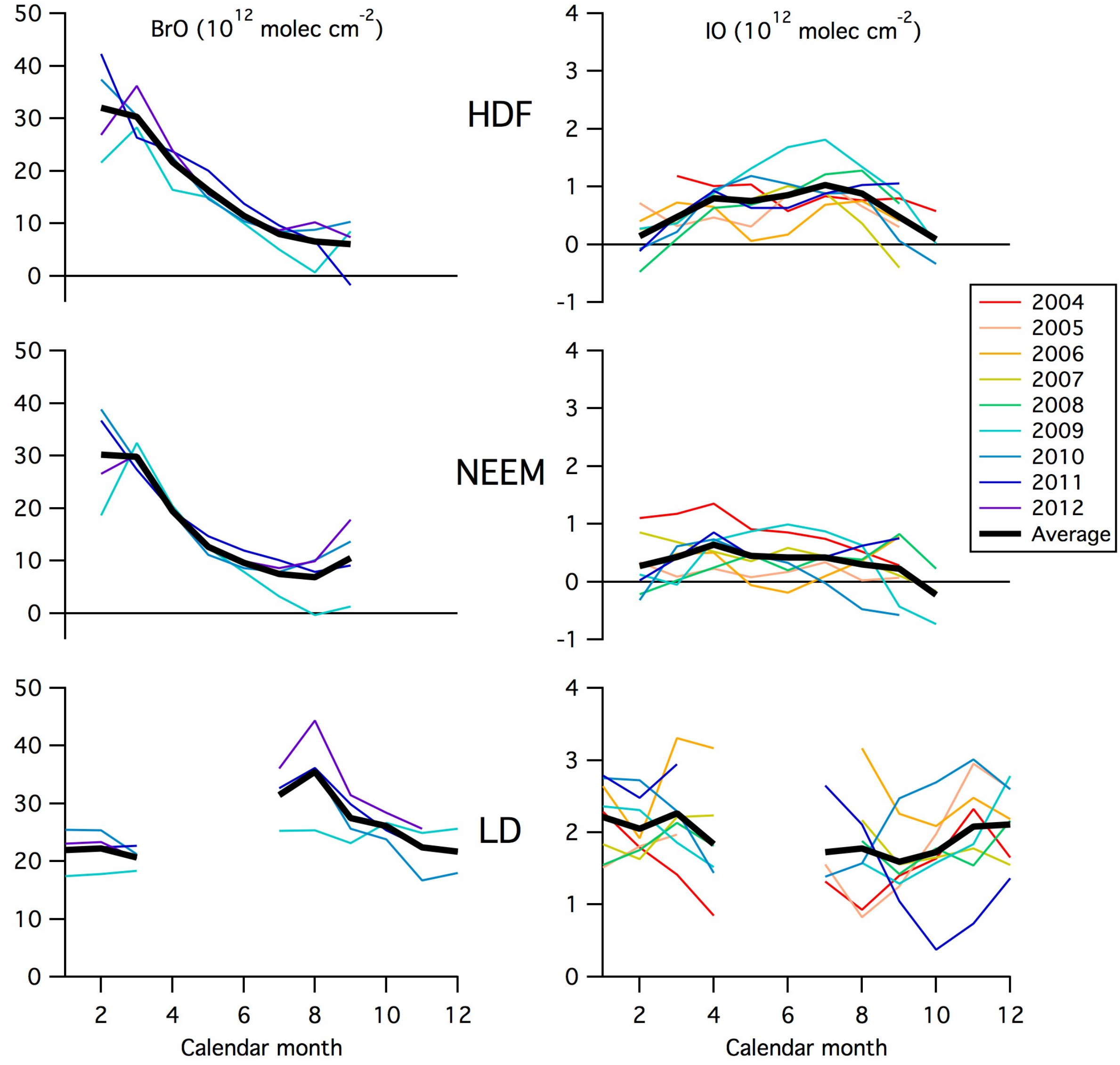

Figure 2. Averaged monthly atmospheric column concentrations for BrO (left column) and IO (right column) for the sampling sites mentioned in the text. The lines show 3-month seasonal running means. Holtedahlfonna (HDF) is in Svalbard, NEEM is in Greenland and Law Dome (LD) is in Antarctica.

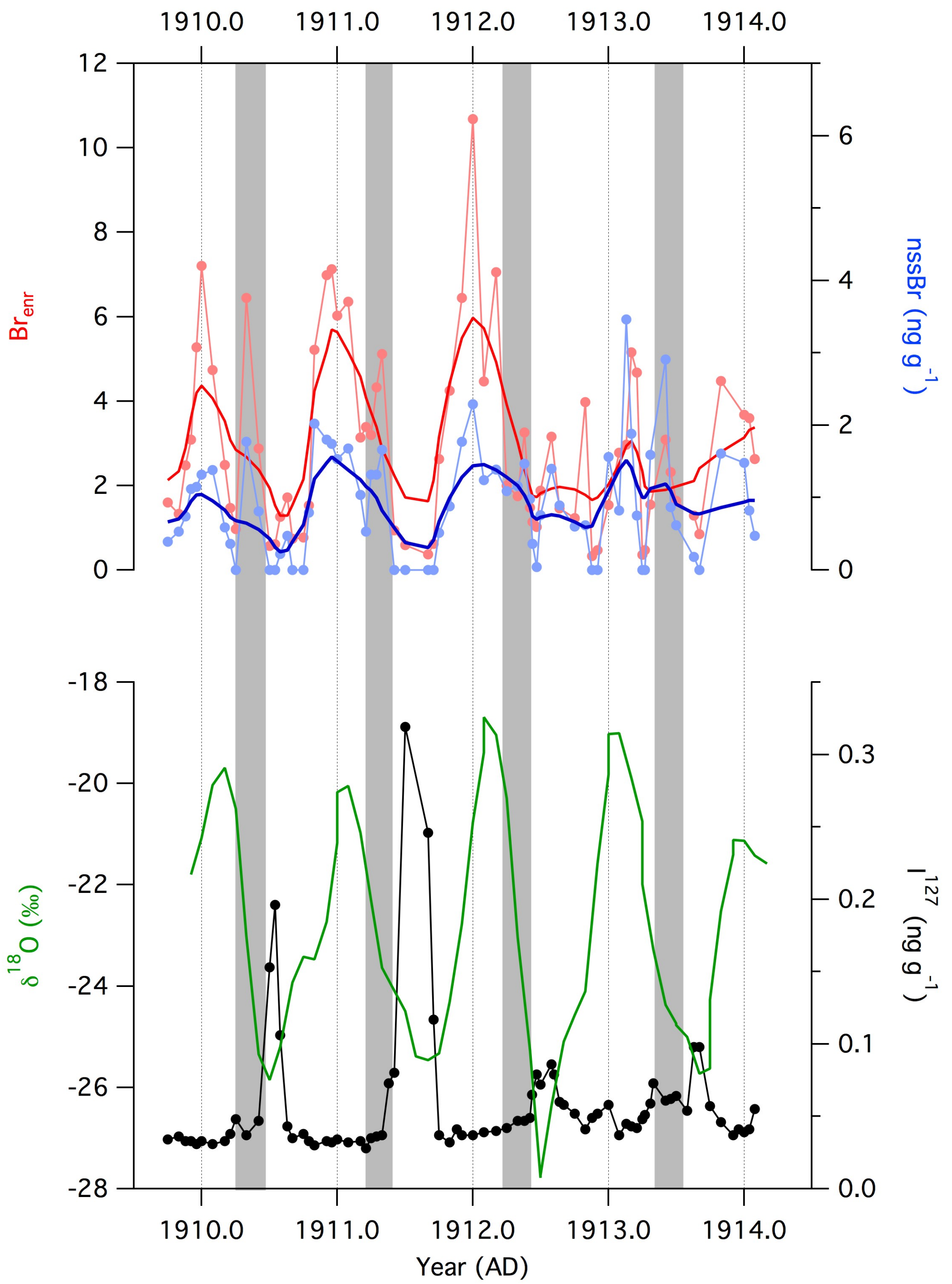

Figure 3. Seasonal variability in bromine and iodine is observed in the coastal East Antarctica Law Dome ice core. Bromine enrichment relative to seawater Br/Na mass values (Br$_{enr}$, red) show the same trend as non-sea salt bromine concentrations (nssBr, blue). For both data sets, individual data (circles) and an 11-point binomial smoothing (thick lines) are shown. Iodine concentration seasonality (black points) is clearly observed with respect to δ^{18}O isotope ratios (green). Vertical grey bars highlight the presence of a late-autumn peak in nssBr and Br$_{enr}$.

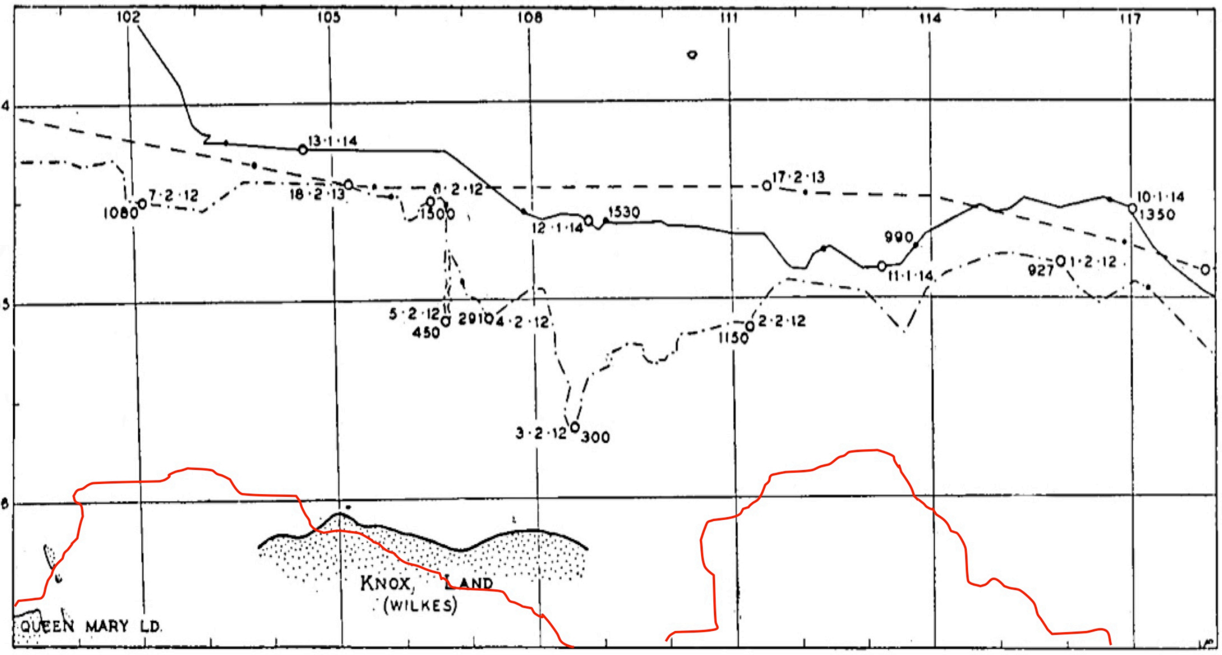

Figure 4. Tracks of the Australasian Antarctic Expedition ship *Aurora* between Adelie Land and Queen Mary Land during the years of the expedition (1911 to 1914) and observations of the Antarctic coastline. The correct location of the Antarctic coastline has been added in red. Image modified from the expedition report under Commonwealth Copyright permission.

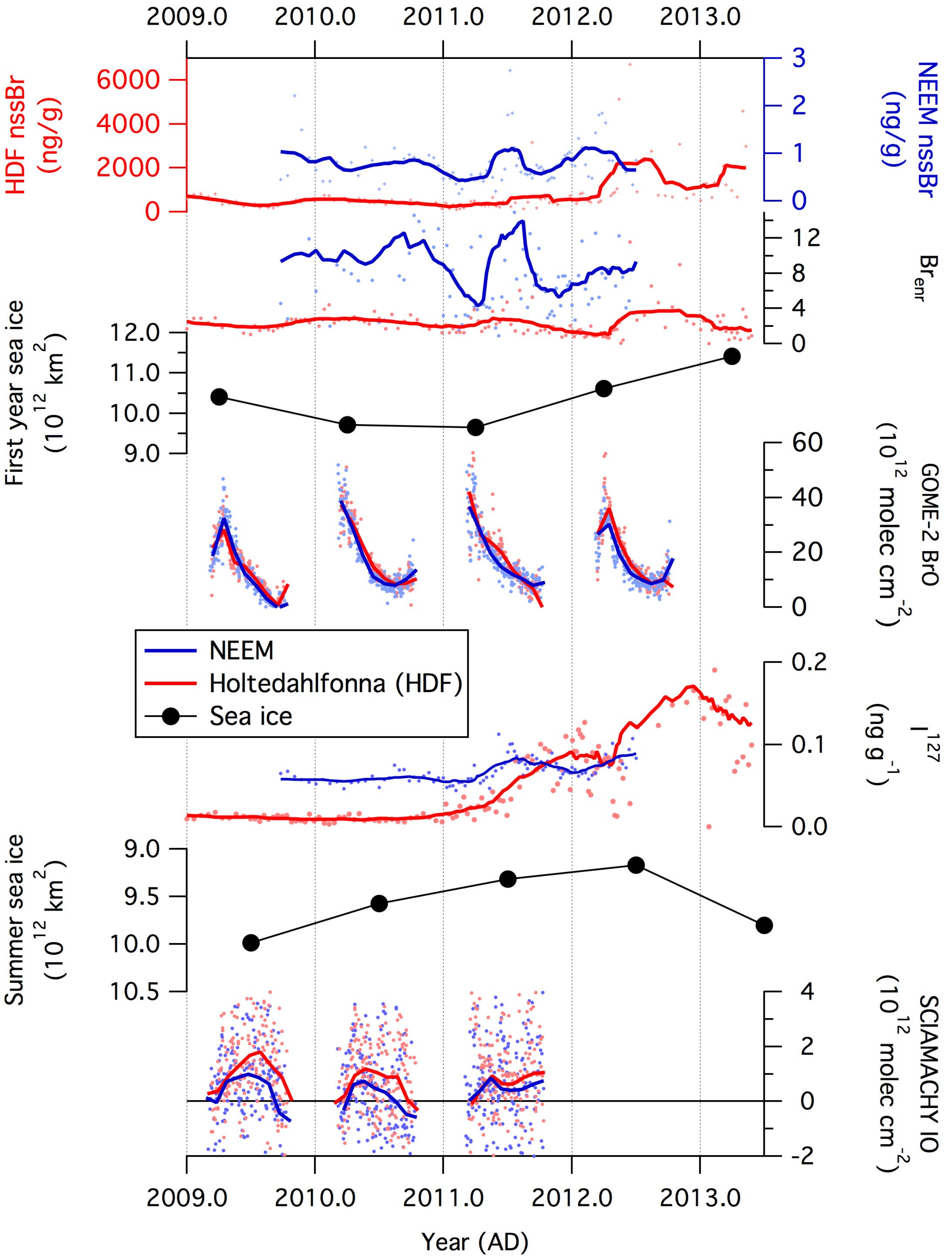

Figure 5. Halogens in the Arctic atmosphere and surface snow compared to sea ice parameters from 2009 to 2013. For all data series, measurements corresponding to the NEEM site (Northwest Greenland) are shown in blue, whereas measurements corresponding to

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), non-sea salt bromine (nssBr) 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.