Author comment on

Review of Bromine, iodine and sodium in surface snow along the 2013 Talos Dome – GV7 traverse (Northern Victoria Land, East Antarctica)

Anonymous Referee #3

We would like to thank Referee 3 for the review and the constructive criticism to the points that have been questioned. We reply to them and made the requested modifications. We acknowledge that an error was found in calculating the sea ice area, this has now been corrected. The introduction has been revised and almost all the suggested references have been added. The nssBr (non-sea-salt bromine) variability is not shown in the plots.

This paper scrutinizes the seasonal cycles of sodium, bromine, and iodine in 7 shallow cores (2 m long spanning the 2010-2014 years) drilled in East Antarctica. The data are discussed with respect to sea-ice halogen sources. Data on bromine and iodine in snow and ice are very welcome since they are still rather rare and are potentially interesting for a better understanding of the halogen chemistry at high southern latitudes in the past, for instance. However, major revisions of the manuscript are needed before I can recommend publication. The first major problem is that there are too many statements in the text that are not correct or oversimplified. Also the problem is that the manuscript totally ignores reveral relevant atmospheric studies conducted in Antarctica. Finally, in the discussion of data (figures 4 to 7) it would be nice to show not only the EF values but also the excess bromine relative to sodium with respect to seawater (or sea-salt aerosol) composition (see below).

Line 38-51: You should better explain to the readers how the examination of the bromine enrichment possibly helps to reconstruct sea-ice extent? Several atmospheric studies showed that not only sea-ice related processes (that are still not fully understood) but also open-ocean sea-salt emissions are important for the bromine chemistry (please cite Sander et al., 2003; Yang et al., 2005).

We acknowledge the presence of open-ocean sources and the related model studies. The 'open-ocean emissions' are now added (along with the references) to the text, however we point out that sea ice is a necessary source for bromine recycling leading to the BrO concentrations observed from satellites and seasonality of bromine (and br enrichment) peaks in ice core records in springtime. The importance of sea ice for bromine recycling is demonstrated in the chemical transport model results presented in Spolaor et al., 2016b. In addition, a more recent paper by Yang et al., 2008 - Sea salt aerosol production and bromine release: Role of snow on sea ice, indicates "that the importance of blowing snow (on sea ice) can be more than an order of magnitude larger than sea salt aerosol production rates from the ocean under typical weather conditions". We therefore also included this reference (being the same author).

The part related to the use of bromine enrichment has been made more clear:

"Although the ocean is the main reservoir of sea salts, various condensed phases of high salinity are found on young sea ice surfaces. During seawater freezing, brine is separated from the frozen water matrix and expulsion processes lead to both upward and downward movement, as temperature decreases (Abbatt et al., 2012). Therefore, high salinity brine, frost flowers and salty blowing snow make newly formed sea ice surfaces a highly efficient substrate for inorganic halides and for their activation and release in the atmosphere (Saiz-Lopez et al., 2012b, Yang et al., 2008). Some studies have pointed out the role of open-water sea salts as a significant bromine source (Yang et al., 2005; Sander et al., 2003).

Reactive halogen species are involved in cyclic reactions between halogen radicals, their oxides and ozone. Reactions R1-3 show the main reactions for bromine. Atomic bromine radicals result from photolysis of molecular bromine, leading to formation of bromine oxide, BrO, through the uptake of ozone:

$$Br_2 \rightarrow 2Br \qquad (1)$$

$$Br + O_3 \rightarrow BrO + O_2 \qquad (2)$$

$$BrO + BrO \rightarrow Br + Br + O_2 \qquad (3)$$

Self reaction of BrO may form 2 bromine atoms (85%) or a Br_2 molecule (15%) which is readily photolyzed. The mechanism has a catalytic behavior that destroys ozone.

High concentrations of tropospheric vertical columns of BrO and IO have been confirmed by SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY) satellite observations over Antarctic sea ice (Schönhardt et al., 2012).

Bromine can then be recycled and re-emitted from halogen-rich condensed phases (such as sea salt aerosol or other saline solutions) or from sea ice surfaces (Pratt et al., 2013), leading to an exponential increase of bromine in the gas phase (Vogt et al., 1996). Such reactions, known as bromine explosions, lead to enhanced bromine in the atmosphere. A recent 1D chemistry model simulation predicted an increase of bromine deposition on surface snowpack after 24/48 hours of recycling over first year sea ice (Spolaor et al., 2016b). Bromine enrichment in snow (compared to sodium, relative to sea water) has therefore been recently used to reconstruct sea ice variability from ice cores both in the Antarctic and Arctic regions (Spolaor et al., 2013a, 2016b). “

Also relevant to your work is the recent atmospheric study conducted (JGR, 2016) at the coast and inland in the same East Antarctic region. In this study, both surface data and satellite observations indicate that in this region whereas the bromine chemistry is indeed maximum in spring, there is only a factor of two differences or less between spring and summer (suggesting again the importance of open ocean emissions in summer).
We believe we have addressed this topic through the previous comment.
The Legrand et al (2016) reference has been added in section 3.2.

This JGR paper also clearly showed that gaseous bromine species (that are water soluble and will be trapped in snow) largely dominate bromine aerosol. These gaseous species are likely responsible for the observed bromine enrichment in snow. Their atmospheric lifetime is far longer than the aerosol one due to a fast recycling on various surfaces (aerosol, snow grain). Therefore I have difficulty to understand the relationship between bromine enrichment in snow and the sea-ice extent ?
We point out that both gas phase and the aerosol are strongly related to sea ice. As they deposit inland, enrichment of bromine with respect to sodium would signal greater sea ice (if depleted aerosol doesn’t dominate the gas phase, see a similar comment made by Referee1). Again, the model study in Spolaor 2016b shows enhancement of bromine as the air parcel travels on FYSI.

For instance, whereas you mentioned in line 64 the noise introduced by transport in using sodium to reconstruct sea-ice, you have also to mention that since the bromine enrichment is related to gaseous species, the non irreversible trapping of the bromine species in snow would strongly handicap their use as proxy of sea-ice: please comment and cite Thomas et al. (2011).
We agree with the Referee on the importance of bromine reemission from the snowpack. We point out that the maxima of bromine in Spring observed from the studies on

seasonality (this work and others, including Legrand 2016) suggest that bromine is not re-emitted significantly (if so, winter concentration would be higher, as for iodine). How much bromine is retained by spring/summer layers was the question addressed by Thomas 2011 and Dibb 2010 and they suggested snowpack reemission in Greenland, Summit. The recent paper by Legrand 2016 found that in (East) Antarctica inorganic bromine snowpack reemission is not significant, by combination of model-snowpit bromide measurements. The topic is now addressed in the introduction, including the related works.

"The stability of bromine in the snowpack was investigated at Summit, Greenland (Thomas et al. (2011), to explain the observed mixing ratios of BrO. Measurements in East Antarctica (Legrand et al., 2016) revealed that snowpack cannot account for the observed gas-phase inorganic bromine in the atmosphere. "

Sander, R., et al. (2003), Inorganic bromine in the marine boundary layer: A critical review, Atmos. Chem. Phys., 3, 1301–1336, doi:10.5194/acp-3-1301-2003.

Yang, X., R. A. Cox, N. J. Warwick, J. A. Pyle, G. D. Carver, F. M. O'Connor, and N. H. Savage (2005), Tropospheric bromine chemistry and its impacts on ozone: A model study, J. Geophys. Res., 110, D23311, doi:10.1029/2005JD006244.

Legrand, M., X. Yang, S. Preunkert, and N. Theys (2016), Year-round records of sea salt, gaseous, and particulate inorganic bromine in the atmospheric boundary layer at coastal (Dumont d'Urville) and central (Concordia) East Antarctic sites, J. Geophys. Res. Atmos., 121, doi:10.1002/ 2015JD024066.

Thomas, J. L., J. Stutz, B. Lefer, L. G. Huey, K. Toyota, J. E. Dibb, and R. von Glasow (2011), Modeling chemistry in and above snow at Summit, Greenland-Part 1: Model description and results, Atmos. Chem. Phys., 11, 4899–4914, doi:10.5194/acp-11-4899-2011.

Line 57 : You should cite here the atmospheric study conducted by Grilli et al. (2013) that showed a less active iodine chemistry in East Antarctica compared to the case of west Antarctica (Saiz-Lopez et al., 2007). Such a difference should enhance the motivation to examine iodine in snow throughout Antarctica (west and East).
Grilli, R., M. Legrand, A. Kukui, G. Méjean, S. Preunkert, and D. Romanini, First investigations of IO, BrO, and NO_2 summer atmospheric levels at a coastal East Antarctic site using mode-locked cavity enhanced absorption spectroscopy, *Geophys. Res. Lett.*, 40, 1-6, doi:10.1002/grl.50154, 2013.
The reference has been added and the sentence has been rephrased:
"Grilli et al. (2013) have shown that ground based IO concentrations in Dumont d'Urville (Indian sector) were more than one order of magnitude lower than in the Atlantic sector (Halley station, Saiz-Lopez et al., 2007), consistent with greater sea ice in the latter."

Line 61-67 : As far as I know, the pioneering finding of a correlation between sea-ice and MSA in snow from Curran et al. (2003) was never clearly confirmed by more recent snow studies. Furthermore, several atmospheric studies reported no evidence of such a link at the decadal scale (Weller et al., 2011; Preunkert et al., 2007).
Weller, R., D. Wagenbach, M. Legrand, C. Elsässer, X. Tian-Kunze, and G. König-Langlo (2011), Continuous 25-years aerosol records at coastal Antarctica: Part 1. Inter-annual variability of ionic compounds and links to climate indices, Tellus, Ser. B, 63, 901–919, doi:10.1111/ j.1600-0889.2011.00542.x.

Preunkert, S., M. Legrand, B. Jourdain, C. Moulin, S. Belviso, N. Kasamatsu, M. Fukuchi, and T. Hirawake, Interannual variability of dimethylsulfide in air and seawater and its atmospheric oxidation by-products (methanesulfonate and sulfate) at Dumont d'Urville (Coastal Antarctica) (1999-2003), *J. Geophys. Res.*, 112, doi:10.1029/2006JD007585, 2007.

We agree and note that a paper currently in discussion with Climate of the Past addresses the issue of sea ice reconstructions from Law Dome (Vallelonga et al, http://www.clim-past-discuss.net/cp-2016-74/). Also, the suggested references have been added.

Line 68-71 : Why do you introduce a discussion on post-depositional effect here ? The existence of post-depositional effect would have no effect on decadal or centennial scales. Why "in particular Greenland" ? Please see and cite the recent work from Olivia Maselli (special issue in CP)

Maselli, O. J., Chellman, N. J., Grieman, M., Layman, L., McConnell, J. R., Pasteris, D., Rhodes, R. H., Saltzman, E., and Sigl, M.: Sea ice and pollution-modulated changes in Greenland ice core methanesulfonate and bromine, Clim. Past Discuss., doi:10.5194/cp-2016-49, accepted, 2016.

We don't completely agree with the Referee, as remobilization in the core can affect the stratigraphy in a non-unidirectional way. Therefore, the discussion on post-depositional effects in kept in the text.

"Greenland" has been removed, and the Maselli paper has been cited.

Line 179 : This number surprises me : 80% ? To what are related the missed (non sea-salt) sodium source that you consider to account for up to 20 % ? I don't think that the crustal source is large enough (at least for present-day climate), see and cite Weller et al. (2008).

Weller et al., Seasonal variability of crustal and marine trace elements in the aerosol at Neumayer station, Antarctica, Tellus 60B, 742-752, 2008.

We agree with the reviewer comment and therefore no crustal correction was applied to the total sodium concentration. But the reference is not added since it refers to measurements done at the Neumayer station, and not near the traverse location.

Line 201-204, please also cite the atmospheric study from Wagenbach et al. (1998)

Wagenbach, D., F. Ducroz, R. Mulvaney, L. Keck, A. Minikin, M. Legrand, J. S. Hall, and E. W. Wolff (1998), Sea-salt aerosol in coastal Antarctic regions, J. Geophys. Res., 103, 0,961–0,974, doi:10.1029/97JD01804.

The reference has been added.

Section 3.2: Please report excess bromine either as Br - 6.2 10^{-3}*Na (or with error calculation Br – 8 10^{-3}*Na in winter and use brome depletion factor in aerosol taken from Sander et al. 2003 or Legrand et al. 2016 for spring and summer).

The non-sea-salt bromine, nssBr has been calculated as [Br]-0.0062[Na] and reported in the new figures (new Fig. 4-5-6). Both Br_{enr} and nssBr show very similar patterns because they are complementary calculations of non-sea salt Br (one absolute, the other a ratio). As in the answer to Referee#1 the core Talos Dome has been removed and it is now shown in the supplementary material on a depth scale.

Line 288-292: Not sure that this is right: at least for bromine the homogeneity is also related to the atmospheric lifetime.

We agree with the Reviewer that the lifetime of the species affects the air-to-snow flux, and that BrO is not the species deposited on the snowpack. However, we believe that the inorganic bromine lifetime in the gas-phase (predicted by models at least 5 days) to be much longer lived than the maximum distance here involved. To support our hypothesis, we observe bromine enrichment well above sea water ratio (>1) all across the traverse area. Therefore, we consider BrO concentration indicative of bromine recycling.

Note that both the BrO concentration spatial distribution from satellites and the calculated fluxes in the snow are annual averages.

Below the new figures:

Figure 1. (a) Schematic map of the traverse area and coring sites, marked with stars. The cores were drilled between Nov 20th 2013 and Jan 8th 2014 (early austral summer). (b) Maximum (left, August 2011) and minimum (right, January 2010) sea ice concentrations in the 130°E-170°W sector for the 2010-2013 time interval covered by the core records (NSIDC data from Meier et al., 2013). The traverse location is marked with an ellipse.

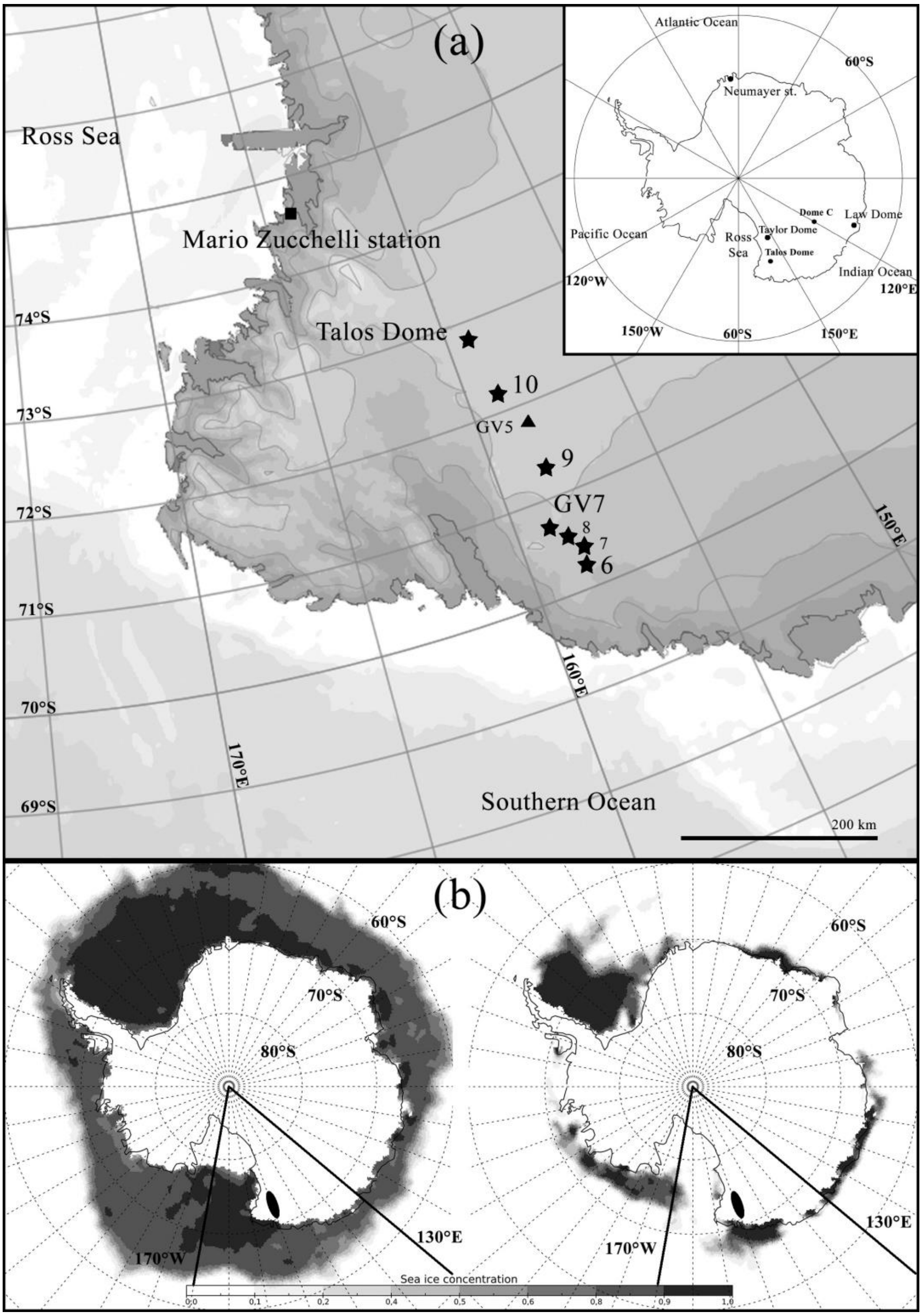


Figure 3. Distribution of bromine enrichment values within cores TD, 10, 9 (blue) and GV7, 8, 7, 6 (red). The dashed line indicates the seawater value (Br_{enr} = 1).

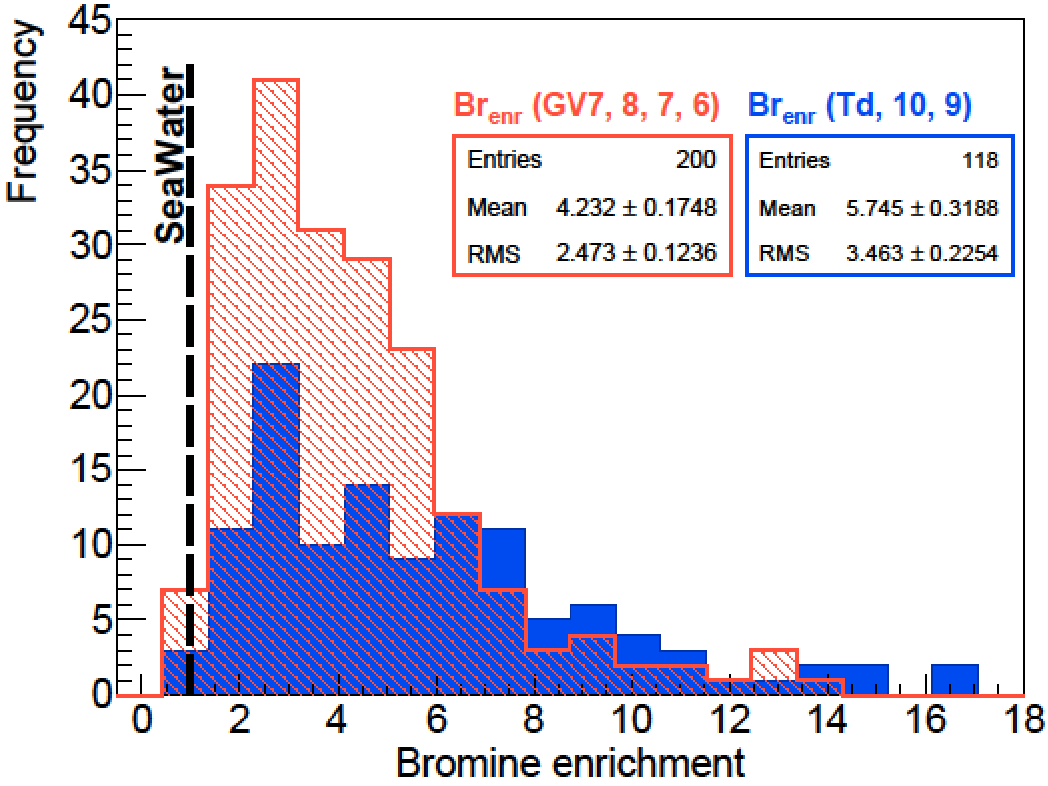


Figure 4. Variability of δ^{18}O (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in cores 10 (left) and 9 (right). Thick lines represent 3-month running means of the raw data (circles).

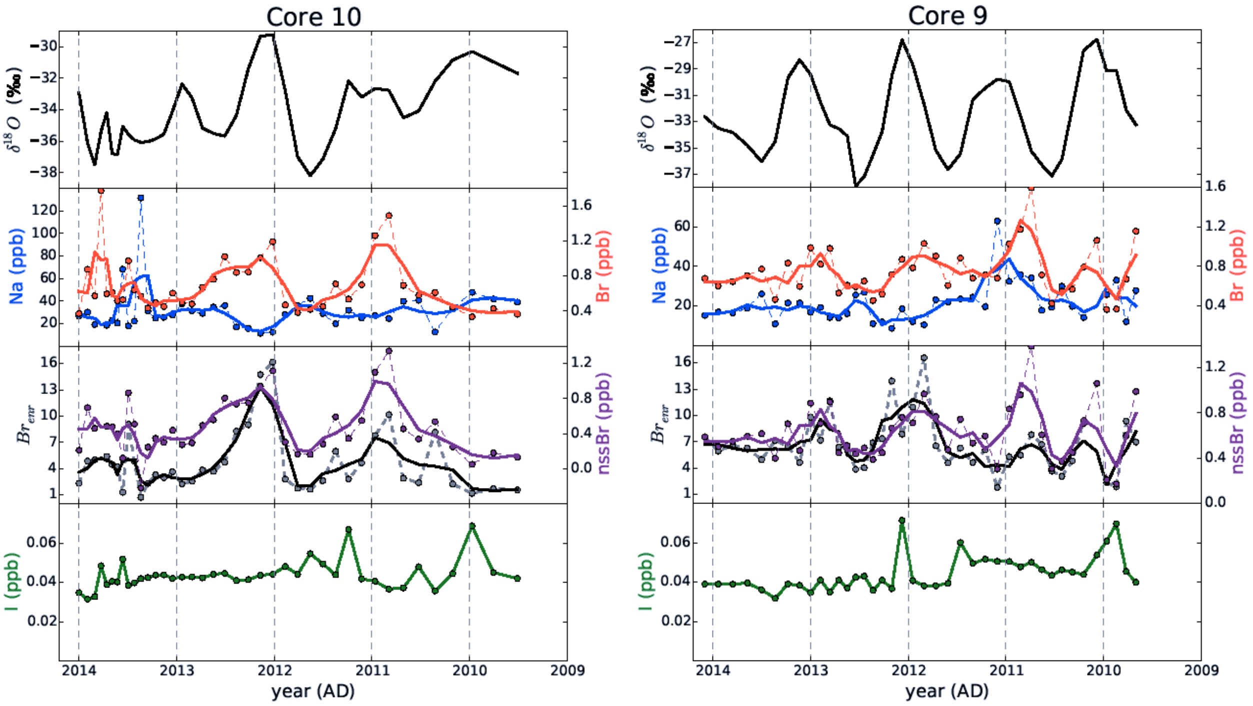


Figure 5. Variability of δ^{18}O (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in cores GV7 (left) and 8 (right). Thick lines represent 3-month running means of the raw data (circles).

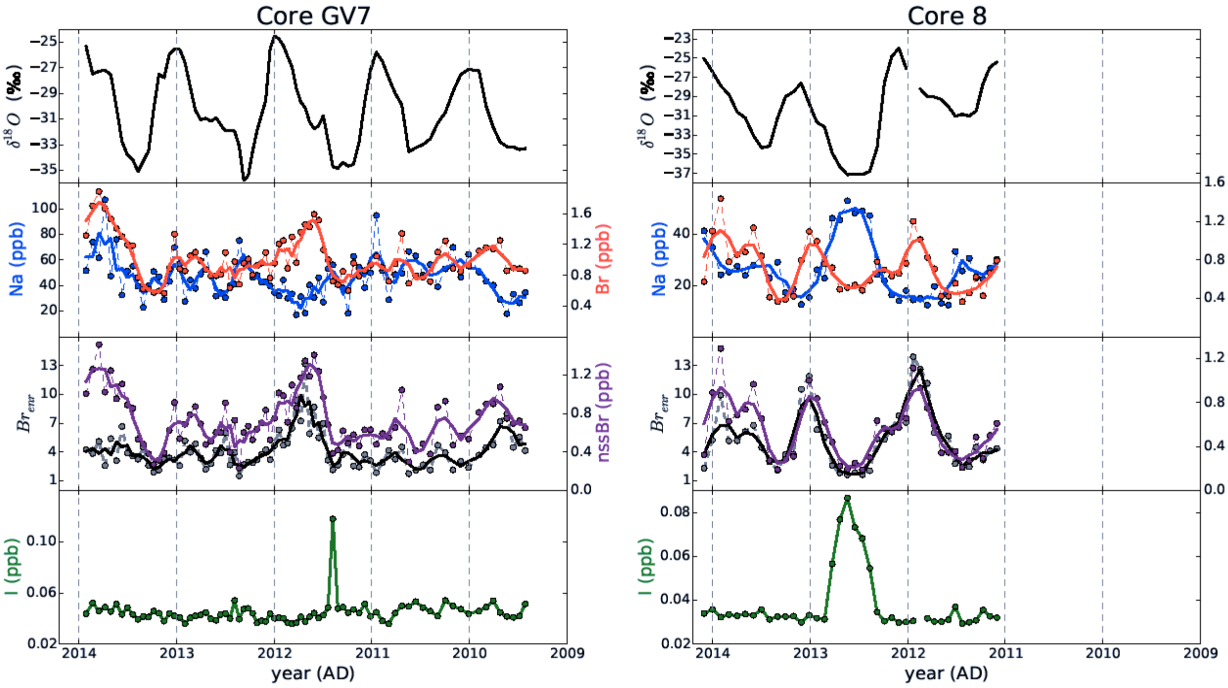


Figure 6. Variability of δ^{18}O (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in cores 7 (left) and 6 (right). Thick lines represent 3-month running means of the raw data (circles).

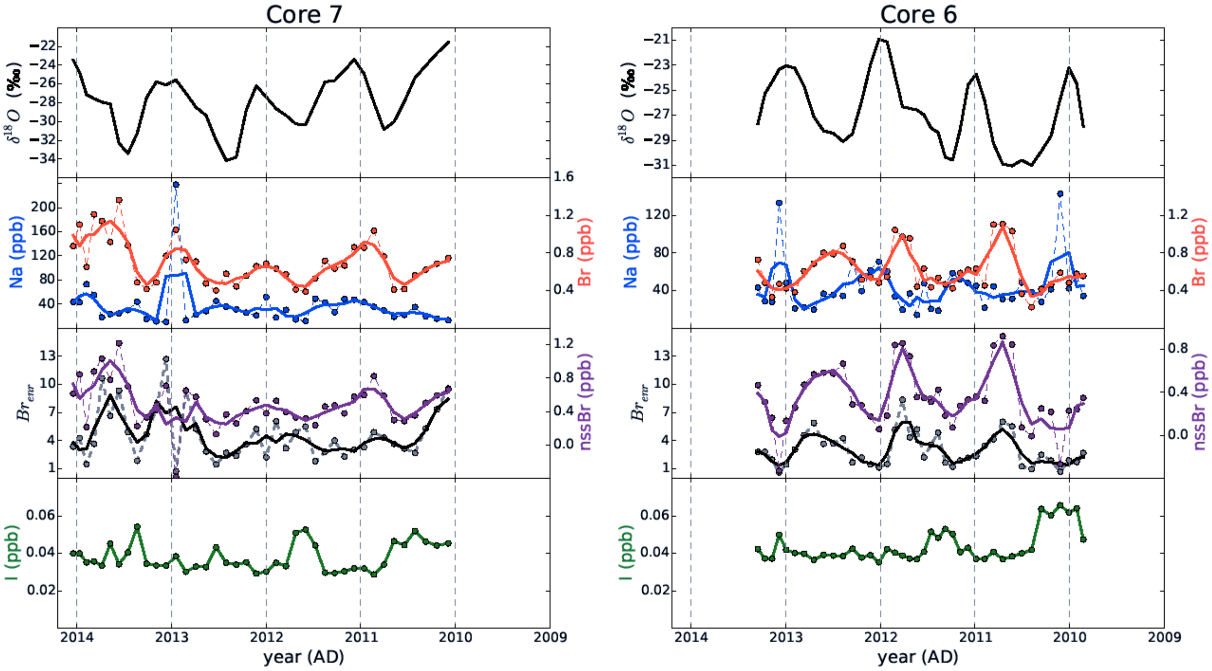


Figure 7. (a) Monthly values of sea ice area (blue) within the 130°E-170°W sector from 2010 to 2013 (±1σ, month variability) and daily average (24 hours) total downwelling spectral irradiance (red), calculated using the TUV model at 71° S, 158° E. Each irradiance calculation was set the 15th day of each month, in 2012. **(b)** Seasonality of annual bromine enrichment along the traverse: the monthly trend shows a seasonal feature with maximum in Spring. Each line refers to a core of the transect (±1σ, shaded blue area). The month averages are displayed in black. The systematic uncertainties associated to the dating are shown as verticals error bars. The magenta band represents the product distribution of normalized sea ice area and insolation, expressed in annual percentage. **(c)** Monthly sea ice area values (blue) from 2010 to 2013, with annual values of FYSI (red) and averaged bromine enrichment (black).

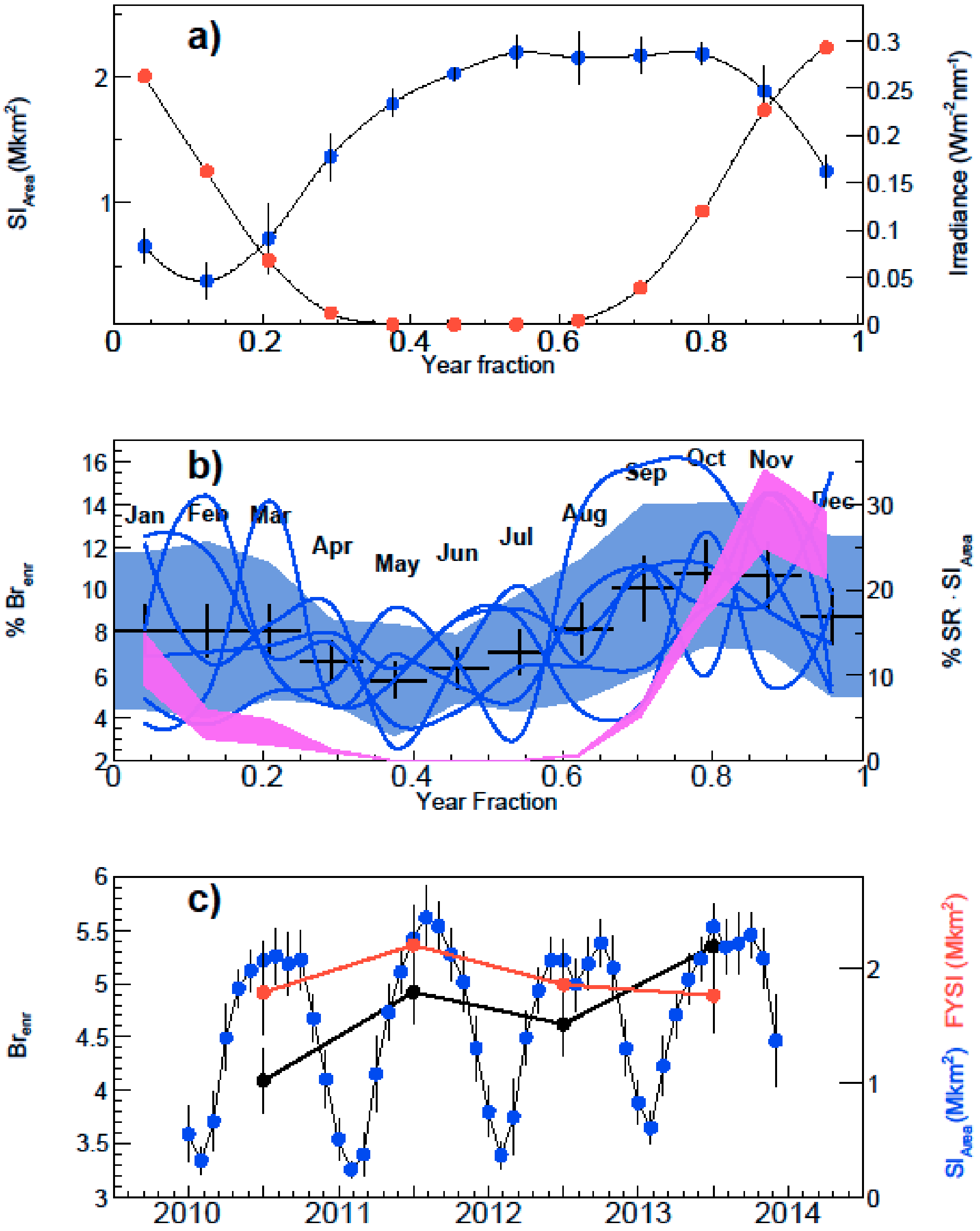
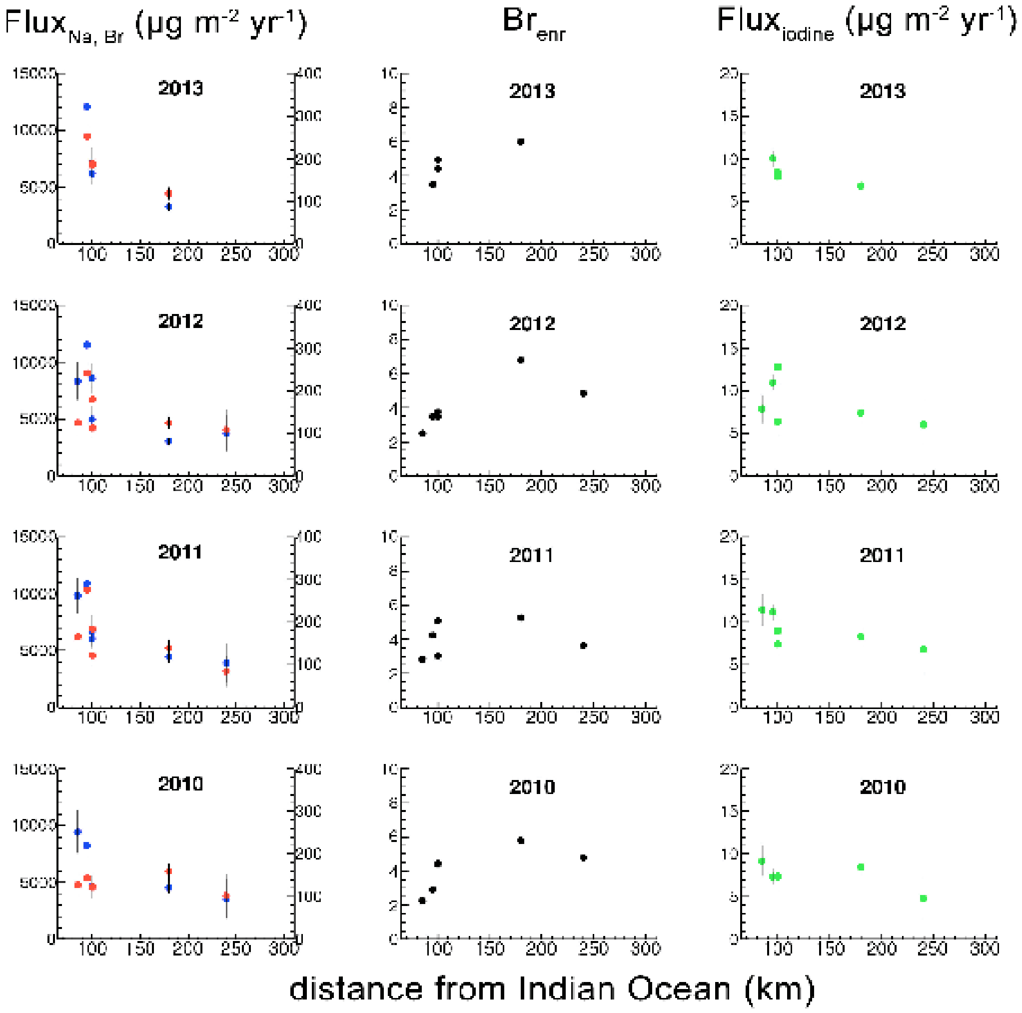


Figure 9. Mean annual fluxes of sodium (blue, left axes), bromine (red, right axes), iodine (green) and bromine enrichment values (black), as a function of distance from the Indian Ocean. Each dot represents a location along the traverse.



Supplementary material

The following figure shows the measurements related to the Talos Dome core.

Figure. Variability of δ^{18}O (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in the Talos Dome core on a depth scale. Thick lines represent 15 cm running means of the raw data (circles).