Author comment on

Interactive comment on "Bromine, iodine and sodium in surface snow along the 2013 Talos Dome – GV7 traverse (Northern Victoria Land, East Antarctica)" by Niccolò Maffezzoli et al.

Anonymous Referee #1

We would like to thank Referee 1 for the review and for the helpful comments that motivate the research on this very current topic. We have responded to the comments and made the requested modifications. Particularly, the link with FYSI has been removed from the abstract and conclusion, and the transport processes issue influencing bromine and sodium (and bromine enrichment) deposition has been addressed (last figure). We acknowledge that an error was found in calculating the sea ice area, this have now been corrected.

It is well-established that the sea ice zone is a hotspot for Br (and with less certainty, I) chemistry. This has been shown by the high concentrations of BrO observed from satellite data in spring, and from ground-based data. The mechanism is understood to be that inorganic Br is activated from salty material (sea ice or aerosol). With this in mind, Spolaor et al (2013b in the present manuscript) found that Br was enriched in interglacial ice and depleted in glacial ice at Talos Dome. They proposed that this resulted from the halogen chemistry over sea ice, and that the enrichment or depletion might be used as an index of sea ice extent in the past. Their mechanism relied on their suggestion that Br/Na would reduce with distance from the sea ice edge, because the enriched material (as gas phase HBr) was deposited faster than the depleted (NaBr) sea salt aerosol. This was a surprising suggestion because previous work (Simpson et al, 2005) had suggested exactly the opposite (for the Arctic): that inland snow would be enhanced due to a longer lifetime of HBr. Clearly it is impossible to consider Br as a sea ice proxy until at least a reasonable understanding of the mechanism leading to temporal changes is understood, so studies attempting to delucidate this are very welcome. The present paper is aimed at doing this, by making a spatial transect (including seasonal information) of Na, Br and I in a part of East Antarctica. Unfortunately the location of the traverse is particularly badly chosen for such a study, because the sites sit between two marine areas, the Ross Sea and the main Southern Ocean. This has the effect that sites that are further from one potential source are nearer to the other, so that even if the data showed very clear trends, opposing interpretations would have been possible. As it happens there is little clarity in the data, which is not entirely the authors' fault but does mean that this is a paper which advances knowledge only incrementally. It is probably justified to consider publishing it after significant changes have been made, if only to indicate the complexity of the problem, and to show how premature it is to consider Br as a sea ice proxy until far more detailed and well-designed experiments and sampling campaigns have been carried out.
The paper itself is relatively short but with a very high number of tables and figures that really don't add to it, so among other things I would recommend losing some of these in the next version. There are also some unjustified interpretations (such as that in the abstract regarding Fig 9), which definitely must be modified.

Comments:
Abstract line 27-28. The last sentence is not justified. This is based on Fig 9c, with 4 data points. No statistics are given but I see no correlation at all, and a rough attempt to plot the data gave an rˆ2 very close to zero, utterly insignificant.
The sentence has been removed.

Sections 1 and 2 are generally OK, with two minor comments:
Line 36, remove the word layer. There is a "layer" of ozone in the stratosphere but there is no layer in the troposphere.
The term "layer" has been removed.

Line 68. The Rothlisberger article in a newsletter is not a good reference here. Better would be reference 3 or one of the other papers by Abram.
Röthlisberger reference has been replaced by Abram et al., 2013.

Line 162-167. While I agree that, taking old and new data into account, there is a tendency (as one would expect) of lower accumulation rates as we move further from the ocean, obviously this is somewhat undermined by the high value of 185 kg mˆ-2 aˆ-1 at TD. In the table the authors try to mitigate this by putting asterisks on "uncertain years", saying that their value is uncertain because the isotope signal is less clear. I don't think Fig 2 really justifies this – the least clear assignment at TD (2012) is at least as obvious as the one for 2011 at site 8 for example, and yet this has no asterisk against it in Table 2. I think a better way to handle this would be to remove the asterisks from the table, but to say that the inconsistency between the accumulation rate derived from the core at TD and that derived from the stake farm and previous measurements suggests that the isotopic assignments of years may be incorrect at TD, and that the profile contains more years than have been assigned.
We agree with the Referee comment with respect to Talos Dome. Therefore, the TD core is not used any further in the flux calculations nor in the %Brenr deposition. Only the profile is shown (on a depth scale) in the supplementary. The asterisks have been removed.
The sentence has been rephrased accordingly:
"The inconsistency between the accumulation rates derived from the core and those derived from the stake farm and previous measurements suggests that the isotopic assignments of years may be incorrect at this site, and that the profile contains more years than have been assigned. This core therefore is not used in further calculations. The fluxes of deposition of sodium, bromine and iodine in the other cores along the transect are calculated using the accumulation rates from this work."

Table 3 is unnecessary. Most of the information is anyway given in the text, but anyway a table like this that mixes different sites has no value that I can see. The table should be removed.
The table has been removed.

Line 189. This sentence is not really correct. Either enrichment or depletion can indicate that the reactions, believed to be focussed on sea ice, have taken place (not just enrichment). In fact the reaction (1) as shown leads only to a depletion of Br from the sea ice. It is only if the Br2 is eventually converted back to HBr that enrichment can occur, if more of this end product gas phase HBr is deposited nullifying the depletion in the aerosol phase. In addition, there are other ways to get such enrichment, as we know from the case of Cl, which is enriched or depleted compared to sodium due simply to production of HCl from the reaction between sulfuric or nitric acid with sea salt (e.g. H2SO4+2NaCl-> Na2SO4 + 2 HCl). A sentence that would be defendible would be "Therefore sea ice presence should lead to Br enrichment (after conversion of activated gas phase Br back to HBr) or depletion, depending whether deposition is dominated by the depleted sea salt aerosol or by the enriched gas phase HBr."
The sentence has been rephrased according to the Referee suggestion, with which we agree. The $Br(g) + HO_2(aq) \rightarrow HBr(g) + O_2$ reaction has been added.

Fig. 3 is OK, but I would have found it more useful if you had shown the distribution for individual sites or groups of sites. As a suggestion, you could show one distribution for sites GV7/8/7/6 (less than 100 km from ocean) and another distribution for the other sites.
Fig. 3 has been modified according to the Reviewer suggestion. The new figure now shows the two distributions of (TD, 10, 9) and (GV7, 8, 7, 6).

Fig 4, TD plot is obviously a problem, since you seem to believe that (Table 2) the years may be misassigned. This undermines your interpretations for this site. I'm afraid you can't have it both ways – either the TD accumulation is really high in which case the statements made about how accumulation varies with distance are not supported, or it is not in which case the year assignments shown in the TD section of this figure are wrong.

We agree on the Reviewer on this point. The Talos Dome core is not used in the following calculations (%Brenr and fluxes) and the variability figure (Fig. 4) has been removed. It is still shown in the supplementary material but plotted on a depth scale.

Fig 8 is really confusing because the map is upside down compared to that used in Fig. 1. In any case a similar figure is shown in Fig 1b. therefore please remove Fig 8, simply incorporating the additional information (basically the red box showing the 130-190E band) into Fig 1b.
We agree with the Referee on the comment. Fig. 8 has been removed and incorporated in Fig1 panel b, which now shows the sea ice concentrations (max and min) and the considered longitude sector. Note that the 'left' longitude sector has been rewritten as 170°W instead of 190°E. Some lat/long values have also been added to both panels as suggested by Referee2.

Line 215 – why is insolation from a site on the opposite side of Antarctica shown here? It is not even at the latitude of the sites here. Furthermore total solar radiation is very unlikely to be relevant, rather it is the radiation at the UV or near-UV wavelengths that might promote the relevant photochemistry. I suggest using a code such as TUV to calculate available radiation at relevant wavelengths.
We agree with the Referee comment and Fig9a+b have been modified accordingly (now Fig 7). The daily average total downwelling spectral irradiance has been calculated using Tropospheric Ultraviolet and Visible Radiation Model (TUV), as suggested, in the [300,500] nm interval. The choice on the wavelength interval was made based on [Saiz-Lopez et al.: Measurements and modelling of I2, IO, OIO, BrO and NO3 in the mid-latitude marine boundary layer, (2006), fig 12]. The daily averages values were calculated for year 2012 (15^{th} day, representative for the month). The model calculations were set at 71° S, 158° E. The normalized trend (Fig 7b, magenta) is very similar and thus the interpretation of combined effects of sea ice and radiation triggering photochemistry.

Line 205, and Fig 9b. It's hard from Figs 4-7 to really see the seasonality, which you describe as max in late spring/summer for Br. Since you must have calculated it to get to Fig 9b, please add a plot of this sort for each site so we can see how consistent the seasonality is at different sites. This could be shown as individual lines underlying the error band in Fig 9b for example, or as a separate panel if this is less confusing.
The seasonality at the different sites are now shown in Fig. 7 (having excluded Talos Dome and year 2013 in core 10, consistent with the previous comments). The blue band shows 1sigma variability of the different cores.

Line 221-3. The comparison of the seasonality with the product of radiation and sea ice extent is interesting but it does not "demonstrate" the dependency of Br enrichment on their combined effect, rather it is "consistent with" the idea that there is such a dependency. Please adjust the text.
The sentence has been rephrased as: "Such comparison suggests that the combined effect of sea ice and insolation drives the seasonality of bromine enrichment."

Lines 225-7. As in the abstract, the correct characterisation of Fig 9c is that, with only 4 years of data, no relationship can be discerned. It is not scientific to say that there is a relationship for 3 years and not for the fourth – statistically this means there is no relationship. You just have to admit that there are not enough data here to know whether Br_enr can be used as an indicator of FYSI. In fact (and related to the next comment) nothing you have written here says why you would expect the enrichment to be related to the FYSI area; what mechanism are you envisaging? If, as in the earlier Spolaor paper, it is via distance from the ice edge (through whatever process) then this should be somewhat reflected in the difference between sites, hence my next comment.
The sentence has been removed as in the abstract/conclusion, but the plot has been left. In the introduction, we now better explained the mechanism linking bromine enrichment to FYSI area. The idea is

that more first year sea ice would lead to bromine enrichment over its surfaces. Depletion can be observed at the deposition site if depleted aerosol dominates gas phase HBr or if HBr is deposited more rapidly.
At glacial/interglacial timescales, the situation is much different than looking at present conditions, since the source (FYSI) is much further away in the glacial (on the basis of more extensive MYSI zone). The interpretation of a glacial/interglacial time serie than relies on a combined effect of source (FYSI/MYSI) and transport processes. The paper Spolaor et al. Canadian Arctic sea ice reconstructed from bromine in the Greenland NEEM ice core, Sci. Rep., 6, doi:10.1038/srep33925, 2016b addresses the topic at such timescales. Unfortunately, it was not possible to test transport mechanisms with this traverse data, since as we move further from one source we approach the other one (see next comment).
The traverse from MZS to Dome C will surely provide more clues on this topic.

Section 3.3 and Fig. 11. I agree that the Br pattern looks similar to the Na pattern. But this then begs the question, what is the pattern of Br_enr. My impression from this figure and the data in Figs 4-7 is that Br enr is probably rather flat with distance. Since this was the issue that Spolaor suggested controlled the TD glacial-interglacial change, it deserves to be shown and discussed in that context. Please add a discussion.
Figure 11 has been modified (now Fig. 9) and now shows the spatial pattern of Brenr in the second column, and bromine and sodium in the first one. The paragraph has been extended to discuss the point in question:
"The pattern of bromine enrichment is linked among other things to the different bromine fractionations during the transport in the gas phase and the aerosol phase, compared to sodium. Unlike sodium and bromine, no decrease is observed for bromine enrichment from our data (Fig. 9, second column), although no clear trend can be inferred. This can be due to the multiple origins of air advection (Ross sea /Indian ocean), to the uneven strength of source areas or because the distances are not large enough for any difference to be reliably observed."

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.

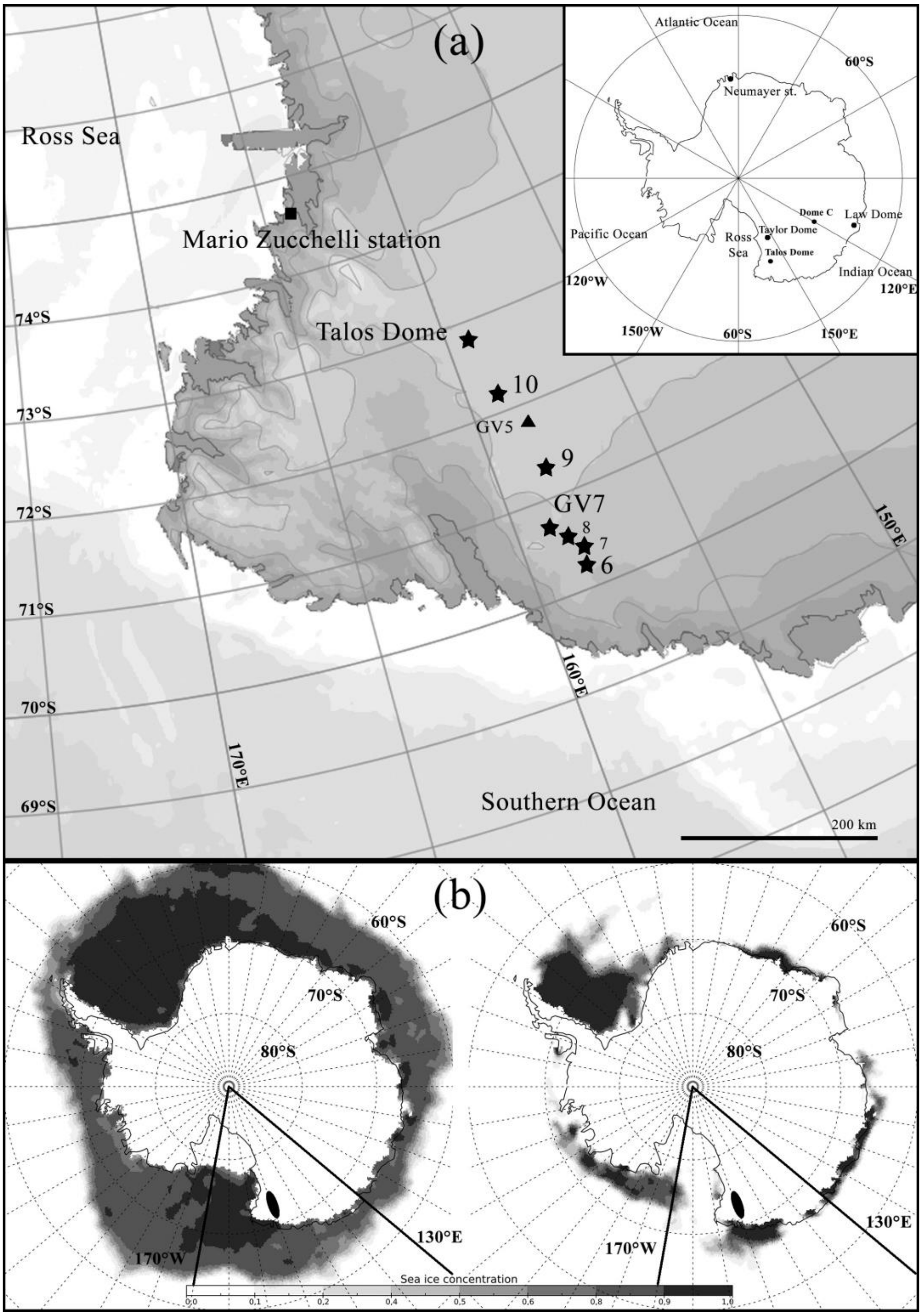


Figure 3. Distribution of bromine enrichment values within cores TD, 10, 9 (blue) and GV7, 8, 7, 6 (red). The dashed line indicates the seawater value (Br_{enr} = 1).

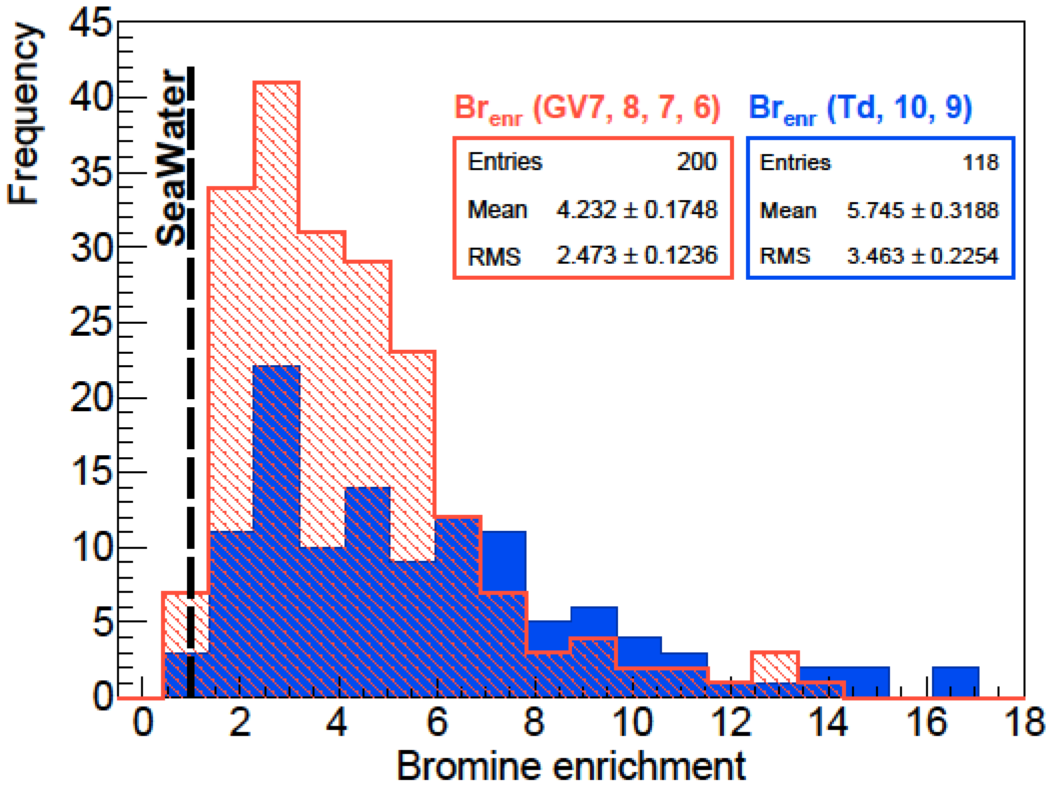


Figure 4. Variability of $\delta^{18}O$ (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in cores 10 (left) and 9 (right). Thick lines represent 3-month running means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

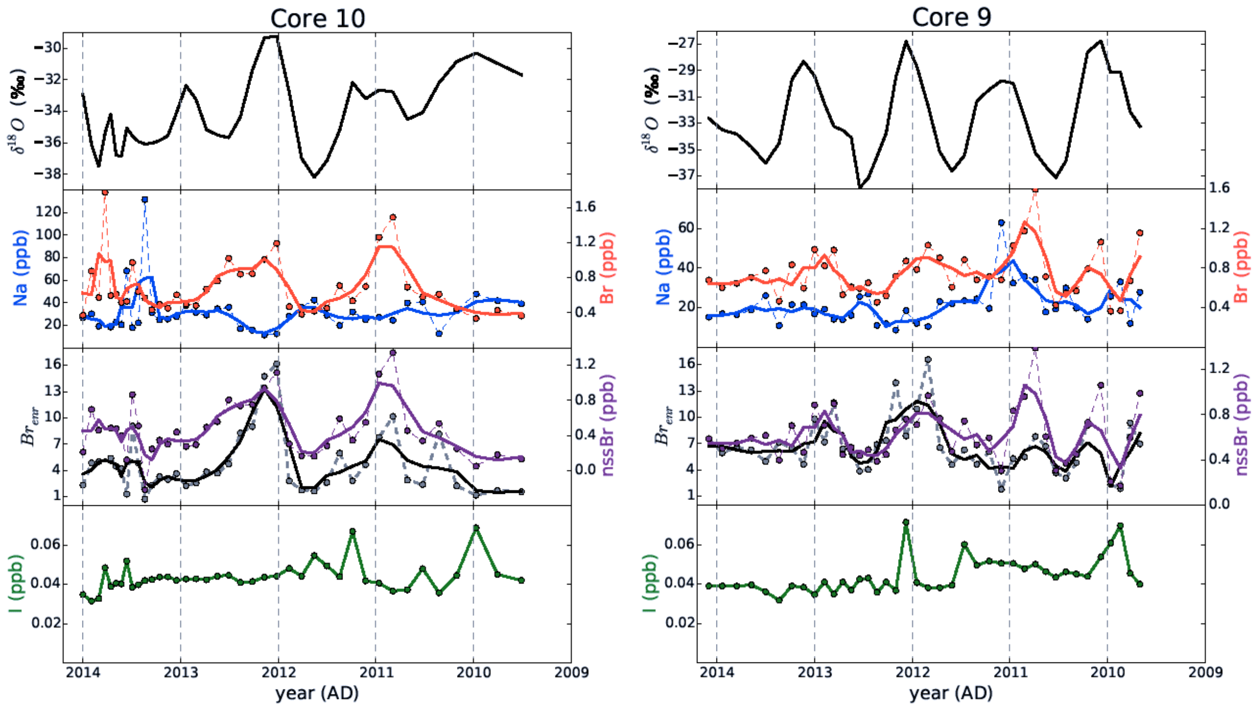


Figure 5. Variability of $\delta^{18}O$ (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in cores GV7 (left) and 8 (right). Thick lines represent 3-month running means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

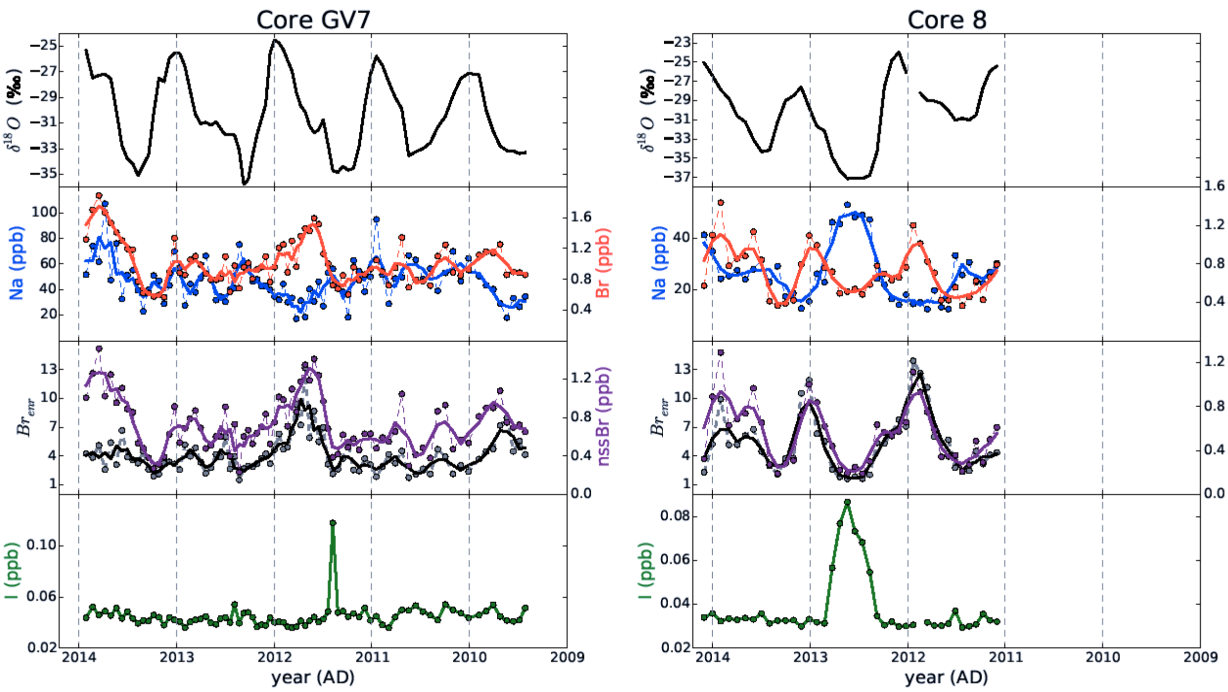


Figure 6. Variability of $\delta^{18}O$ (upper panel), Na (middle top panel, left axis), Br (middle top panel, right axis), Brenr (middle bottom panel, left axis), nssBr (middle bottom panel, right axis), and I (bottom panel) in cores 7 (left) and 6 (right). Thick lines represent 3-month running means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

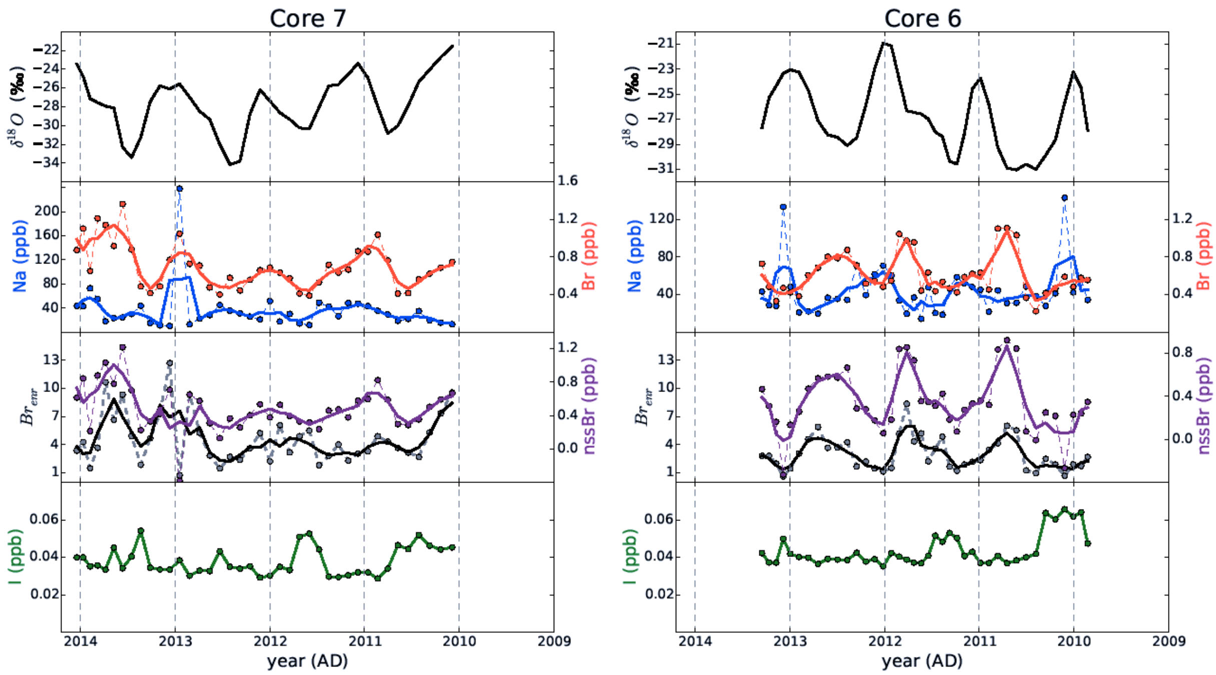


Figure 7. (a) Monthly values of sea ice area (blue) within the 130°E-170°W sector from 2010 to 2013 (±1σ, month variability) and daily average (24 hours) total downwelling spectral irradiance (red), calculated using the TUV model at 71° S, 158° E. Each irradiance calculation was set the 15th day of each 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).

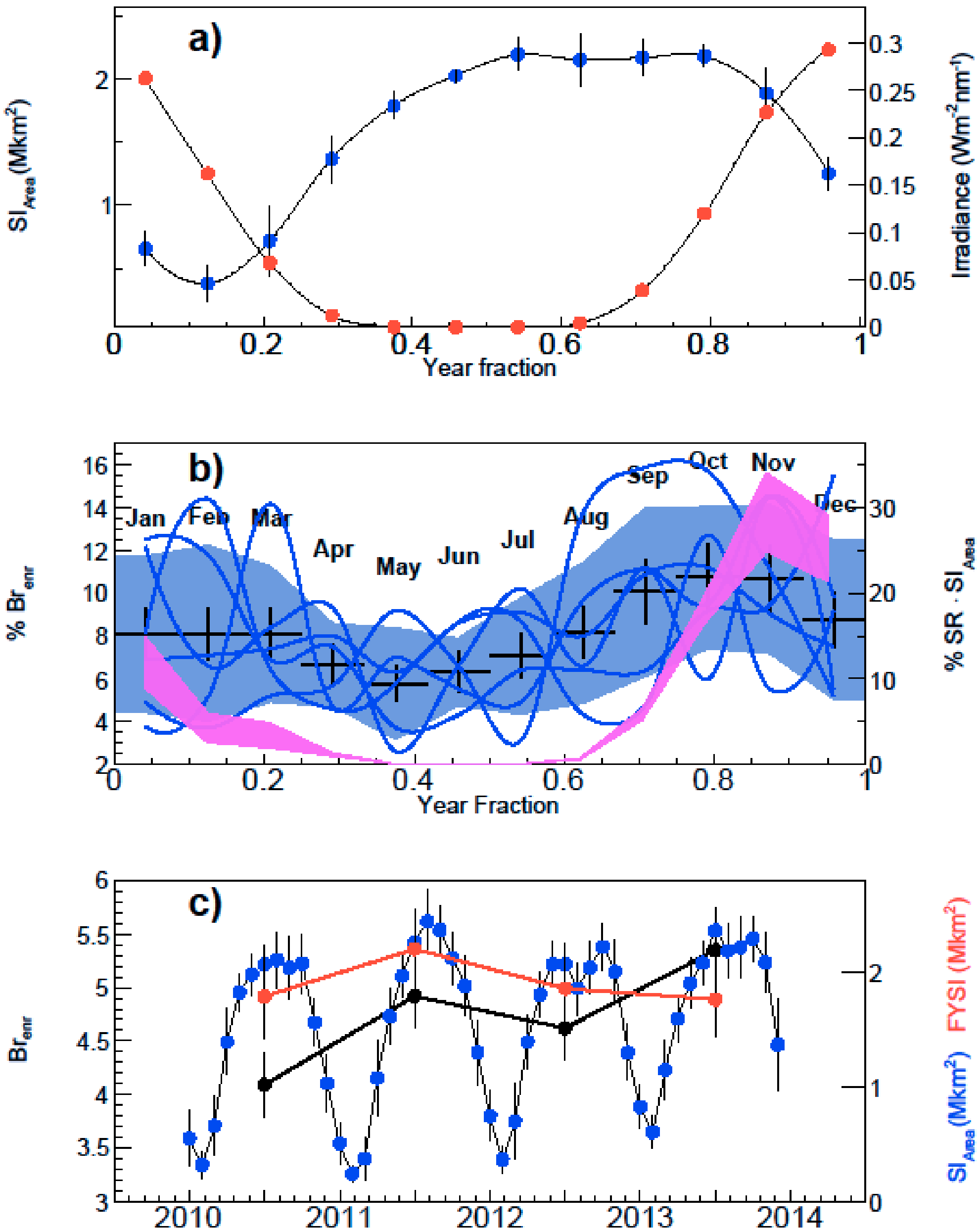
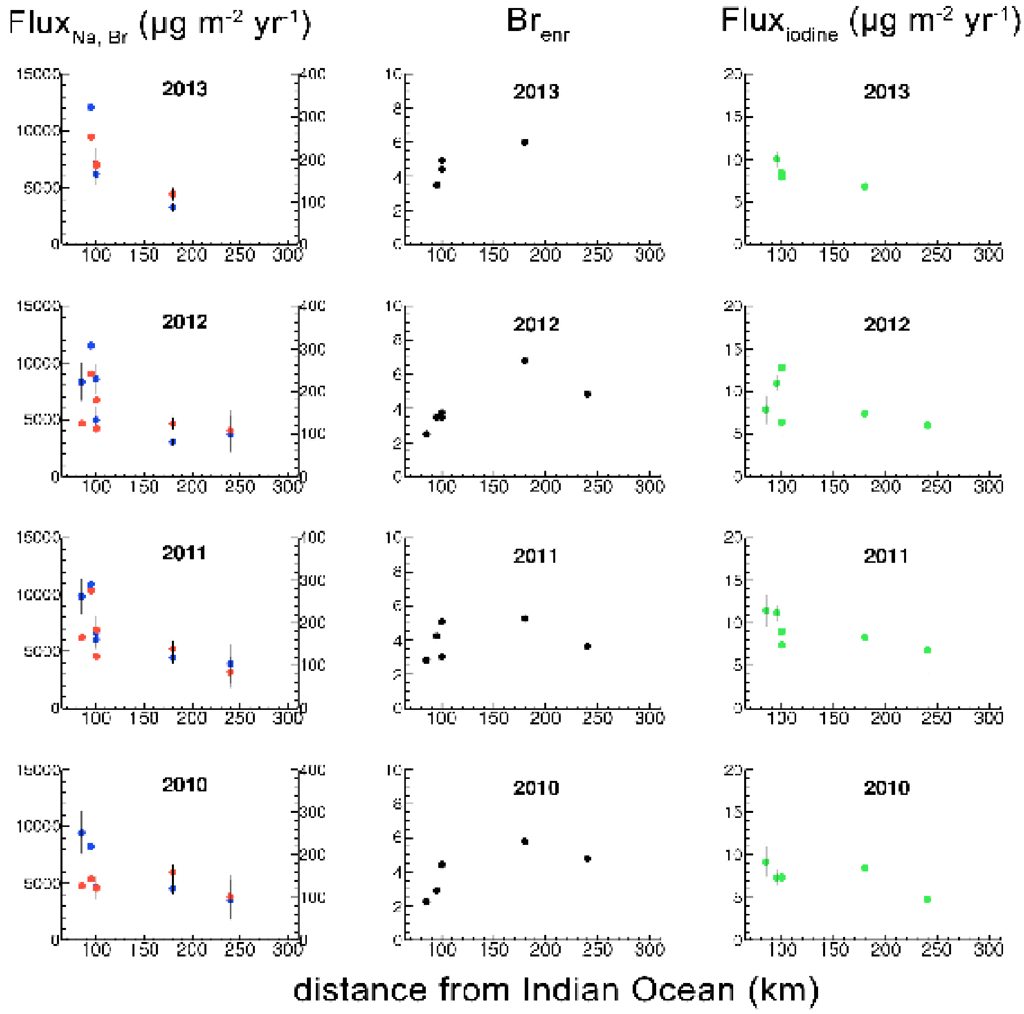


Figure 9. Mean annual fluxes of sodium (blue, left axes), bromine (red, right axes), iodine (green) and bromine enrichment values (black), as a function of distance from the Indian Ocean. Each dot represents a location along the traverse.



Supplementary material

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

Figure. Variability of $\delta^{18}O$ (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).