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Climate of the Past
Discussions

Interactive comment on "Sea ice and pollution-modulated changes in Greenland ice core methanesulfonate and bromine" *by* O. J. Maselli et al.

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Maselli and coauthors present a study investigating the behavior of two possible sea ice proxies, Br and MSA, from two Greenlandic ice cores, Tunu and Summit. This is an interesting dataset and discussion, however I hold some significant doubts regarding the interpretations and methods. Most of my concerns relate to the production and interpretation of the MSA record. This would be the first time that a convincing MSA record has been published from Greenland ice cores, and the first time ever that such data has come from a continuous melting system. Given the significance of such data, it is surprising that the technique description and validation is so limited. I also have doubts regarding the assumption to calibrate Br trends using MSA, as the two have

different production processes with respect to sea ice. Further, such a calibration is performed for a period where there is no independent reliable observational data. Can the authors be sure they are not comparing proxy with different meaning? There is a lot of impressive data presented in this work but the authors should not put the cart before the horse: A thorough demonstration of the reliability of the data presented; a more complete investigation of the divergent trends between MSA and Br, and between Tunu and Summit; and a more detailed consideration of the potential impacts of acidity on the stability of Br and MSA in ice cores, would make this work a considerable contribution to the literature and our understanding of these important possible sea ice proxies. The following comments on the manuscript are divided into topics instead of referring to particular lines or sections. Major comments MSA record Many papers have been written about the measurement of MSA (Legrand et al., 1993; Curran et al., 2001) as well as the problems of stability and mobility (Abram et al., 2008; Smith et al., 2004; Curran et al., 2002) as well as challenges of interpretation (Abram et al., 2013, Wolff et al., 2006; Legrand and Mayewski, 1995). Given the length of time that the community has required to tackle the distribution and stability of such a challenging ion, a thorough validation of the measurement method is required. Have replicate measurements been carried out? Have parallel discrete samples been measured (ie, samples that have not been exposed to the melter?). How do these results compare to other recent observations of MSA in Greenland (e.g Kuramoto et al., 2011, Jaffrezo et al., 1994)? Is it possible that MSA is destabilized at the melthead or when acid is added to the meltstream? These are critical questions as there is no pre-existing MSA record for comparison and in this manuscript MSA is used as a calibratiuon reference for the Br data. ——————————————

Several updates to the manuscript have been added in order to address the concerns of the referee regarding the reporting of the MSA measurement technique and its validation – since it is the first time the ESI/MS/MS analytical technique has been combined with a continuous, online sampling of an ice core. The following three plots have been added to the supplementary section of the paper and referenced in the manuscript.

A plot comparing the MSA record from this study and that from Legrand 1997 (Legrand et al., 1997) - both collected near Summit (as mentioned in the text) has been added to the Supplementary material and referenced in the manuscript (see Figure R 1). The Legrand record is from the GRIP ice core drilled at the location 7234'N, 3738'W in 1993, 35 km NE of the Summit-2010 ice core site. The MSA samples from the GRIP core were isolated in the field, 1-2 hours after the ice cores were retrieved and subsequently processed via discrete sample ion chromatography. In comparison, the Summit-2010 ice core was measured using the new technique of continuous melting of the ice core combined with continuous analysis by electrospray triple-quad mass spectrometry (ES/MS/MS - as described in the manuscript). As was mentioned in the text, the analytical technique of ES/MS/MS for discrete MSA ice core samples is well established; studies using this technique were published by the Saltzman group over 10 years ago (Saltzman et al., 2006) so the new part of the technique is using the ES/MS/MS in continuous mode.

The tight overlap between the low frequency trend of the two MSA series demonstrates that the new, continuous measurement technique is able to achieve a comparable accuracy in MSA concentration measurements to the discrete technique. It also demonstrates that negligible amounts of MSA are being lost during the continuous melt method (by destabilization at the melt-head as the review suggests). No acid is added to the melt stream that feeds the MSA into the ES/MS/MS so MSA would not be degraded or destabilized in this way either- as the reviewer suggests. The reviewer also questions the validity of using the Summit-2010 MSA record as a calibration for the Br record since there “is no pre-existing MSA record for comparison”. We believe that the Summit-2010 MSA replicates the ‘pre-existing’ Legrand GRIP MSA record (which is also from the Summit region). It was for this reason that the Summit-2010 MSA record was not presented as unique record of MSA from Summit, instead it was used so that an accurate comparison between MSA and Br could be drawn since they were measured simultaneously from the same ice core.

To demonstrate the reproducibility of the MSA measurements and thus the robustness of the online, continuous technique, several plots have been included in the supplementary section which show replicate MSA measurements from the same depth of the Tunu ice core (Figure R 2). Each section of the ice core was cut into multiple longitudinal sticks so that replicate measurements of all chemical species could be performed at any depth. The same stick in each core section was melted and analyzed to give the primary record of all the chemical species measured online. Replicate measurements were then performed using the ice sticks which ‘overlapped’ the depths of interest. The online, continuous MSA technique reproduces both the high and low frequency components of the MSA record extremely well in the duplicate analyses even though the duplicate measurements were often performed days or even months apart. The records demonstrate both the high precision and temporal stability of the technique. Replication at such high resolution also demonstrates that the high frequency component of the MSA is actually real variability of MSA preserved in the ice core and not just the noise of the analytical technique. The entire MSA record from the Tunu ice core was also reproduced by discrete analysis of MSA samples collected from the CFA system. The discrete samples were collected as the continuous measurements were performed by directing part of the sample stream into an autosampler collection system just before they entered the continuous analyzer. The samples were then frozen and later measured using ion chromatographic separation and the ESI/MS/MS detection. In this plot (Figure R 3 and added to the supplementary section) the continuous data have been averaged over the same depth range covered by each discrete sample and then both series plotted as the average age over that depth range. Over the 1750-2012 C.E. period the Tunu discrete measurements were, on average, 7% higher than the online measurements (dashed lines indicate average values over the 1750-2012 period). Both the discrete and continuous samples experienced identical conditions from ice melt to collection so the reason for the offset in measured concentration is likely due to differences in post-processing of the data (such as calibration) and not due to loss of MSA in the continuous, online technique. ———————————

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Br measures Line 143. In the text the authors refer to Bromine as the sum of all bromine species that could be present into ice core samples. Equation 4 shows a calculation for Br enrichment, which has been used previously through the work of Spolaor and coauthors (2013) whereas in this manuscript the authors always use total bromine for discussion. Total Br follows sea salt and its components such as sodium. It is the difference, or the additional amount of Br produced beyond the sea salt component, that must be evaluated, at least if you want to consider Br as a sea ice tracer. ——— ————————————

We do not agree that it is the bromine (Br) in excess of the sodium concentration (exBr(Na)) or Br enrichment relative to sodium (enrBr(Na)) that must be used to consider Br as a sea ice tracer. Unfortunately, the use of sodium to try and extract the pure sea water component of the Br is complicated by the fact that a lot of sodium comes from the sea ice surface as well as from the open ocean. Sodium itself has been used as a sea ice proxy in several prominent studies (Wais Divide Project Memebers, 2013; Wolff et al., 2003) because, like Br, sodium is incorporated into the brine encapsulated within the sea ice which can then soak into the snow that sits on the surface of the sea ice and subsequently be blown aloft to produce the atmospheric sodium signal seen in the ice core. In addition, the sodium concentration is fractionated upon the formation of the ice when mirabolite ($Na2SO4$) is precipitated out of the brine solution at -8C (Abbatt et al., 2012). In saying this, the records of Total bromine and enrBr(Na), for example, do look similar except for two dips in the enrBr(Na) at years ~1954 and 1990 where the total sodium signal has maxima and the low frequency variability is not as great in the enrBr(Na) record (Figure R 4). As bromine is a relatively new proxy for sea ice, this plot has now been included in the supplementary section so it can aid comparison to the work of Spolaor (2013a, 2014, 2016) and this discussion added to Sect. 4 of the manuscript. The reviewer states that “Total Br follows sea salt and its components such as sodium”. This study has found that while there are similarities between the

total bromine and total sodium records it is not clear that they follow each other. Below is a plot (Figure R 5) comparing the total bromine and total sodium records from the Summit-2010 ice core. To avoid confusion between the bromine enrichment as defined by Spolaor and coauthors (2013b) or Brexc defined by Spolaor (2016) and exBr described in this study, the label of exBr has been changed to nsiBr (non sea ice Bromine) within the manuscript. ——————————————————— ————-

Br summer peak and biological production Br emission from sea ice is well documented from both satellite observations of BrO and aerosol measurements. It is detected from the beginning of March, the arrival of solar radiation, to early June. The data show a maximum in Br in mid-June (also shown in figure S1). The results are in agreement with those obtained from NEEM (Spolaor et al., 2014) of maximum Br enrichment in summer. The authors claim that biological production could be a factor influencing the total Br concentration however I am not convinced of this for the following reasons: MSA, biologically produced, has its greatest snow concentration during spring, with consistently lower values during summer. Ardyna et al 2013 (Biogeosciences, 10, 4383–4404) report annual time series of surface chlorophyll for the Arctic and show that the main production is concentrated in spring with less production in summer. There could be an influence of biogenic bromine in spring but this is not supported by satellite observations, where the highest atmospheric concentrations are over sea ice. Release of biogenic bromine from sea ice through percolation is quite unlikely due to the low porosity of Arctic spring sea ice (Zhou et al 2013, JGR: Oceans, Vol. 118, 3172–3189, 2013) Finally, during summer satellites do not detect BrO in the polar atmosphere. ——————————————

We agree that biogenic sources of bromine are likely insignificant in the ice core records. The text of Sect. 4.1.4 has been reworded to try and better reflect this. —————————————————————————-

MSA/Br correction (line 331) The authors suggest a correction for Br using MSA in the preindustrial era. To do this, a linear relationship has been used between the two parameters. I am not convinced about this approach because the relationship between Br, and its enrichment over seasonal sea ice is not linear but logarithmic. This is explained by Br chemistry over sea ice – very briefly, one Br radical produces two radicals causing the explosion. The relationship between MSA and the location of the sea ice edge, or as proposed by the authors, with open water leads in the ice pack, is linear. What is the correlation between Br and MSA? What is the relationship used? No chart has been presented in the paper although this is one of the central discussions of the manuscript. ————————————

In the reviewer's explanation of the bromine explosion event they say that "one Br radical produces two radicals causing the explosion". We think that they mean one Br2 molecule produces two radicals as this is the mechanism as we understand it. The Br2 is produced when one non-reactive atmospheric Br species is adsorbed onto the ice surface (HOBr) which, when it reacts with the Br salt in the ice (BrÂŕ) releases Br2 and subsequently two reactive atmospheric Br radicals are produced (Frieß, 2004). The mechanism is labelled as a 'bromine explosion' because there is an exponential increase in reactive atmospheric bromine species. Also, it is important to note that this bromine release mechanism only occurs in acidic ice substrates (Frieß, 2004). It is important to note that in this study total bromine is measured – which is not isolated to just the reactive atmospheric species released in the bromine explosion events, so it wouldn't be expected that there is a exponential (or logarithmic as suggested by the reviewer) relationship between the atmospheric Br species measured in this study and the Br species in the sea ice. In fact it is primarily the soluble, non reactive bromine species which would be able to be transported the large distances to the ice core sites on the surfaces of aerosols and thus preserved in the ice core. Supplementary figures have been added which describe the process used to 'correct' the total bromine record using the MSA (Figure R 6). The figures include the correlation between MSA and Br which was used to determine the sea ice component of the bromine signal. From the Summit-2010 correlation it is easiest to see that the relationship between Br and

MSA does indeed appear to be closer to linear than either logarithmic or exponential. Also, the fitting function that was used to fit the MSA time series (a 264 point stienman function in the original manuscript) has been updated to a 9th order polynomial fit to simplify the analysis - the final record of the non-sea ice component of the bromine (exBr or nsiBr) is unchanged by this update. ——————————————————————————-

In Fig 3 (and other work in the literature) it is shown that MSA can undergo remobilization (the seasonal cycle of MSA is changed completely) and smoothing in the ice. How much does this interfere with the Br correction? Again I mention my comment about the dangers of comparing a proxy with a proxy. ————————————

In Figs. 3 and S3 we demonstrate that both the bromine and MSA signal show a seasonal shift along the length of the ice core. The shift is on a sub-annual scale for both species so that the annual average value for each species appears to be unchanged. For this reason, the comparison between MSA and bromine was performed at an annual, not sub-annual resolution so the remobilization of the species along the length of the ice cores should not significantly effect this comparison. Although comparing proxy with proxy may be 'dangerous' it is common practice: such as the comparison between sodium and bromine that the reviewer suggests as a more appropriate way to develop the sea ice proxy. ————————————————————————————-

Do MSA and Br represent the same source processes at the two sites investigated? Abram et al. (2013) have reviewed at least 5 different interpretations for MSA records around Antarctica alone. In this work, how can the authors correct a proxy (Br) influenced by the presence of seasonal sea ice with a proxy (MSA) that seems to quantify open water leads in the ice pack? ————————————

Areas of open water in the ice pack (OWIP) become relaminated with fresh sea ice (unless they represent a polynya) and it is the newest sea ice which is most saline and thus the major source of bromine enriched aerosol. In this case the size of the OWIP influences the amount of fresh sea ice that is formed in these zones. In this way the two source processes are linked but are not identical. ——————————————————————————————-

Again my comment that more careful attention must be given to the discrepancies between the records. In figure 2 there is a positive correlation until 1870 for Summit while for Tunu it persists until 1950. Then the correlation between Br and MSA seems negative. Why there is this discrepancy between the two cores? Tunu is a low accumulation site, Summit is far away from the coast; how much should these two sites be expected to demonstrate a similar sea ice signal? Are they even sampling the same sea ice regions? ——————————————

We are not suggesting that the two sites have the same sea ice signal. Indeed, while there are similarities between the Br and MSA records at the two sites, they are distinctly different (as was demonstrated when the time series were fitted with the 3-step linear regression and the fitting parameters summarized in Tables S1and S2). As was shown by the air mass back trajectories the sea ice source regions for each ice core are on different sides of Greenland and at different latitudes so it is understandable that the sea ice signals are different – as discussed in the text. ——————————————————————————-

It has been demonstrated that sea ice cannot be reconstructed from MSA in central East Antarctica (Wolff et al., 2006) – a similar level of criticism needs to be applied to records from central Greenland ——————————————

In their 2006 manuscript, Wolff (Wolff et al., 2006) stated that MSA from a central East Antarctic site (Dome C) could not be used as a sea ice proxy since MSA can be lost to the atmosphere post-deposition at very low accumulation sites. The EPICA Dome C (EDC) ice core used in the Wolff study has an average accumulation rate of 25 kg m-1 yr-1(Augustin et al., 2004) which is much lower than the accumulation rates of both Greenland ice cores used in this study. Indeed Wolff references the work of

Weller (2004) who was able develop a relationship between %MSA(and nitrate) loss and average snow accumulation for a series of Antarctic ice cores. Extrapolation of this relationship predicts 0% MSA (and nitrate) loss at accumulation rates of >105 kg.m-1.yr-1. The average accumulation rates for ice cores used in this study were: Summit-2010; 0.22 m yr-1 (220 kg m-1 yr-1) and 0.11 m yr-1 (110 kg m-1 yr-1) which are both larger than the minimum accumulation rate needed to ensure 0% post-depositional loss of MSA (and nitrate) according to the work of Weller (2004). For this reason post-depositional loss of MSA has not been included in this manuscript. However, comment as to why the post-deposition loss of MSA is not considered has now been included in the manuscript (Sect 3.2) ——————————————————————————-

Br after 1950: The authors have investigated the Br increase of Br after 1950 in both cores. In the Summit core Br increases significantly from 1930 while in the Tunu core the increase is sharper and starts around 1950. The authors investigated different possible explanations, suggest- ing that anthropogenic pollution plays an extremely marginal role compared to biogenic contributions and acidity which can play a more central role. As discussed previously biological production can contribute to total bromine emission but a major influence on Br deposition is not supported by satellite observations of BrO. Acidity can play a role in the process, primarily for halogen recycling in sea salt aerosols and not so much for heterogeneous recycling on sea surfaces. Nevertheless, acidity is dependent on sea ice to have any effect: without sea ice the role of acidity would be zero. Therefore, the first order influence on Br recycling is from sea ice and a second or third order influence may be attributed to acidity. The links drawn between nitrate and Br are extremely interesting but the data presented does not satisfactorily describe the influence of acidity. The authors are correct that the data points to more of an influence from nitrate than from sulphate, but none of the correlations in Fig 9 are strong, even if some are significant. How much of the significance between Br and nitrate can be ascribed to autocorrelation based on their seasonality? ——————————————

The types and locations of the sources of nitrate and bromine and distinctly different, so it is unlikely that the correlation between the magnitudes of the low frequency components of the two species is dominated by autocorrelation based solely on their seasonality (See Figure 8a). The reviewer also questions whether the correlations determined in Fig. 9 (between only the high frequency components of the acidic species and the bromine) may be dominated by the the fact the two species show the same seasonality. However, the correlations were performed on annual averages of the bromine and nitrate so the seasonal characteristics of each species are essentially removed before the correlations were performed. The reviewer also suggests that biological production of bromine is not a major influence on deposited Br since it is not supported by satellite BrO observation. Satellite observations of this reactive form of atmospheric Br show that BrO is confined to areas directly above sea ice - minimal BrO is observed inland. As the bromine records generated in this study were from inland ice core sites this shows that bromine is transported inland – but must not be in the form of the species that are observed by the satellites – BrO. So, as the reviewer noted, “biological production can contribute to total bromine emission” and biological production is related to sea ice coverage and the amount of open water in the ice pack (OWIP), which is what is promoted in this study. Indeed more discussion has been added reference to the influence of nitrate in fixating the bromine into the snowpack in summer as the likely cause of the summertime bromine maximum observed in the ice core (more details included in the reply to reviewer 1) The manuscript describes the influence of nitrate in promoting more bromine to be released from the sea ice than would be in the absence of the anthropogenic species in addition to helping to fix the bromine in the snow pack. To aid in this discussion we have incorporated a plot into Figure 8 (Figure R 7) showing a direct comparison between the nitrate records and the nsiBr (non sea ice bromine) in addition to expanding the discussion of the links between nitrate and bromine in the emission, transport and deposition of bromine (Sect. 4.2.3) ———————————————————————————-

Back trajectory and sea ice correlation Back trajectories shown in Figure 5 indicate

that for Summit the main atmospheric pattern, or the source regions, originate from the south and south-east of Greenland while for Tunu the main source is Baffin Bay with sporadic incursions from southeast Greenland. Figure 6 shows correlation maps of monthly sea ice concentration (SIC) derived from the HadISST1 ICE dataset from 1900-2012. Why is it that the area used for correlation is different to the south and south-east secotrs of Greenland, where the Summit back-trajectories originate from? ———————————————

We thank the reviewer for this observation – indeed the secondary source region (as mentioned in the text) was highlighted for both ice core sites in figure 6 and 7 - this was a mistake and has been corrected in the manuscript. Now the primary source regions (as determined from the back trajectories from Fig. 5) are outlined in black on figures 6 and 7 and the lower, OWIP plots have been updated to display the OWIP values for the indicated source regions. The figure captions have been updated to try and make this more clear and more detail has been added to the analysis of the correlations between the MSA and OWIP records. In addition, the resolution of the maps has been increased to aid visualization. ——————————————————————————————-

For panel b of figure 6, how is the correlation value in the graph (0.45) related to the data in the satellite maps, where none of the data approach a value of 0.45? For Tunu (Figure 7), as for Summit, the main correlation with sea ice is detected in northeast Greenland where BT analysis do not suggest an atmospheric source region. On what basis was the correlation window chosen? Again, why does the graph in panel b include a correlation of r=0.53 when this value is not shown in the correlation maps? For both sites, what would the correlations be if “outliers” were included? ———————————————

The correlation values displayed in the lower, line plots are for the correlation between the area of Open Water in the Ice Pack (OWIP) within the black squares (the back-trajectories source regions) and the MSA time series. The upper, correlation maps are displaying the direct correlation between the Sea Ice Concentration values (SIC) at each latitude and longitude displayed and the MSA time series. So these two parts of the figure are distinctly different, that is why the correlation values in the maps and the line plots are not related. ———————————————————————————-

Line 101. Bromine is not normally measured in low resolution due to interference from 40Ar39K. What were the relative sizes of baseline to signal and was there a significant background when quantifying Br in low resolution? ————————————————

The bromine was measured at medium resolution - this resulted in sufficient mass separation between Br 79 and 40Ar39K to avoid interference between the two species. This has been corrected in the manuscript. ———————————————————————-

Line 225. Why has bromine been referenced to chloride? Chloride can undergo atmospheric reactions and is not recommended for evaluating Br enrichment. For consistency, as well as due to its stability, sodium should be used. ———————————————

The manuscript has been updated to include the bromine enrichment relative to sodium as well as chlorine. ——————————————————————————-

Line 472. Although the effect of springtime Arctic haze is well described, the high springtime concentrations of sulphate and nitrate cited by the authors may be associated with biological production. Lehrer et al 1997 conducted their study in Ny-Alesund, a research facility right on the coast. Such a site is therefore susceptible to oceanic productivity, especially in connection to the springtime opening of sea ice in the adjacent fjord. ————————————————

Discussion about the cause of the seasonal nitrate cycle has now been added to the manuscript. “Although there are biological sources of nitrate in the ice core aerosol

source regions, in a recent study focused on the and record in the Summit-2010 ice core, Chellman et al. (2016) concluded that the preindustrial (1790-1812 C.E.) seasonal cycle was driven by biomass burning emissions. However, in the modern era (1930-2002 C.E.) oil-burning emissions became the dominant source of in the snowpack. The change in the dominant source due to industrialisation is the cause of the shift in timing of the seasonal cycle.” ————————————————————————-

Line 557-559. Br and its enrichment in ice cores has been used for reconstructing sea ice changes in recent periods in the Arctic. The authors haven’t provided a satisfying explanation for why bromine doesn’t work at Tunu or Summit but does work at other Arctic sites. Acidity should play a role in influencing reactive halogens such as bromine but without sea ice no reactions will occur. It is further dissatisfying that the large acid peaks observed in the record do not have a consistent effect on either Br or MSA. ————————————————

Figure R 4 has been added to aid direct comparison between the previous studies that used Br enrichment and this study which used total bromine. Also more discussion has been included which hopefully helps to explain how the large amounts of anthropogenic nitrate will effect the deposition of the bromine in the snow and thus distort the low frequency component of the bromine record from what it would be if it was purely a sea ice proxy. The fact that the large acidity peaks do not appear to have a consistent effect on the bromine records supports our conclusion that it is not total acidity (nitric acid + sulphuric acid + other minor acids) which effects bromine activation on the snow/ice but more specifically just HNO3. ———————————————————————-

Figure 2. It would be easier to look at the data if they do not overlap. ———————————————

Figure 2 has been replotted (Figure R 8) so that the data does not overlap. The time-series are plotted so that the magnitude of the preindustrial variability is the same at each site. ——————————————————————————-

FIGURE CAPTIONS

Figure R 1. Comparison between the MSA record from the the GRIP ice core drilled in 1993 (Legrand (1997)) and the Summit-2010 ice core drilled in 2010 (this study). Figure R 2. Demonstration of the reproducibility of the MSA online, continuous measurements performed on the Tunu ice core. Two different depths of the Tunu ice core are shown where the replicate analysis was performed by melting a secondary stick of ice cut from the same ice core and overlapping in depth: (a) Six 'overlap' ice cores were melted sequentially to replicate the MSA record over the depth 8-14 m.(b) Two 'overlap' ice cores were melted sequentially over the depth 186.2-187.9 m. Zooming in on a small section of the record at each depth demonstrates that the high frequency signal is real (not noise) and well replicated by the continuous MSA technique. Figure R 3: Comparison between discrete and continuous, online measurements of MSA measurements from the Tunu ice core. Figure R 4. Total bromine and bromine enrichment (relative to sodium) from the Summit-2010 ice core. The time-series have been plotted to match the signal variability in the preindustrial era (1750-1850 C.E.). Figure R 5. Total bromine and total sodium records from the Summit-2010 ice core. The concentrations of sodium were measured as, on average, 60 times greater than that of bromine and the temporal trends of both species is also quite different. The time-series have been plotted to match the signal variability in the preindustrial era (1750-1850 C.E.). Figure R 6: Summary of the technique used to determine nsiBr: the amount of Bromine in excess of what is expected from a purely sea ice source.(a,b) Blue dots, blue fit line: correlation plots between total bromine and total MSA in Summit-2010 and Tunu ice cores, respectively over the preindustrial period 1750-1880 C.E.. Red dots, yellow fit line: Correlation plots between total bromine and smoothed MSA time series shown in c and d.(c,d) Annual MSA record fit with 9th order polynomial. (e,f) Comparison between the total bromine record (black) and the bromine predicted from the smoothed MSA,

Br linear relationship determined in a and b (blue) – the bromine from a purely sea ice source. The difference between the blue and black lines is the amount of bromine in excess of what is expected from a purely sea ice source (nsiBr; See Fig. 8). Figure R 7: Upper panels: Comparison between bromine in excess of what is expected from a purely sea ice source (nsiBr, black) and nitrate. The temporal similarities between the nitrate and nsiBr records are high and indicate that nitrate is a likely driving force for the enhanced release of bromine species from sea ice sources. Lower panels: Comparison between the calculated nsiBr record and excess lead (exPb, purple) measured in the ice cores. The lower panels also show the upper limit to the amount of bromine that could be derived from leaded fuel combustion by assuming exPb:Br ratio of 1:2 after 1925 (blue). After 1970, when world consumption of leaded gasoline began to fall, nsiBr concentrations continued to rise at both ice core sites far above the concentrations that could be explained by leaded gasoline sources. Figure R 8: Annual record of bromine (thin blue) and MSA (thin red). Annual record of bromine (thick blue) and MSA (thick red) with outlying spikes removed using a 25 year running average filter described by Sigl et al. (2013). All records were fit with a 3 step linear regression and the results of the fits which identify the timing of inflection points are summarized in Table S1.The time-series have been plotted to match the signal variability in the preindustrial era (1750-1850 C.E.).

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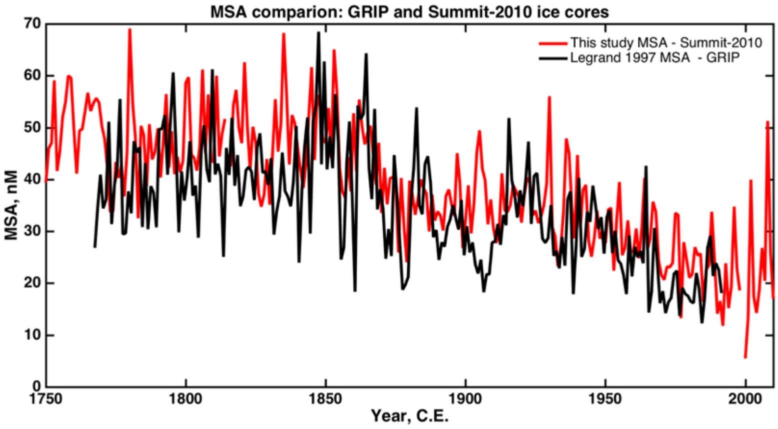
MSA comparion: GRIP and Summit-2010 ice cores
This study MSA - Summit-2010
Legrand 1997 MSA - GRIP
MSA, nM
0
10
20
30
40
50
60
70
1750
1800
1850
1900
1950
2000
Year, C.E.

Fig. 1.

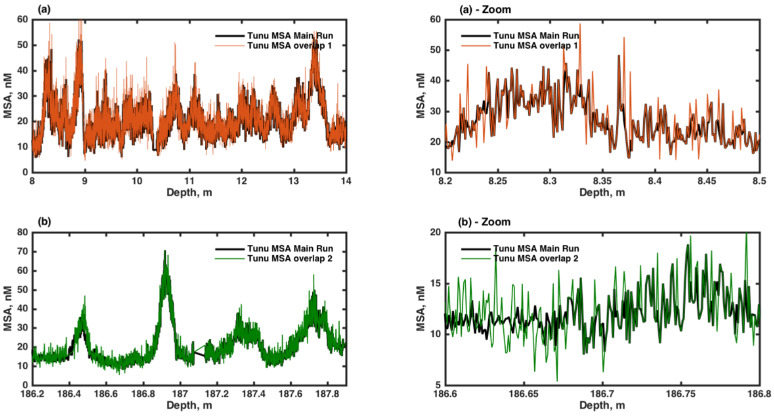
(a)
Tunu MSA Main Run
Tunu MSA overlap 1
MSA, nM
Depth, m
(a) - Zoom
Tunu MSA Main Run
Tunu MSA overlap 1
MSA, nM
Depth, m
(b)
Tunu MSA Main Run
Tunu MSA overlap 2
MSA, nM
Depth, m
(b) - Zoom
Tunu MSA Main Run
Tunu MSA overlap 2
MSA, nM
Depth, m

Fig. 2.

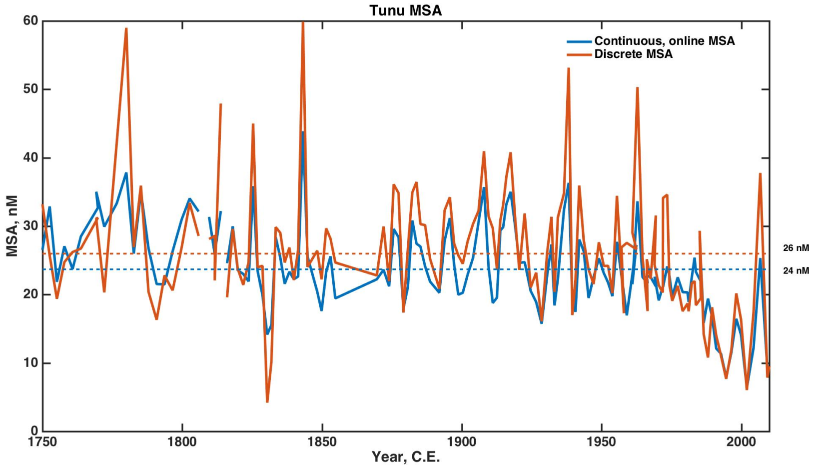
Tunu MSA
Continuous, online MSA
Discrete MSA
MSA, nM
0
10
20
30
40
50
60
26 nM
24 nM
1750
1800
1850
1900
1950
2000
Year, C.E.

Fig. 3.

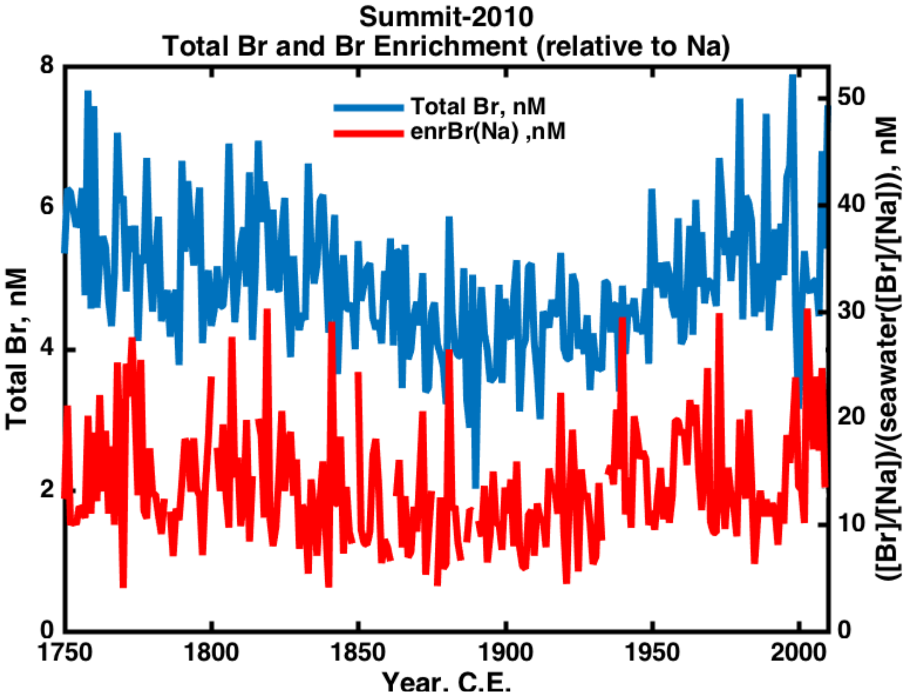
Summit-2010
Total Br and Br Enrichment (relative to Na)
Total Br, nM
enrBr(Na) ,nM
Total Br, nM
0
2
4
6
8
([Br]/[Na])/(seawater([Br]/[Na])), nM
0
10
20
30
40
50
1750
1800
1850
1900
1950
2000
Year. C.E.

Fig. 4.

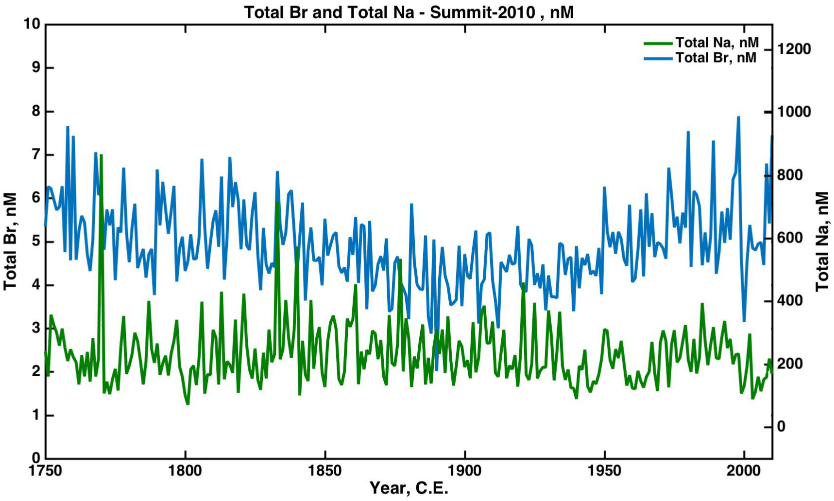
Total Br and Total Na - Summit-2010 , nM
Total Na, nM
Total Br, nM
Total Br, nM
Total Na, nM
Year, C.E.
0
1
2
3
4
5
6
7
8
9
10
0
200
400
600
800
1000
1200
1750
1800
1850
1900
1950
2000

Fig. 5.

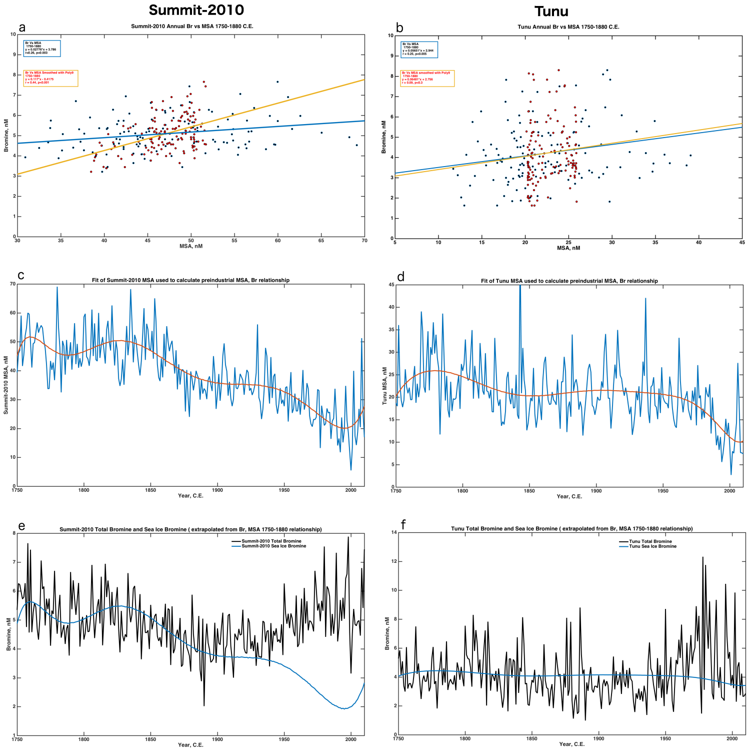
Summit-2010
Tunu
a
Summit-2010 Annual Br vs MSA 1750-1880 C.E.
Br Vs MSA
1750-1880
y = 0.02776*x + 3.786
r=0.26, p<0.003
Br Vs MSA Smoothed with Poly9
1750-1880
y = 0.117*x - 0.4175
r = 0.44, p<0.001
Bromine, nM
MSA, nM
b
Tunu Annual Br vs MSA 1750-1880 C.E.
Br Vs MSA
1750-1880
y = 0.05651*x + 2.944
r = 0.25, p<0.005
Br Vs MSA smoothed with Poly9
1750-1880
y = 0.06481*x + 2.756
r = 0.09, p<0.3
Bromine, nM
MSA, nM
c
Fit of Summit-2010 MSA used to calculate preindustrial MSA, Br relationship
Summit-2010 MSA, nM
Year, C.E.
d
Fit of Tunu MSA used to calculate preindustrial MSA, Br relationship
Tunu MSA, nM
Year, C.E.
e
Summit-2010 Total Bromine and Sea Ice Bromine (extrapolated from Br, MSA 1750-1880 relationship)
Summit-2010 Total Bromine
Summit-2010 Sea Ice Bromine
Bromine, nM
Year, C.E.
f
Tunu Total Bromine and Sea Ice Bromine (extrapolated from Br, MSA 1750-1880 relationship)
Tunu Total Bromine
Tunu Sea Ice Bromine
Bromine, nM
Year, C.E.

Fig. 6.

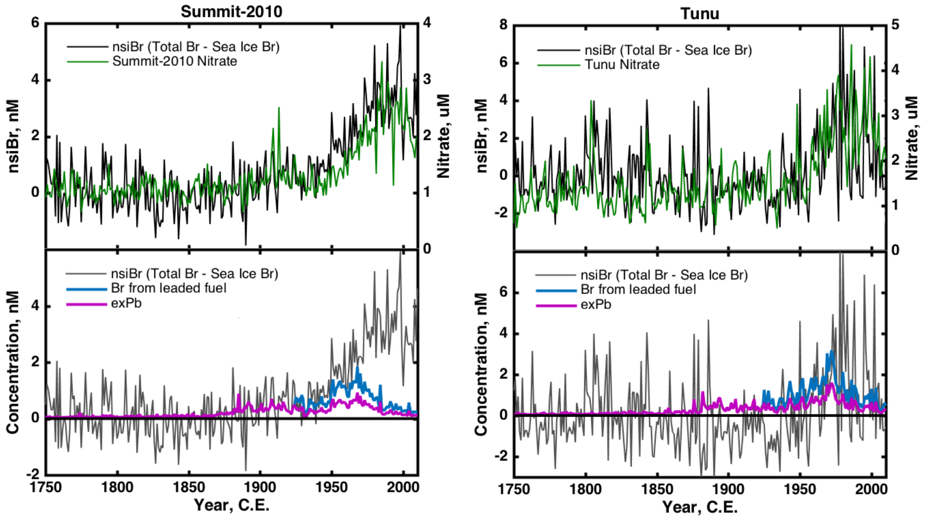
Summit-2010
nsiBr (Total Br - Sea Ice Br)
Summit-2010 Nitrate
nsiBr, nM
Nitrate, uM
nsiBr (Total Br - Sea Ice Br)
Br from leaded fuel
exPb
Concentration, nM
Year, C.E.
Tunu
nsiBr (Total Br - Sea Ice Br)
Tunu Nitrate
nsiBr, nM
Nitrate, uM
nsiBr (Total Br - Sea Ice Br)
Br from leaded fuel
exPb
Concentration, nM
Year, C.E.
1750
1800
1850
1900
1950
2000

Fig. 7.

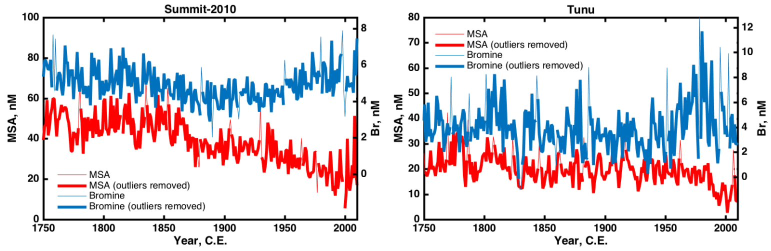
Summit-2010
MSA, nM
Br, nM
MSA
MSA (outliers removed)
Bromine
Bromine (outliers removed)
Year, C.E.
Tunu
MSA
MSA (outliers removed)
Bromine
Bromine (outliers removed)
MSA, nM
Br, nM
Year, C.E.
1750
1800
1850
1900
1950
2000

Fig. 8.