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Climate of the Past Discussions
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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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Chapter 2.1: Accurate absolute dating is pivotal for the subsequent correlation analyses. Please provide a reasonable error estimate for both ice cores and assess the potential impact on the correlations shown in Figs. 5-7. ——————————— The age error estimates for both ice cores have been added to the manuscript. The Tunu ice core was dated with an error of 1 year and Summit-2010 has an error estimate of 0.33 years. To assess the potential impact of the ice core dating errors on Figs. 6 and 7 (Fig. 5 does not involve the ice core records),We have re-plotted the maps using MSA time scales shifted to either extreme of the timescale error estimates (Figure R 1). The results of this analysis show that the timescale shifts do not change the ar-

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eas of positive and negative correlation between sea ice concentration and the MSA records, but do change the magnitude of the correlation in some areas. I have only performed this analysis over the shorter, satellite time period (1979-2012) as this is where the effect would be seen most dramatically. The correlation for the longer record (1900-2012) is dominated by the large, low frequency changes in the MSA record and so is not dramatically affected by a temporal shift of up to 1 year. These plots have been added to the supplementary section of the manuscript and referenced in the text. ———————————————————————————————-

Chapter 2.4, page 7, line 146-150 and Fig. 5: Did you use 10 day back trajectories (as stated in chapter 2.4) or 10 hr back trajectories as mentioned in Fig 5 (the latter seems unreasonable unless extremely high wind velocities prevailed) – please clarify. ——— ——————————— 10 day back trajectories were used – as correctly described in Chapter 2.4 of the text. The figure captions of Fig 5 and S4 have both been corrected to also say that 10 day (not 10 hour) trajectories were used. ——————————— ———————————————————-

Chapter 3.1, page 8, line 179-182 and Fig. 2 and Table S1: Please briefly describe the way you performed the "3 step linear regression" and how you identified the points of inflection. The following has been added to Sect. 3.1 to explain how the '3 step linear regression' was performed: ——————————————— The "3 step linear regression" was performed by simultaneous linear least squares fitting of 3 straight lines joined by 'inflection points' to the data sets. The variables of the fitting procedure were the slopes and intercepts of each line as well as x-axis locations at which the total function switched from one linear section to the next (the inflection points). Initial guess values were supplied for each variable to help the fitting procedure reach reasonable values. ———————————————————————————————-

Chapter 3.1, page 9, line 224-232 and Fig. S2: Albeit unusual, negative bromine enrichment relative to chlorine might as well be caused by a (positive) Cl enrichment relative to Na. Corresponding Cl vs. Na scatter plots could be instructive. ————

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———————— We thank the referee for this observation. Cl vs. Na scatter plots have been added to the supplementary figure and the following discussion included in the manuscript. “Both sites also show a (small) positive enrichment of chlorine relative to sodium, which is amplified at small sodium concentrations. Chlorine containing aerosols are expected to undergo similar chemical processing to bromine containing aerosols but the enrichment factors of bromine (relative to sodium) are much larger which is likely due to the high solubility of bromine species such as HBr (Sander et al., 2003). Alternatively, the chlorine enrichment could be interpreted as a sodium depletion of the aerosols particularly in those of small diameter where both concentrations are low; this would amplify the bromine enrichment (relative to sodium) but would not explain the bromine enrichment relative to chlorine. It is likely that both halogens undergo some degree of enrichment and the sodium undergoes some depletion in the aerosols, though it is difficult to determine this from the data.” ————————————————————-

Chapter 4.2: While the increase of nss-related bromine (exBr) in the industrial era is scrutinised at length, I am missing an explanation for the late summer bromine maximum in the preindustrial era (although this point is insinuated in chapter 4.2.3 line 512-517). Note that this interesting finding is in contrast to the observed BrO concentration maximum in coastal Antarctic regions occurring mainly in spring (at Halley around October/November with an apparent small secondary maximum in March/April; Saiz-Lopez et al., Science, 317, 348-351, doi:10.1126/science.1141408, 2007). Surprisingly, however, in both Polar Regions bromine activation seems to roughly coincide with the respecting seasonal nitrate maximum (i.e. October/November for coastal Antarctica, see Wagenbach et al., J. Geophys. Res. 103(D9), 11007-11020, 1998). Do you think, a similar mechanism is valid in (still pristine) coastal Antarctica? ———————————— While there may be a concentration threshold at which nitrate begins to significantly influence the bromine activation it is likely that the nitrate-bromine interaction mechanism is the same in pristine coastal Antarctica as it is in the preindustrial Arctic (which too was more ‘pristine’ than during the industrial period). We

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have unpublished data from West coast Antarctic ice cores that show seasonal bromine maxima in Oct/Nov (with secondary peaks ∼June) which, as the Reviewer notes is coincident with the seasonal nitrate maximum (Nov/Dec) and the satellite observations of BrO maxima in the neighboring sea ice. This may suggest that while the BrO emission from the sea ice is initiated by the increased spring insolation (as it also is in the Arctic), the deposition of the Br inland and its fixation into the snow is linked to its interaction with nitrate. This is supported by the work of Thomas et al. (2012) whose study of the cycling of NOx and bromine species in the snowpack at Summit concluded that the presence of snow nitrate would suppress the emission of BrO from the snow pack and into the interstitial air – in essence helping to preserve the bromine in the snow pack. More discussion highlighting these differences between Antarctic and Arctic records has been included in the manuscript to try and provide the explanation the reviewer requires regarding the summer maximum in Br. ————————————————————-

Chapter 4.2.3, page 18, line 518-519: To be honest, I cannot realize from these figures that nitrate and bromine records “differ dramatically” in the industrial era! An additional plot showing explicitly Br vs. nitrate could be enlightening. ———————————— A plot comparing total Br and Nitrate at both sites has been included in the supplementary (Figure R 2) and referenced in the manuscript. The two time-series have been plotted to match the variability in the preindustrial era 1750-1850 C.E.. Hopefully this figure now supports the statement that Br and nitrate records are different – particularly at Summit. The difference is not as great at Tunu because the sea ice did not change as dramatically at Tunu as it did at Summit. ————————————————————-

Minor points: Page 4, lines 63-65: write Br-/Na+ or Br/Na (but not Br-/Na). ———— In the reference to which the discussion is referring the author (Spolaor et al., 2013) uses (Br-/Na) since the form of the bromine measured is as bromide (it is isolated by ion chromatography) whilst the sodium is measured directly

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by ICPMS so it is in its neutral form (Na). So the manuscript has not been changed as it is reflecting the discussion of Spolaor (2013). ——————————————————————————-

Page 9, line 226: Sander et al. (2003). The manuscript has been updated

Page 11, line 296: It is actually Fig. 5b (and not Fig. 6b). The manuscript has been updated ——————————————————————————-

Page 15, line 400 and 407: The correct name is 1,2 dibromethane or 1,2 dibromethylen (i.e. BrH2C-CH2Br, abbreviated DBE) – 1,2 diethyl bromide nonexistent. ——————————————— This mistake has been corrected in the text at both locations. DEB changed to 1,2-dibromoethane (DBE). The cited references were also updated as they were not included in the reference list (Berg et al., 1983; Nriagu, 1990; Oudijk, 2010) ——————————————————————————-

Page 25, line 725-728: Please refer to the respecting final paper (not the discussion paper): Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M., Crutzen, P. J., Duce, R. A., Hönninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V. C., and Van Dingenen, R.: Inorganic bromine in the marine boundary layer: a critical review, Atmos. Chem. Phys., 3, 1301-1336, doi:10.5194/acp-3-1301-2003, 2003. The manuscript has been updated ——————————————————————————-

Table S1 (caption): inflection (not infection – witty typo!). The manuscript has been updated, thanks. ——————————————————————————-

Figure Captions

Figure R 1: The effect of the timescale error on the correlation between ice core annual MSA concentrations and Sea ice concentration. The time scales for the MSA records at each ice core site were shifted to either extreme of the error in the time series dating and the correlation maps replotted. The effect of shifting the time series is to

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change slightly the magnitude of the correlation at each location but not the sign of the correlation.

Figure R 2: Comparison between nitrate and bromine records at both ice core sites. The time-series have been plotted to match the signal variability in the preindustrial era (1750-1850 C.E.). The difference between the two time-series is most dramatic at the Summit-2010 site because the sea ice record changes most dramatically at this site also – and sea ice is the underlying driver of the bromine record.

References

Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M., Crutzen, P. J., Duce, R. A., Hönninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V. C. and Van Dingenen, R.: Inorganic bromine in the marine boundary layer: a critical review, Atmos. Chem. Phys., 3, 1301–1336, doi:10.5194/acp-3-1301-2003, 2003. Spolaor, A., Vallelonga, P., Plane, J. M. C., Kehrwald, N., Gabrieli, J., Varin, C., Turetta, C., Cozzi, G., Kumar, R., Boutron, C. and Barbante, C.: Halogen species record Antarctic sea ice extent over glacial-interglacial periods, Atmos. Chem. Phys., 13, 6623–6635, doi:10.5194/acp-13-6623-2013, 2013. Thomas, J. L., Dibb, J. E., Huey, L. G., Liao, J., Tanner, D., Lefer, B., von Glasow, R. and Stutz, J.: Modeling chemistry in and above snow at Summit, Greenland – Part 2: Impact of snowpack chemistry on the oxidation capacity of the boundary layer, Atmos. Chem. Phys., 12(14), 6537–6554, doi:10.5194/acp-12-6537-2012, 2012.

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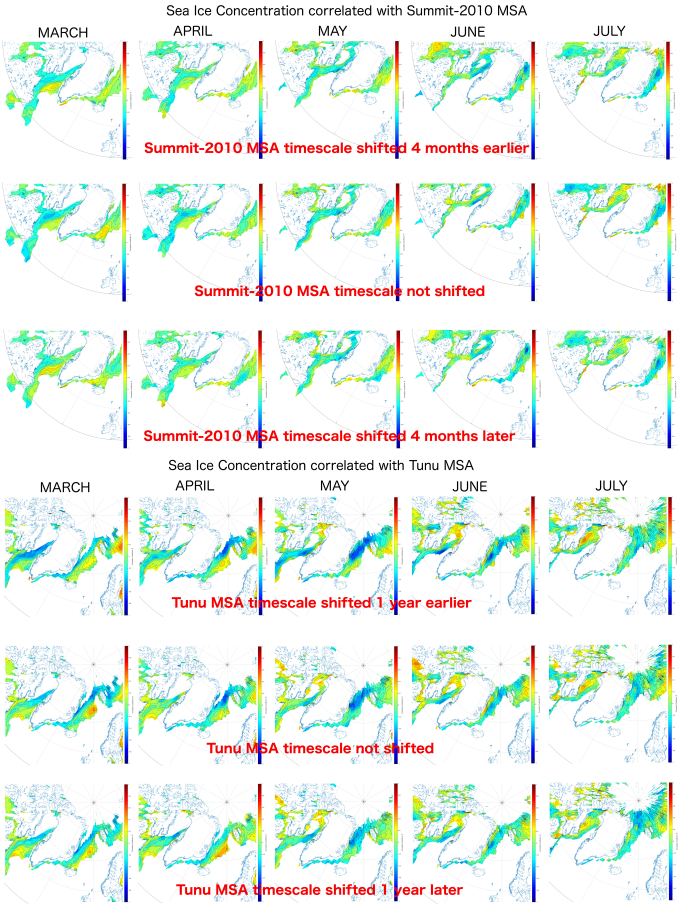
Sea Ice Concentration correlated with Summit-2010 MSA
MARCH
APRIL
MAY
JUNE
JULY
Summit-2010 MSA timescale shifted 4 months earlier
Summit-2010 MSA timescale not shifted
Summit-2010 MSA timescale shifted 4 months later
Sea Ice Concentration correlated with Tunu MSA
MARCH
APRIL
MAY
JUNE
JULY
Tunu MSA timescale shifted 1 year earlier
Tunu MSA timescale not shifted
Tunu MSA timescale shifted 1 year later

Fig. 1.

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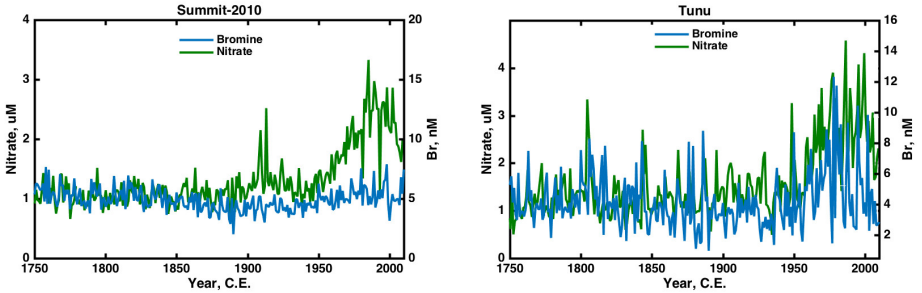

Fig. 2.

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