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Atmospheric
Chemistry
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Discussions

Interactive comment on “Iodine and Bromine speciation in snow and the effect of elevation” *by* B. S. Gilfedder et al.

B. S. Gilfedder et al.

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We would like to thank reviewer 2 for the time taken to review our manuscript and for the useful and interesting suggestions.

Reviewer 2: the data set is quite limited. Answer: we release our data set is quite small, we had planed to do some replicate studies this past winter, however due to the very warm conditions in southern Germany, there was very little snowfall over the entire transect (Elsa Weg) in the Black Forest. Unfortunately when there was snow it did not last long and we felt that the shallow snow pack increased the risk of contamination. Definitely further studies should be conducted to verify our initial results.

Reviewer 2: IC-ICP-MS should be written in full in the abstract. Answer: IC-ICP-MS has been extended to its full name in the abstract: ion chromatography-inductively

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coupled plasma mass spectrometry.

Reviewer 2: Iodine enrichments in aerosols are derived from the gas phase rather than bubble bursting. Answer: We agree that the iodine enrichments relative to seawater are a gas phase phenomenon as the bubble bursting can only account for an enrichment of approx. 50. This section of the introduction has been changed to read:

Bubble bursting and ejection of iodine rich material from the ocean surface microlayer is one possible mechanism for the iodine enrichments (Seto and Duce, 1972), although this can only produce, at maximum, an enrichment factor of approximately 50. Therefore, condensation of gaseous biogenic iodine compounds onto (or forming) aerosols is required to explain the large iodine enrichments observed in aerosols and rainfall (Woodcock et al., 1971; Moyers and Duce, 1972; Duce and Hoffman, 1976; O'Dowd et al., 2002; Baker, 2005).

Page 1000 l. 9: The incorrect reference to figure 1 has been replaced with the correct reference to Figure 2a. Thanks for picking this up.

Reviewer 2 page 1002, l. 16: Maybe you want to add the bromine enrichment to that figure as well (with a different scale). Answer: We have added the bromine enrichments to the figure with a different scale.

Reviewer 2: discussion of fig 5: simply from looking at the figure one might get the impression that the EF peaks at 800m and then declines with altitude. Could you comment on that?

Answer: On reanalyzing the data it appears that it is only possible to interpret the last part of the profile as a decrease in EF's if the sample from 934 masl is ignored. In fact, by fitting a 2nd order polynomial trend line to the data gave an r sq. value of 0.87 for iodine and 0.8 for bromine. It is difficult to interpret this change as removing the sample from 934 masl only leaves 2 data points. This is especially true considering that the positive linear relationship for the first 8 points is so strong. Also, a decrease in enrichment after 800 masl would somehow insinuate that Na was becoming enriched in the snow relative to iodine and bromine, which we do not have a mechanism for that we can support with data. In part the change in EFs with increasing altitude is due to the ‘decay constant’ of the exponential decay curves being lower for Na than for either Br or I. Speculatively we feel the most likely reason for the differences in the Na and halogen trends (and hence the rapid change in the enrichments factors) is the strong updrafts usually associated with orographic lifting, especially over such a short horizontal distance and large altitude change. Perhaps the rapid decrease in vapor pressure and increase in super saturation (particularly with respect to ice) led to rapid activation (probably sublimation of super cooled vapor) of small iodine/bromine enriched and Na depleted aerosols. Such distributions have often been observed in the marine environment (Moyers and Duce, 1972). However, this is rather elaborate and we don’t have any size-segregated aerosol or cloud microphysics data from the study site to back it up and as such has not been included in the manuscript. Of course we can never rule out some contamination by anthropogenic Na, being winter and all roads in the Black Forest are heavily salted. However, if this were to play a large role then one would not expect the strong and significant relationships noted here. Rather it would promote a random pattern of points due to different degrees of contamination. As such, in the revised manuscript we have suggested the possibility for decreasing Efs after ˜ 800 masl, but state that we do not have enough data to conclude weather the last points are anomalous or if a real decrease does occur and that more measurements should be made.

reviewer 2: p. 1004, l. 24: Pechtl et al., 2006 discuss mechanisms to change the iodate:Iodide ratio but not organic-I.

Answer: We referenced Pechtl et al., 2006 here because it shows the importance of org-I in reproducing iodate/iodide speciation. However, as suggested by the reviewer we have removed this reference from this location.

Reviewer: 1005, l. 20: "These same species.." - can you be certain that these are the same species or only the same peaks?

Answer: We can be certain as possible using the methods available for iodine speciation at such low levels. The conductions used in the IC-ICP-MS were identical and ion chromatography is a standard method for separating ionic species. Moreover, the columns are prefabricated by Dionex and so are very consistent in their retention. It is also unlikely that the retention parameters of each species to the stationary phase are so similar that we don't see any peak overlaps. For example, iodoacetic acid and iodopropionic acid have very similar retention times and we cannot adequately separate them for quantification; however we can qualitatively see that the two peaks overlap rather than coming at exactly the same time and as such know there are two different species. However, in saying this it is impossible to definitively tell using this method if the peaks are really only one species or a number of species with identical retention times. The only way to really be sure if they are individual species would be to employ a number of analytical procedures such as 1: enrich these compounds some $>$1000 times (which would require $>$1000L of sample water assuming 100% recovery) to get enough material and 2: analyze the resulting material with instruments such as H-NMR, C-NMR, and take a mass spectra. The main problem with doing all this is that we don't have a machine for the concentration step or enough sample material.

the DOI has been added to Baker (2004)

Reviewer: Consider moving the supplementary material Figure 1 into the main text. Why is the exact altitude only given for one sample?

Answer: The altitude is given for the point where there appears to be a change in the % organo-I fraction with altitude. This has now been removed to avoid any confusion. This graph is not included into the main text as it does not show a very clear trend, first decreasing until 718m and then increasing again. We prefer to leave this figure in the supplementary material available for interested persons, rather than obscure the message of the main text with further speculation about why we observe such trends.

Reviewer: Supplement Table 1: How strongly - if at all - diluted are the melted samples before analysis?

Answer: The samples are not diluted at all. They are simply allowed to warm to room temperature (so that the injection volume is not affected) and then analysed. This is one of the strong points of this method, it does not require any additives before speciation analysis. We have also added to the methods that we used 187Re as the internal standard for total halogen concentrations.

We have fixed the spelling mistake in supplementary table 1: orano-I has been replaced with organo-I. Thanks for pointing this out.

Reviewer 2: p. 1006, l. 9-17: The bromine size paradox cannot be explained by the mechanism suggested in the paper as many or even most fine particles in the marine boundary layer are not of marine origin, so that the mechanism should not rely on some sea-salt specific processes. Also note, that large sea spray droplets also carry a substantial amount of organic material as rising bubbles scavenge material from below the surface micro layer which then gets incorporated also in large sea spray droplets (see, e.g., Turekian et al, 2003, JGR, 108, 4157, doi:10.1029/2002JD002053).

Answer: We now agree that the bromine enrichments in small aerosols cannot be solely explained by the organic bromine, as it appears that even in studies where they only measured bromide (by ion chromatography with conductivity detection) the enrichment still exists. We believe that organo-Br may play a role and should be investigated further, but our data do not allow us to draw conclusions on this matter. Therefore we have removed this section from the manuscript. It now reads:

The majority of the total bromine is bromide, of which the majority is most likely from ocean water as suggested by relatively little depletion or enrichment compared to this source. The organically bound bromine in snow (max. 32%) may be derived from the ocean surface layer as discussed above for iodine or between reactive bromine species such as BrCl and organic material.

Reviewer 2: add error bars to the figures and give more information on the methods.

Answer: The method section has been significantly expanded. We analysed replicate or in one case triplicate samples of the first 4 samples from the profile with a maximum relative standard deviation (RSD) of 1.3 % for total iodine and 4.8 % for bromine. The individual standard deviations have been used for calculating errors for these first 4 samples and then the highest standard deviation (4.8 %) was taken when propagating errors for the remaining samples. Unfortunately we did not analyze any replicates for speciation. However, we have made many other analyses using the IC-ICP-MS method, primarily for lake water. Replicate analysis of these samples usually gives RSD's of $<$2% for both iodine species and therefore we have taken 2 % as the error when propagating the error for organo-I and enrichment factors. This is consistent with iodine speciation RSD's from other IC-ICP-MS studies (Heumann et al., 1994). The RSD for bromide was larger, usually between 2-7 % because bromine was 2 isotopes of about equal abundance and one of the isotopes (81Br) has significant interferences. We have used a RSD of 7 % for propagation of errors for organo-Br and enrichment factors. We have included these points, as well as further details on the analytical method, into the methods section of the manuscript.

Reviewer 2: The discussion in section 4.1 is a bit weak and the reader is left alone in finding out why the relationship is linear or not or should be linear or not and why there are these differences for different compounds as shown in figure 2 and 4.

Answer: We have looked closely again at the data and found that all elements show better regression statistics (r sq values) if the data (both metal and halogen) is fitted with exponential decreases curves. The exponential fits are significantly better than either the linear or inverse trends and are common for all elements, which seams to fix the problem of different elements following different curves. We have made this change in the manuscript, and also suggested two possible mechanisms for forming such a curve: constant removal with height due to a rainout effect and also dilution of the elemental concentrations by deposition of water vapor during snow crystal growth. To model these processes more comprehensively we definitely require significantly more data such as supersaturations, updraft speeds, drop/snow crystal size distributions etc.

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