

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 the first reviewer for the insightful comments on our manuscript. We have made most of the changes suggested by the reviewer as outlined below.

Reviewer 1 makes the interesting (and correct) observation that it is not the actual elevation that affects the iodine and bromine concentrations in the snow, but removal by precipitation induced by increasing supersaturation in the atmosphere as the cloud mass is forced to higher altitudes. We agree with this and thank the reviewer for the insight. The manuscript no longer presents elevation as the removal mechanism but rather the precipitation associated with orographic lifting and subsequent increase in supersaturation within the cloud masses. We note however that orographically induced precipitation is likely to be different (more intense) than from, say, normal precipitation over the lowlands. In particular, the strong updrafts associated with orographic lifting

Interactive
Comment

over such a rapid increase in altitude, and hence the rate of supersaturation increase, are expected to be more intense than experienced by lowland snowfall. As such the new version of the manuscript reflects that the decrease in iodine and bromine with height is related to orographically induced precipitation and that this orographically induced precipitation is a strong influence on iodine concentrations in snow.

Reviewer 1 suggests that the metal data is not really needed for the manuscript and is not introduced at the beginning of the paper. The metal analysis was not the initial intention of the study, and we definitely would need more data to incite a natural or anthropogenic source of these elements. However, we were looking for a way to test whether the Na-halogen correlation was a reflection of the marine origin of these elements or due to simply a common atmospheric scavenging/removal process (as suggested by the reviewer of another one of our papers). As we show in this paper, all of the elements are very well correlated (further highlighted in the revised manuscript), reflecting that they are all internally mixed within the snow and that the correlations observed between Na and the halogens cannot be used here to infer a marine source. The halogen-metal correlations were the only way we could show that the removal process was not halogen specific, but rather an overall removal process. Indeed, the second reviewer suggested that perhaps diffusion of gaseous iodine/bromine into/out of the snow at the lower temperatures experienced at higher altitudes may be a mechanism for the decreasing concentrations with altitude, however this cannot be the case as the metals cannot partition into the gas phase and the correlations would be lost if temperature dependent partitioning was to play a role. As such, we prefer to keep the metal data in the manuscript. We have included further details on the analytical procedure in the methods section including reference material analysed and relative standard deviations and have also added error bars to the appropriate graphs.

Reviewer 1: Bubble bursting is not the dominant mechanism for the iodine enrichment in aerosols.

We fully agree with this. The relevant part of the manuscript introduction has been

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changed to read:

Bubble bursting and ejection of iodine rich material from the ocean surface microlayer is one suggested mechanisms for the iodine enrichments (Seto and Duce, 1972). However, this can only produce, at maximum, an enrichment factor of ~50. Therefore, condensation of gaseous biogenic iodine compounds onto (or forming) aerosols must be the dominant mechanism for the iodine enrichment (Woodcock et al., 1971; Moyers and Duce, 1972; Duce and Hoffman, 1976; O'Dowd et al., 2002; Baker, 2005).

The text on p 999 should be altered to make it clear that Campos (1997) studied changes in iodine speciation only.

The text relating to Campos (1997) now reads:

It has been shown that no significant changes in iodine speciation occur in samples stored for up to two months (Campos, 1997).

Reviewer 1: Please give some more details of standard reference material BCR611. I believe it is a groundwater reference material.

This is the only standard reference material that we have been able to find for fresh water with low ($<10 \mu\text{g/l}$) concentrations of iodine. The limited reference materials for aqueous iodine species is currently quite a problem, as even BCR611 only gives indicative values for total iodine and iodide. Apparently there was no iodate in the sample.

More information on this reference material has been added to the methods section and now reads:

The accuracy of total iodine, total bromine, bromide and iodide concentrations were checked using standard reference material BCR-611. BCR-611 is a groundwater reference material with a certified bromide level of $93 \pm 4 \mu\text{g/l}$. It also gives indicative values for total bromine ($107 \pm 11 \mu\text{g/l}$), total iodine ($9.3 \pm 1.3 \mu\text{g/l}$), and iodide ($9.0 \pm 1.1 \mu\text{g/l}$). More information on this reference material can be found at the European In-

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stitute for Reference Materials and Measurements website: <http://www.irmm.jrc.be>. All of our values were consistently within the error given in the certificate except for total bromine which was slightly lower (bromide $93.5 \mu\text{g/l}$, total bromine $94 \mu\text{g/l}$, iodide $9.4 \mu\text{g/l}$, and total iodine $9.65 \mu\text{g/l}$). We believe that our value for total bromine is more realistic than the reference material average of $107 \mu\text{g/l}$, as this high concentration would imply a relatively large proportion of organically bound bromine in the groundwater, which is unlikely.

Spelling error ‘monotonous’ has been corrected with ‘mountainous’. We agree this is a much more appropriate and accurate description of the Alps.

Reviewer 1: “dust” is a very vague term when applied to the metals studied here. Is this intended to mean soil-derived mineral dust? Many of the metals reported here (e.g. V, Mn, Zn, Pb) have significant atmospheric sources from anthropogenic activity rather than soil uplift.

The reference to dust has been removed. The origin of all of these metals (natural vs anthropogenic) is outside the scope of this paper, and would require a considerably larger data set to make any authoritative assessment (including analysis of Al as a tracer of continental material). The metals are used only to show that the removal process is not confined to iodine and bromine, suggesting that the iodine and bromine are mixed with these other elements (shown by high correlation coefficients) and are removed in unison.

In figure 2 the data points are only for the sampling tour on the 11 and 12th of February. This has been made clearer in the figure caption.

Error bars have been added to all appropriate graphs (i.e. figs 2, 4, 5, and supplementary material figs 1 and 2) and represent 1 standard deviation of the analytical error.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 995, 2007.