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Iodine and Bromine speciation in snow and the effect of elevation

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Abstract

Iodine is an essential trace element for all mammals and may also influence climate through new aerosol formation. Atmospheric bromine cycling is also important due to its well-known ozone depletion capabilities. Despite precipitation being the ultimate source of iodine in the terrestrial environment, the processes effecting the distribution, speciation and transport of these elements are relatively unknown. The aim of this study was to determine the effect of orographic lifting on iodine concentrations and also quantify inorganic and organic iodine and bromine species. Snow samples were collected over an altitude profile (~800 m) from the northern Black Forest and were analysed (IC-ICP-MS) for iodine and bromine species and trace metals (ICP-MS). All elements and species showed a significant (r^2>0.65) inverse relationship with altitude despite the short (5 km) horizontal distance of the transect. In fact, total iodine more than halved (38 to 13 nmol/l) over the 800 m height change. The results suggest that orographic lifting of cloud masses has a major influence on iodine levels in precipitation and is perhaps more important than lateral distances in determining iodine concentrations in terrestrial precipitation. The microphysical removal process was common to all elements. We also show that organically bound iodine is the dominant iodine species in snow (61–75%), followed by iodide. Iodate was only found in two samples despite a detection limit of 0.3 nmol/l. Two unknown but most likely anionic organo-I species were also identified in IC-ICP-MS chromatograms and comprised 2–10% of the total iodine. The majority of the bromine was inorganic bromide with a max. of 32% organo-Br.

1 Introduction

Iodine is an essential nutritional element for all mammals, including humans. A lack of dietary iodine intake can lead to iodine deficiency disorders such as goiter and in more severe cases, cretinism, which can cause both mental and physical disabilities (Dobson, 1998; Slavin, 2005). Iodine transport from the oceans by clouds and

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aerosols and subsequent precipitation as rain or snow is one of the primary factors influencing iodine levels and availability on the continents (Whitehead, 1984; Fuge and Johnson, 1986; Moran et al., 2002). However, there is conflicting evidence regarding the terrestrial processes effecting iodine concentrations in rainfall and particularly with the suggestion that iodine levels decrease with distance from the ocean (Fuge and Johnson, 1986; Krupp and Aumann, 1999; Schnell and Aumann, 1999; Slavin, 2005). Most studies concentrate on lateral distances and to the best of our knowledge there has been only one other study focusing on the effect of elevation on iodine levels in precipitation (Duce et al., 1965). Iodine in rainfall is not a simple product of sea spray as observed for Cl, with large (100–10 000) enrichment factors in both rain and aerosols compared to ocean water (Duce et al., 1965; Duce et al., 1967; Winchester and Duce, 1967; Woodcock et al., 1971; Sturges and Barrie, 1988). It is thought that bubble bursting is the dominant mechanism for the iodine enrichment although release of gaseous biogenic iodine compounds and subsequent iodine aerosol formation undoubtedly also contributes (Woodcock et al., 1971; Moyers and Duce, 1972; Duce and Hoffman, 1976; O'Dowd et al., 2002; Baker, 2005). However, although research on iodine in rainfall is still limited, iodine levels and particularly speciation in snow is almost non-existent. Snow is an important factor in the hydrological cycle during winter at higher latitudes and as such warrants further attention. One explanation for the lack of speciation data is undoubtedly the very low concentrations of individual iodine species in rain and snow and therefore methods for reliable speciation are often complex or unavailable. However, with the wide spread use of ICP-MS and the ability to couple an ion chromatograph to this extraordinarily sensitive instrument (Gilfedder et al., 2006) it is possible to measure anionic iodine and bromine species into the sub nmol concentration range. One of the features of this method is that many interfering ions, such as Cl, are separated from the element of interest and therefore the sensitivity of individual species is even greater than observed for total concentrations. Iodine speciation in the liquid phase is also of interest for atmospheric iodine cycling as there is a discrepancy between most model calculations, which suggest that iodate should

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be the dominant iodine species in the particulate phase (Vogt et al., 1999; McFiggans et al., 2000), and field observations which show that organically bound iodine and iodide are the dominant iodine species (Baker et al., 2001; Baker, 2004, 2005; Gilfedder et al., 2006). Recent modeling work to reconcile this discrepancy further highlights the potential importance of organo-I in atmospheric chemistry cycles (Pechtl et al., 2006). For example, organo-I has implications for the sea/atmosphere fractionation mechanism that concentrates iodine in aerosol and rain and perhaps for iodine's effectiveness in destroying tropospheric ozone (Duce and Hoffman, 1976; Baker, 2005). Bromine is also of interest in atmospheric research due to (1) its well-known ozone depletion capabilities, and (2) the interesting observation that activated bromine (Br_2) is librated from larger size aerosols causing bromine depletion relative to seawater, whereas small aerosols tend to be enriched in bromine (Sander et al., 2003). In this work we investigate the changes in iodine, bromine species (including the organically bound fraction), and metal concentrations in snow with altitude. The primary aims of this study are to clarify the role of microphysical landscape features (mountains) on the distribution of iodine and bromine as well as determine the dominant iodine species in snow.

2 Methods

A transect for snow sampling was selected in the northern Black Forest between the village of Ottenhöfen (326 masl) and the summit of the highest peak in the area; "Hornisgrinde" (1164 masl). This transect was chosen to minimize the horizontal distance (5 km) and maximize changes in elevation. Fresh snow was collected on the 11 and 12 of February 2006 in LDPE bottles at selected locations between Ottenhöfen and Hornisgrinde along the hiking track "Elsa Weg". Back trajectories (HYSPLIT model; http://www.arl.noaa.gov/ready/hysplit4.html) of air masses arriving at the site were calculated for the previous six days with a new trajectory starting each day at 0h UTC using an altitude of 500 m above the ground level and the FNL meteorological database

(Fig. 1). The data show that the majority of the precipitation sampled was derived from the Atlantic Ocean. Also, the weather system had passed from the low lands to the west of the sampling site before being orographically lifted over the Black Forest mountain range. All samples were collected from open areas and clearings in the forest. Four samples were also taken on 26 January 2006 at a height of 1034 masl (Mummelsee) and again four additional samples were taken in mid April (14 April 2006) from very old snow deposits at 796 masl and above on the same transect. This remnant snow was only present due to the elevation and all snow from lower altitudes had previously melted. It appeared to be recrystallised into small ice particles and had probably undergone partial melting and refreezing. It also contained small debris from the surrounding forest on the surface which was discarded by filtering.

The snow was thawed, filtered (0.45 μm) and stored at 4°C until analysed (max. 1 month). It has been shown that no significant speciation changes occur in samples stored for up to two months (Campos, 1997). Samples were allowed to warm to room temperature and were then analysed for total iodine, bromine and metals (Li, V, Mn, Co, Rb, Zn, As, Mo, Pb, Ba, Sb and U after acidification with suprapur HNO_3) by an inductively coupled plasma–mass spectrometer (ICP-MS). Iodine and bromine species (iodide, iodate, bromide, bromate and organically bound I/Br) were analysed by coupling an ion chromatograph to the ICP-MS (IC-ICP-MS). Organically bound iodine and bromine was calculated as total iodine minus the sum of the inorganic species (i.e. Org-I = total I − (I^- + IO_3^-)). Iodine and bromine species were quantified using a Dionex AS16 column with an AG16 guard column, 35 mmol NaOH eluent, a flow rate of 0.9 ml/min and cyclone spray chamber on a Perkin Elmer quadrupole ICP-MS. This method has a detection limit for aqueous iodine species of about 0.3 nmol/l and each sample has a run-time of only 12 min. Moreover, no sample pretreatment is required. Unidentified organic iodine species were observed in all chromatograms; while not strictly correct these species have been quantified based on the iodide calibration curve. This should not pose a large problem as all iodine atoms are converted to I^+ in the plasma prior to quantification with the mass spectrometer. Total iodine, total bromine, bromide

and iodide concentrations were checked using standard reference material BCR611. This reference material is certified for bromine, but only gives indicative values for iodine. However, all of our values were consistently within the error given in the certificate. Sodium was analysed by a Perkin Elmer flame AAS after acidification with
5 HNO_3.

3 Results

Total iodine concentrations in snow samples were slightly higher than or similar to other existing studies (Duce et al., 1965; Jickells et al., 1991; Moran et al., 1999; Gilfedder et al., 2006), but decreased significantly with elevation (r^2=0.77; Fig. 1a). Over the 864 m
10 height change from Ottenhöfen (326 masl) to Hornisgrinde (1164 masl) total iodine levels decreased consistently from a maximum of 38 nmol/l to 13 nmol/l, respectively.
    IC-ICP-MS iodine speciation analysis showed similar results to total iodine. Iodide concentrations decreased linearly with increasing altitude from 11.4 nmol/l at Ottenhöfen to 3.9 nmol/l at Hornisgrinde (r^2=0.88; Fig. 2a). No iodate was observed in
15 any of these snow samples. Organically bound iodine also decreased with altitude, with maximum concentrations at Seebach (400 masl; 28.8 nmol/l) and then steadily decreased to 9.1 nmol/l at Hornisgrinde (Fig. 2a). Organically bound iodine was the most abundant iodine species in all samples (61–75% of total iodine), with no clear change in percentages with altitude (Supplementary Fig. 1). Interestingly, two unidenti-
20 fied organo-I species were consistently found in IC-ICP-MS chromatograms in all snow samples between the iodide and iodate peaks (Fig. 3). It is thought that these peaks are anionic organic iodine compounds due to their consistent separation by the anion exchange column and stable behavior. The larger of the two peaks had a retention time of 6.8 min and the smaller peak eluted at a slightly shorter time of 5.4 min. These
25 peaks generally accounted for 5–10% of the total iodine concentrations and also displayed an inverse linear relationship with altitude (supplementary material Table 1 http: //www.atmos-chem-phys-discuss.net/7/995/2007/acpd-7-995-2007-supplement.pdf).

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Total bromine concentrations showed much the same pattern as iodine, decreasing steadily with altitude from 129 nmol/l at Seebach to 38.8 nmol/l at Hornisgrinde (Fig. 2b). Bromide was also inversely correlated with altitude with an r^2 value of 0.91. Organically bound bromine was not so well correlated with altitude (r^2=0.63), however the trend is still clear, as with all other species: decreasing concentrations with increasing altitude. Percent organically bound bromine displayed no relationship with altitude (r^2=0.02; data not shown). In contrast to iodine, the majority of bromine in snow was inorganic bromide (68–81%). Bromate was not observed in any of the samples, whereas organically bound bromine accounted for 18–32% of the total bromine.

Metal concentrations also decreased with altitude. In fact, many of the metals even showed a stronger inverse relationship with altitude than iodine and bromine. Manganese, Na, Co, Rb, Zn, Ba, and U tended to follow a decay curve described by the general equation M_{et}=m/alt + b whereas Li, V, As, Mo, Sb, and Pb decreased linearly with altitude (i.e. M_{et}=m*alt + b). Also, significant positive (p<0.001) correlations between all elements, including iodine and bromine, were observed (Supplementary material Table 4). All data can be found in sup. Table 3 (http://www.atmos-chem-phys-discuss.net/7/995/2007/acpd-7-995-2007-supplement.pdf) and Li, Co, Na and Pb are plotted in Fig. 4.

Total iodine concentrations in the four snow samples taken in January from the surface of a small frozen lake at 1036 m (Mummelsee) were similar (although slightly lower) to those taken in February. Organo-I accounted for 53–62% of the total iodine in these samples and again no iodate was observed. The only notable observation for bromine from these samples is that the percent organically bound bromine is nearly identical to all other samples and is therefore relatively invariant with time (ca. 30%). The snow sampled in April contained significantly lower iodine (av. 3.9 nmol/l) and bromine (av. 33.4 nmol/l l) concentrations than the previous sampling tours and showed no significant relationship with altitude. These anomalously low results are undoubtedly due to partial melting and refreezing and other post depositional changes. It is thought that, due its large ionic radii, iodine is excluded from the recrystallizing ice and

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hence is preferentially leached from the snow during partial melting. Organo-I composed approximately 50% of the total iodine with iodide being the next most abundant species. Iodate was also observed in two chromatograms, although it was only responsible for at maximum 16% of the total iodine. Interestingly, we also observed the same

5 unidentified iodine peak (retention time 6.8 min) between the iodate and iodide peaks as noted above. This suggests that this species is stable and can remain in the snow during melting-refreezing events.

   Molar iodine and bromine enrichment factors (EF) relative to seawater may be able to trace the origin of these elements (Winchester and Duce, 1967; Woodcock et al.,

10 1971). EFs are calculated by dividing the halogen to sodium ratios in snow by halogen to sodium ratios in seawater (e.g. I/Na in snow divided by I/Na sea). When these enrichment factors are calculated, it is immediately apparent that iodine is highly enriched in snow (average EF 204, max. 281). EFs appear to increase linearly with elevation until 796 masl (r^2=0.95), whereafter the relationship collapses (Fig. 5). In contrast to

15 iodine, bromine enrichment factors range from slightly depleted (0.7) at Ottenhöfen to no enrichment or only slightly enriched over the remainder of the transect (max. 1.4). Bromine enrichment factors also increase linearly with altitude up to 796 masl, whereafter the relationship is again lost (data not shown). The apparently random behavior of these last three points is due to Na following an exponential decrease curve rather

20 than the linearly trend displayed by I, Br and associated species. We can also calculate iodine enrichment factors relative to bromine (I/Br in snow divided by I/Br in sea). These EFs (av. 602, max 665) show that iodine is more enriched relative to bromine than to sodium, however there is no relationship with altitude (r^2=0.3; data not shown). Enrichment factors for iodine relative to bromine from the January samples were lower

25 than those taken in February, averaging 402.

4 Discussion

4.1 Microphysical processes

There is growing evidence that suggests iodine concentrations in rainfall are not simply related to distance from the ocean (Krupp and Aumann, 1999; Moran et al., 1999; Michel et al., 2002). While back trajectories are not given in any of these studies and the authors assume that the closest ocean is the source of rainfall, the data still appears to be relatively robust. The data presented here indicates that, compared to lateral distance, elevation has a large effect on the total iodine concentrations as well as the individual iodine species in snow. In fact, iodine concentrations more than halve over a horizontal distance of only 5 km. Moreover, the systematic decrease in concentration is not confined solely to iodine and bromine as the 12 metals also analysed displayed a similar pattern. Duce et al. (1965) also found a relatively linear relationship between height and iodine concentrations in Hawaii, however the scatter in the data points were much greater than observed in this study. Interestingly, (Reithmeier et al., 2006) have also suggested recently that, based on differences in ^{129}I concentrations between Zürich and the Fiescherhorn ($\sim$4000 masl) glacier Switzerland, that radiogenic iodine is removed with altitude. Our data suggest that depletion of elements due to orographic lifting is a general atmospheric microphysical processes rather than element specific and for iodine and bromine this is a linear relationship. This is supported by the significant correlations between all of the elements, which also indicate that iodine, bromine and metals are internally mixed within the snow crystals. Such an altitude dependence for iodine is perhaps not unexpected considering that some of the areas most effected by iodine deficiency disorders are (or in some cases, were, before introduction of iodinated salt) located in monotonous regions such as the Alps or the Himalayas (Stewart, 1990; Slavin, 2005). Perhaps the height or altitude that a weather system must cross will have the largest influence on iodine concentrations in precipitation rather than the distance traveled.

While it perhaps appears logical that iodine, bromine, Li, V, Zn, As, Mo, Sb, and

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Pb decrease linearly with altitude due to a rainout effect, this is not in fact the case. As a simplification, as the cloud of interest rises, it cools. Cooling lowers the vapor pressure of the air, increasing the supersaturation in the atmosphere and increasing the rate of nucleation, snow crystal growth and hence snowfall. This should in theory consistently deplete the cloud in its elemental constituents as the cloud gains altitude, but not in a linear fashion. Assuming that the elemental abundance is homogeneous between snow crystals, the concentration in the cloud, and hence falling snow, should steadily decrease as the cloud undergoes orographic lifting. Elemental depletion in the cloud mass continues as the cloud rises, so that less and less iodine is available for inclusion in snow. The element concentrations in the deposited snow should therefore conform to an inverse decay function ($y=m/x + b$). In fact, this exact trend is observed for Na, Co, Rb, Zn, Ba. At this stage we only have data from one vertical profile, and therefore cannot, as yet, determine if the non-linear and linear patterns are an elemental specific fractional effect between water vapor and snow crystals (Borys et al., 1988) or a random effect of sampling and analysis.

4.2 Speciation

Iodine is of particular interest in atmospheric chemistry due to its possible role in new aerosol formation (O'Dowd et al., 2002), tropospheric ozone depletion (von Glasow and Crutzen, 2003), atmosphere-ocean interactions (Duce and Hoffman, 1976) and more generally as an important constituent of tropospheric chemical cycles. While there has been a large research effort to quantify the gaseous iodine flux species from the ocean and their role in new particle formation in recent years, most of these studies have concentrated on inorganic speciation in the particulate and aqueous phase. Indeed, atmospheric models indicate that iodate should be the only stable long-term iodine species in particles and the aqueous phase (Vogt et al., 1999; McFiggans et al., 2000; Saiz-Lopez et al., 2006). However, it is becoming apparent that organically bound iodine is a major, if not the most important species in small aerosol particles, rain, and snow (Baker et al., 2000; Baker, 2005; Gilfedder et al., 2006; Pechtl et al.,

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2006). It is obvious from the data presented here that organically bound iodine is the dominant species in snow from the northern Black Forest, accounting for between 60–75% of total iodine. To date, there appears to be three plausible mechanisms for the formation of organically bound iodine in the atmosphere; 1) ejaculation of iodo-organic rich material from the ocean surface micro-layer into the atmosphere during bubble bursting, whereafter the small droplets evaporate leaving a small aerosol which may subsequently deliquesce and become a cloud droplet (Seto and Duce, 1972; Cavalli et al., 2004); 2) biogenic iodine gases emitted from the ocean (e.g. CH_3I, I_2 or CH_2I_2) are photolysed to $I°$ which, after a series of reactions, ends up as IO, I_2 or HOI (von Glasow and Crutzen, 2003). These species may easily bind to atmospheric organic material, either gaseous (e.g. terpenes and/or isoprene (Greenberg et al., 2005)) or particulate matter; 3) Biogenic terrestrial organo-I emissions (Dimmer et al., 2000); these can probably be neglected in this study due to very little terrestrial biological pro-ductively during the European winter. The second mechanism may reduce the impact of iodine on ozone depletion in the troposphere by reactions between highly reactive iodine species and organic material. Mechanisms 1 and 2 could also be occurring si-multaneously, which may lead to two organically bound fractions, those associated with secondary iodo-organics, and those associated with higher molecular weight material from the ocean surface. An interesting finding is the two unknown, most likely organic, peaks observed in the snow IC-ICP-MS chromatograms. These same species have also been observed in rain from Lake Constance, Germany, Patagonia, Chile and in a glacier core from the Fiescherhorn glacier (Gilfedder et al., 2006). This supports our earlier suggestion that these are important iodine species in the atmosphere, and may even be globally ubiquitous. Unfortunately, it has not been possible to identify these peaks with the standards available to date. These species may be formed by photolysis of iodo-organics derived from primary aerosols or by secondary gas phase reactions.

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. While our dataset does not measure aerosols directly and therefore we cannot make any firm statements as to organo-bromine in aerosol and the bromine size paradox, perhaps we can speculate briefly here on this issue. Firstly, the paradox is that large particles ($>1\mu$m) display a characteristic bromine depletion relative to seawater due to acid catalyzed bromine activation (formation of volatile Br$_2$) while small particles ($<1\mu$m) typically display bromine enrichment factors of 2–10 relative to ocean water (Sander et al., 2003). This is in contrast to theory which suggests that smaller particles, which are more acidified than their larger counterparts, should display even larger bromine deficits. However, organic material and particularly humic-like substances such as found in the ocean micro-layer tend to consolidate on acidification. As such, rather then becoming volatile, bromine bound to organic material would condense in acidifying aerosols. The enrichment of organically bound bromine in smaller aerosols is probably a fractionation effect during bubble bursting with the larger aerosols more closely representing bulk seawater (forming when the cavity created after bubble bursting collapses) whereas the small aerosols may more closely represent the microlayer due to ejaculation of small droplets from the breaking bubble skin.

4.3 Origin of the iodine and bromine

Finally we consider the enrichment factors and the possible origin of iodine in snow. Iodine in snow is highly enriched relative to both iodine/bromine and iodine/sodium ratios in seawater. Similar enrichments are well documented in marine aerosols and rain samples and is thought to be a function of both fractionation at the ocean surface during bubble breaking and emissions of biogenic iodine gasses (Duce et al., 1965; Duce et al., 1967; Woodcock et al., 1971; Sturges and Barrie, 1988; Baker, 2004, 2005). The observation that the snow sampled here display almost identical enrichment factors as marine aerosols (Duce et al., 1965; Baker, 2005) tend to suggest that iodine and bromine in snow originate from deliquescence of these aerosols. As such, we hypothesize that iodine is transported to the continents from the ocean primarily by aerosols

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and aerosol derived droplets. It is interesting to note that iodine enrichment factors in precipitation are also large in the winter, when biological productivity in the ocean is generally low at mid to high latitudes (O'Dowd et al., 2004). This suggests that at least a part of the enrichment is due to physical mechanisms such as bubble bursting rather
5 than purely biological. As mentioned above, it is likely that the enrichment of iodine in aerosol, rain, and snow is related to both biological and physical mechanisms.

5   Conclusions

Iodine is an essential element for all mammals and may also be involved in new aerosol formation. We have presented here iodine and bromine speciation and total metal
10 concentrations in snow over an altitude profile ranging from 326 to 1164 masl in the northern Black Forest. Iodine species (total I, I$^-$ and org-I), bromine species (total Br, Br$^-$, org-Br) and metals decrease consistently over the height change within only 5 km horizontal distance. In fact iodine concentrations more than halve over this distance. Therefore, it is suggested that orographic lifting of cloud masses and subsequent pre-
15 cipitation is the major influencing factor on iodine and other elemental concentrations in precipitation. This may reconcile previous data, which has been ambiguous as to the relationship between iodine concentrations in rainfall and distance from the coast in that orographic cloud lifting may be the dominant influence rather than horizontal distance.
20   Iodine:sodium ratios in snow from the northern Black Forest indicate that iodine is highly enriched compared to iodine:sodium ratios in ocean water, whereas bromine ranges from slightly depleted to slightly enriched relative to seawater. Based on these enrichment factors and their resemblance to marine aerosol it is proposed that iodine and bromine in snow are derived from deliquescence of marine aerosol and subse-
25 quent riming of snow crystals with these droplets. The metals are most likely derived from dust nuclei which are vital for the formation of snow.
  In contrast to atmospheric models, which predict iodate as the only stable iodine

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species in particulate and aqueous phases, organically bound iodine was the most abundant iodine species in snow, followed by iodide. No iodate was found in the snow samples from January or February although a small amount was observed in two samples of very old snow in April. The organic iodine probably originates from a combination of 1) ejaculation of iodine-rich oceanic microlayer into the atmosphere as well as 2) addition of gaseous or (gas phased derived) reactive iodine species to preexisting organic molecules. Active species such as HOI, I_2 and IO are likely candidates for such reactions. It is clear from this and previous studies that organic iodine is an important part of the atmospheric iodine cycle and as such warrants further attention.

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Iodine and Bromine speciation in snow

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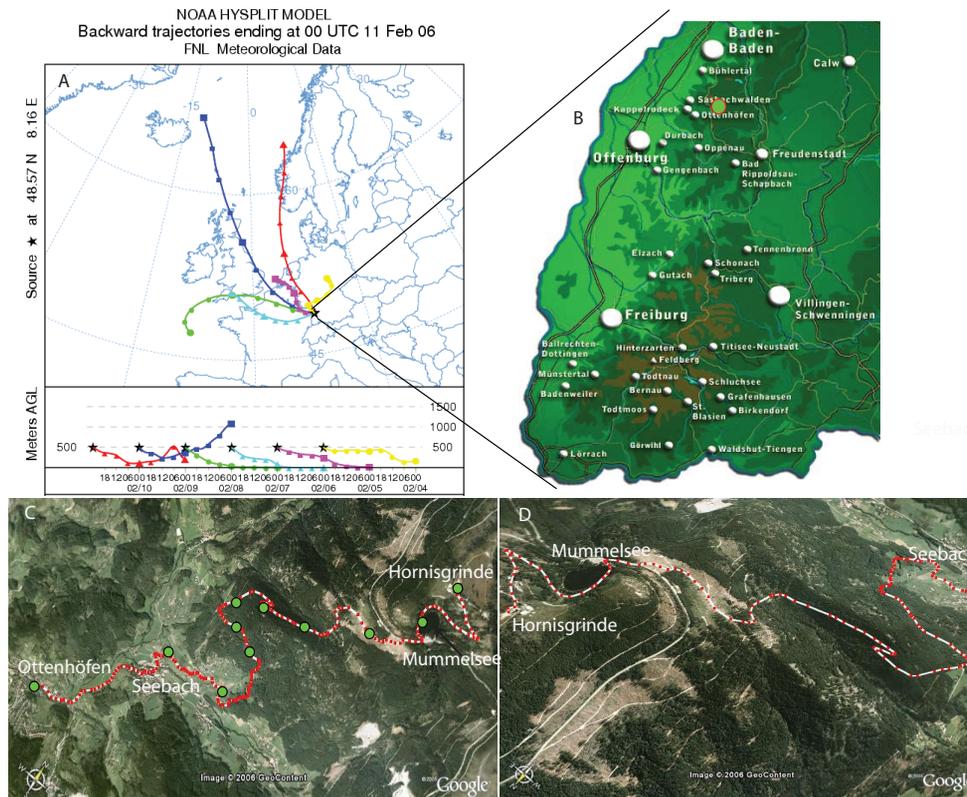
Fig. 1. (A) Europe map with sampling site and 6 day back trajectory for air parcels arriving at Ottenhöfen, **(B)** The Black Forest mountain range and sampling site, **(C)** and **(D)** Sampling transect and sampling sites (green circles) from Ottenhöfen (326 masl) to Hornisgrinde (1164 masl).
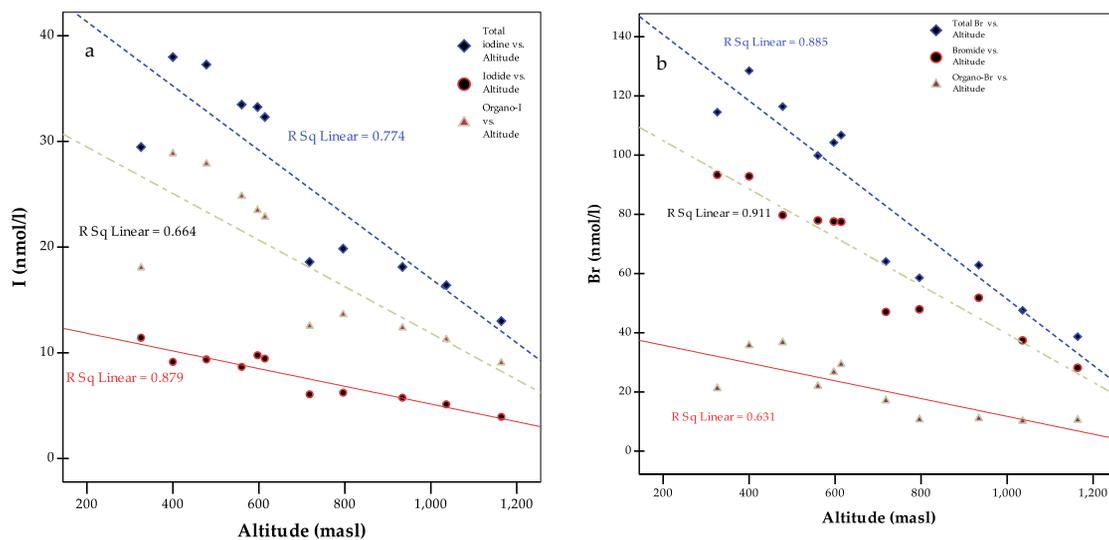
Fig. 2. (a) Total iodine, iodide and organically bound iodine in snow vs. altitude. **(b)** Total bromine, bromide, and organically bound Br in snow vs. altitude.

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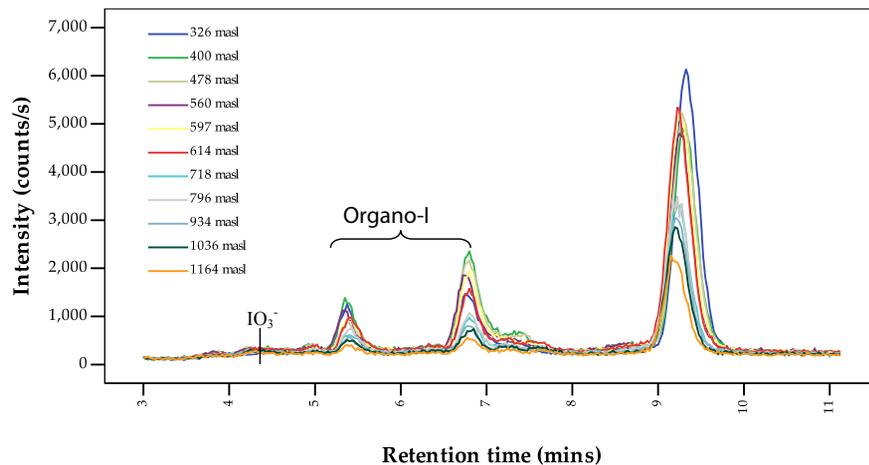
Fig. 3. IC-ICP-MS chromatogram of iodine species in snow. Iodate less than 0.3 nmol/l. Largest iodide peak 11.4 nmol/l.

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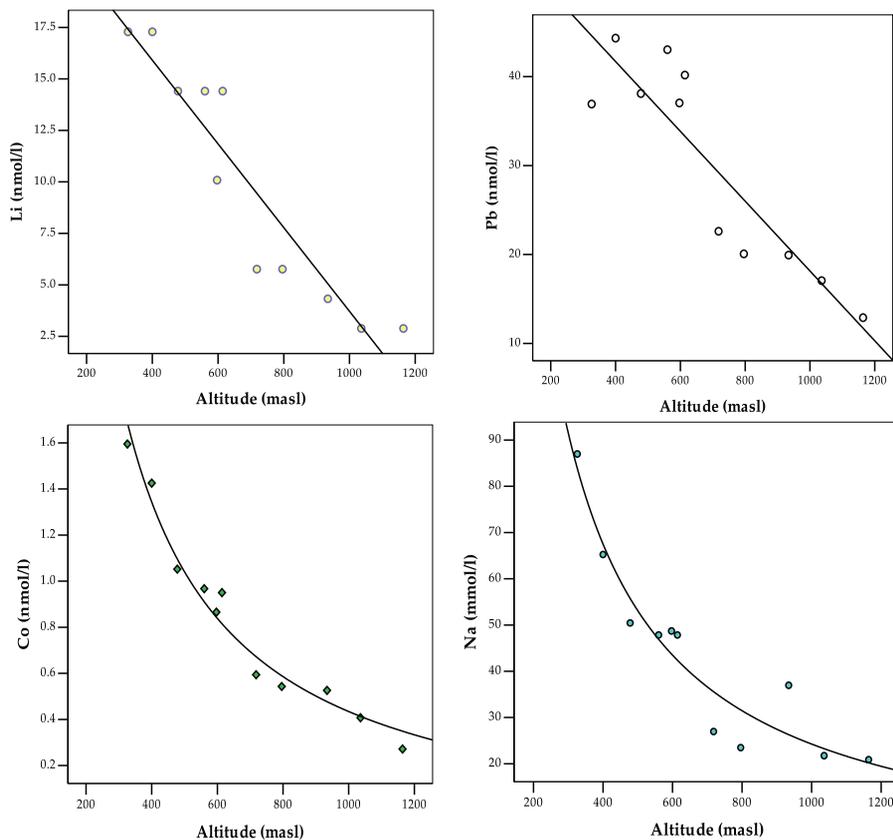
**Fig. 4.** Lithium, Co, Pb and Na concentrations vs. altitude in the northern Black Forest, Germany.
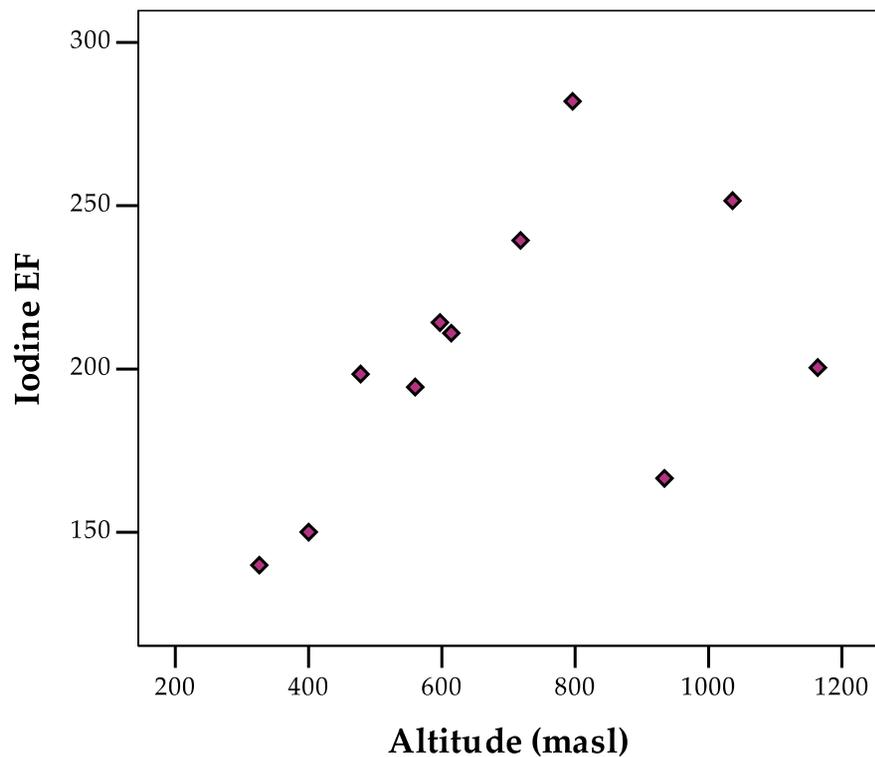
Fig. 5. Iodine enrichment factors relative to seawater Na concentrations.

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