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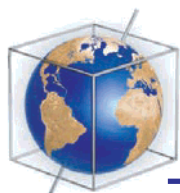
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Transfer of atmospheric boron from the oceans to the continents: An investigation using precipitation waters and epiphytic lichens

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[1] **Abstract:** The variation of B concentration in atmospheric deposition was studied from the analysis of 35 individual rain events, 17 snow packs, and 17 lichens sampled over NE North America (south from Hudson Bay) and Asia (from the coast of Bangladesh to the high Himalayas of Nepal). Rain samples show a range of B concentration between 0.3 and 9.4 $\mu\text{g/L}$ (average of $1.8 \pm 1.7 \mu\text{g/L}$), excluding two rains with higher B contents of 17 and 37.5 $\mu\text{g/L}$, most likely reflecting anthropic contamination. Snowpacks and lichens which average atmospheric deposition over periods of a few months to a few years show a smaller range of variation, from 0.1 to 2.3 $\mu\text{g/L}$ (average $1.1 \pm 0.8 \mu\text{g/L}$) for snowpacks and from 1 to 25.9 ppm for lichens. The lichens have elemental ratios (such as B/Cl) similar to the average of rains, showing that they are good monitors of atmospheric B deposition without significant biofractionation of elements. This is also demonstrated by their halogen contents, which follow the systematics of the atmospheric distribution of these elements previously derived from the study of rains and atmospheric particles. Though individual rains do not show systematic decrease in B concentration with distance to the sea, this behavior is clearly shown by samples having longer integration times, snowpacks, and lichens. The snow and lichen data show that seawater is a major source of atmospheric B. Using the lichen data, the enrichment factor (normalized to Na) of marine air masses relative to seawater is estimated to be ~ 13 (average B/Na of 5.6×10^{-3}). This implies that the fractionation factor of atmospheric suspended marine particles relative to seawater ($F^X = (X/\text{Na})_{\text{particle}} / (X/\text{Na})_{\text{seawater}}$) is 0.177. Thus B transfer from seawater to the atmosphere occurs mostly via degassing of sea salts, the residence time of gaseous B being estimated at 15.9-fold that of particulate B. The distribution of B in the atmosphere between gaseous B and degassed sea salts can be used to model the large range of B concentrations measured in single rain events by selective removal of one of the two B components. In this model, unfractionated marine air masses can reach the continents with very variable B concentrations, between ~ 0.2 and $\sim 20 \mu\text{g/L}$.

Keywords: Boron, concentration, atmosphere, lichens, aerosols, rains.

Index terms: Evolution of the atmosphere; geochemical cycles; chemical evolution; atmosphere.

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Theme: Geochemical Earth Reference Model (GERM) **Guest Editor:** Hubert Staudigel

1. Introduction

[2] Because atmospheric B measurements are scarce and difficult to make, the atmospheric behavior of B is still poorly understood. It has been suggested from previous studies of B concentrations in atmospheric gas and particles over the sea and inland that the major source of atmospheric B was the degassing of sea-salt particles. The flux of marine B from seawater to the atmosphere was estimated to $\sim 200 \times 10^{10}$ g/yr, which stands for approximately half of the total atmospheric B flux [Duce, 1996]. Volcanic B emissions are the source of the other half of B input to the atmosphere, while anthropogenic sources due to coal burning and agricultural fires represent only minor contribution [Duce, 1996]. The major fraction of the atmospheric B is gaseous, commonly considered to be essentially in the form of boric acid ($B(OH)_3$), with a gas to particulate ratio for B ≈ 74 [Fogg and Duce, 1985].

[3] Though coastal rains may show B enrichments by a factor of 2 or more compared to rain sampled at distance from the sea [Carrier and Brezonik, 1978; Fogg and Duce, 1985] and are known to be enriched in B relative to seawater ($(B/Na)_{rain}/(B/Na)_{sea} \approx 11$ [Gast and Thompson, 1959; Fogg and Duce, 1985]), the role of the oceans either as a source or as a sink for atmospheric B is still debated. This is first due to the fact that coastal rains show a strong variability in B concentrations, i.e., from 0.3 to 12 ppb B at Narragansett, Rhode Island [Fogg and Duce,

1985]. In addition, experimental and thermodynamic treatments of the evaporation of marine B come up with contradictory views. Laboratory experiments, in which air was blown over a container of seawater and collected for analyses of particles and gas, have shown that $\sim 1-2\%$ of the B was recovered in the condensed phase at $12^\circ C$. This proportion increased to $\sim 9-10\%$ if the experiment was conducted at a lower temperature of $0^\circ C$ [Gast and Thompson, 1959]. These results suggested that the ocean was a source of B, that the rate of B degassing was directly proportional to that of water vaporization, and that the B concentration in rain was a function of the condensation temperature. However, a different view based on experiments and thermodynamic calculations was favored later, in which the ocean was considered as a sink for atmospheric B [Nishimura and Tanaka, 1972; Nishimura et al., 1973; Savenko, 1977]. These two different views might be reconciled by taking into account the role of temperature [Duce, 1996] since the Henry law's constant would favor B volatilization from the atmospheric sea salt at $T > 20^\circ C$, and for $T < 20^\circ C$ it would condense on the particles.

[4] In this study the variations of atmospheric B concentrations were investigated using rainwaters, snows, and lichens sampled along transects from the sea inward to the continent in North America and Asia. Major elements and halogens were also analyzed together with B in order to constrain the evaporation processes from seawater and the different possible

sources of atmospheric B. Whereas rain samples represent a snapshot of the precipitation chemistry at a given time, snowpacks yield an average of 2–3 months. Furthermore, lichens might average B atmospheric deposition of both gas and particles over periods of a few years, thus giving access to B atmospheric signals free from short-timescale perturbations, as might be the case for individual rain events. Lichens are, in fact, a symbiosis between fungi and algae: they derive moisture and nutrients exclusively from air so that they are efficient biomonitors because of (1) their perennial photosynthetic activity, (2) their slow metabolism, and (3) their high nonselective capacity to remove matter from the atmosphere acting as natural filters [Deruelle and Lallemant, 1983].

2. Sampling

[5] Rain, snow, and lichen samples were collected from urban and nonurban areas at various distances from the ocean (0–800 km) and on two different continents (North America and Asia).

2.1. Rain and Snow Samples

[6] The collectors are open only when it starts raining/snowing [Simonetti *et al.*, 2000a, 2000b]. All samples were kept in cleaned Teflon bottles and stored at 4°C in the laboratories after filtration to 0.45 microns. No sample was acidified except in the case of snowpacks (NE North America; Table 1) into which a small amount of distilled nitric acid was added [Simonetti *et al.*, 2000a, 2000b]. Replicate concentration analysis by inductively coupled plasma-mass spectrometry (ICP-MS) and ion chromatography after several months of storage yielded reproducible results (standard deviation varying from 0 to 0.1), showing the stability of the sample solutions (Figure 1).

2.1.1. Asia

[7] Every rain event was collected at the time of the first drops. Single rain or snow events were sampled in Nepal and Bangladesh between 1993 and 1997 (Table 1) by using an inert plastic funnel and a Teflon bottle precleaned with the rainwater itself. Composite events ($n = 6$; Table 1) representing more than 2 months of rainfall during the 1997 monsoon were also sampled in Kathmandu (Nepal). In this latest case, the collector used to get the integrated rains was always exposed to rain and dry deposition. Nevertheless, it was during the monsoon period; therefore the dry deposition was probably scarce. The chemistry (major cations and anions; O, H, and Sr isotopes) of these water samples has been reported elsewhere [Galy, 1999].

2.1.2. NE North America

[8] During the 1994 winter, snow packs were sampled along a north-south transect in the boreal forest of Québec between Hudson Bay and Montréal. These samples represent an integration of 2–3 months of precipitation. Precipitation samples (snow, freezing rain, and rain) representing either single or integrated events (Table 1) were collected during the 1998 winter at a meteorological station close to Montréal. The chemistry (major cations, trace elements; Pb and Sr isotopes) and the detailed sampling procedures of these water samples have been reported previously [Simonetti *et al.*, 2000a, 2000b].

2.2. Epiphytic Lichens

[9] All lichen samples were taken from tree branches using nylon tweezers and stored in clean sealed plastic bags. In the laboratory, samples were either freeze-dried or dried in an oven at 105°C for ~4 hours [Carignan and Gariépy, 1995]. All samples were fruticulose specimens of *Evernia* sp. (Figure 2), *Bryoria* sp., or *Usnea* sp. (Table 2). In Asia, epiphytic

Table 1. Trace Element Contents in $\mu\text{g/L}$ in Precipitation Waters

Sample	Sampling Date	Altitude, m	Distance From Coast, ^a km	B	Cl	Na	Ca	Mg
<i>North America (Québec)</i>								
Lac Laporte (snowpack)	March 1994		650	2.3				7.8
Lamothe (snowpack)	March 1994		500	2.2				16.9
Matagami (snowpack)	March 1994		410	1.0				8.9
Evans (snowpack)	March 1994		340	1.5				18.3
Opinaca (snowpack)	March 1994		220	1.6				67
Chisasibi (snowpack)	March 1994		105	1.8				138
Khoury (snowpack)	March 1994		45	2.0				118
LAS-97-4 (snow)	Dec. 25, 1997		800	0.2				2.7
LAS-98-7 (freezing rain)	Jan. 7, 1998		800	0.1				8.2
LAS-98-8 (freezing rain)	Jan. 8, 1998		800	0.1				6.2
LAS-98-9 (freezing rain)	Jan. 10, 1998		800	0.7				7.7
LAS-98-10 (snow)	Jan. 13, 1998		800	1.6				16.6
LAS-98-12 (snow)	Feb. 12, 1998		800	0.3				18.7
LAS-98-13 (rain)	Jan. 16, 1998		800	1.0				16.3
LAS-98-14 (snow) ^b	Feb. 20 and 25, 1998		800	0.4				9.5
LAS-98-15 (snow)	March 2, 1998		800	1.1				18.3
LAS-98-16 (snow-rain)	March 9, 1998		800	0.3				5.0
<i>Asia (Nepal-Bangladesh)</i>								
Orage (Kathmandu: rain)	May 29, 1993	1310	600	1.3	418	501	1319	92
LO 225 (Paigutang: snow)	June 5, 1993	4107		1	209	113	417	39
NAG 1 (Kathmandu: rain)	Nov. 10, 1995	1310	600	0.7	131	120	1258	100
NAG 2 (Pokhara: rain)	Nov. 10, 1995	885	700	0.2	181	131	341	15
NAG 50 (Kathmandu: rain)	Aug. 7, 1995	1310	600	17	511	221	6020	119
NAG 51 (Kathmandu: rain)	Aug. 9, 1995	1310	600	4.4	138	60	4320	100
NAG 52 (Kathmandu: rain)	Aug. 19, 1995	1310	600	3	191	99	970	29
NAG 53 (Kathmandu: rain)	Sept. 22, 1995	1310	600	3	330	140	7198	250
NAG 54 (Kathmandu: rain)	Sept. 29, 1995	1310	600	1.4	199	90	2361	90
NAG 55 (Kathmandu: rain)	Nov. 10, 1995	1310	600	0.4	479	349	1118	80
BGP 1 (Dhaka: rain)	July 29, 1996	50	100	9.4	1631	949	1836	131
BGP 2 (Dhaka: rain)	July 31, 1996	50	100	0.4	35	34	349	24
BGP 9 (Mahastan: rain)	Aug. 3, 1996	50	150	0.6	184	117	180	22
BGP 10 (Mahastan: rain)	Aug. 4, 1996	50	150	2	152	51	80	7
BGP 16 (Mahastan: rain)	Aug. 6, 1996	50	150		826	407	1274	107
BGP 17 (Mahastan: rain)	Aug. 7, 1996	50	150	1.3	206	60	132	17
BGP 24 (Bhola: rain)	Aug. 11, 1996	50	150	2	1719	1212	1615	226
BGP 25 (Bhola: rain)	Aug. 11, 1996	50	150		1769	860	1110	117
BGP 26 (Bhola: rain)	Aug. 11, 1996	50	150		1337	584	814	80
BGP 27 (Bhola: rain)	Aug. 11, 1996	50	150		925	423	617	58
BGP 28 (Bhola: rain)	Aug. 11, 1996	50	150		631	320	481	46
BGP 29 (Bhola: rain)	Aug. 11, 1996	50	150		755	395	433	56
BGP 30 (Bhola: rain)	Aug. 11, 1996	50	150		581	407	2024	39
BGP 31 (Bhola: rain)	Aug. 11, 1996	50	150		1195	453	449	39
BGP 32 (Bhola: rain)	Aug. 11, 1996	50	150	1	131	78	144	53
BGP 33 (Bhola: rain)	Aug. 11, 1996	50	150		5290	2476	1102	114
BGP 35 (Rupgani: rain)	Aug. 13, 1996	50		5.4	1326	828	1892	136
GK 1 (Kathmandu: rain)	May 16, 1996	1310	600	2.1	369	193	2016	122
GK 2 (Kathmandu: rain)	May 20, 1996	1310	600	3.3	3099	2081	4188	430
GK 3 (Kathmandu: rain)	June 9, 1996	1310	600	1.2	386	154	946	92
GK 4 (Kathmandu: rain)	June 21, 1996	1310	600		46	76	28	29
GK 5 (Kathmandu: rain)	July 7, 1996	1310	600	1.5	266	126	786	44
GK 6 (Kathmandu: rain)	Aug. 3, 1996	1310	600	1.9	805	2646	2717	80
GK 7 (Kathmandu: rain) ^c	Aug. 12, 1996	1310	600	37.5	291	2002	12280	284

Table 1. (continued)

Sample	Sampling Date	Altitude, m	Distance From Coast, ^a km	B	Cl	Na	Ca	Mg
GK 8 (Kathmandu: rain) ^c	Sept. 9, 1996	1310	600	1.8	184	30	41938	756
MO 17bis(Chepe Valley: rain)	May 2, 1997	1000	700	1.2	64	83	862	146
MO 46(Chepe Valley: snow)	May 6, 1997	3800	700	2	184	64	481	46
MO 62 (Chepe Valley: rain)	May 7, 1997	3310	700	0.3	57	18	361	32
MO 76 (Chepe Valley: rain)	May 8, 1997	2690	700	1	67	90	277	10
KTM1 (Kathmandu-rain) ^b	June 25 to July 9, 1997	1310	600	1.6	124			
KTM2 (Kathmandu: rain) ^b	July 10–24, 1997	1310	600	2.4	326			
KTM3 (Kathmandu: rain) ^b	July 25 to Aug. 5, 1997	1310	600	0.4	429			
KTM4 (Kathmandu: rain) ^b	Aug. 6–24, 1997	1310	600	0.7	670			
KTM5 (Kathmandu: rain) ^b	Aug. 25 to Sept. 7, 1997	1310	600	1.4	713			
KTM6 (Kathmandu: rain) ^b	Sept. 8–29, 1997	1310	600	1.4	489			

^aDistances from the sea are calculated for North America samples from Hudson Bay. The distance given here for the Montréal samples is also from Hudson Bay although the distance from the Atlantic Ocean is slightly shorter. For Asia samples the distances are calculated from the bay of Bengal.

^bIntegration of several precipitation events.

^cThese two measurements were not reported in the figures because of anomalous high nitrate concentration, maybe indicative of pollution.

lichens were sampled during spring 1997 in three different valleys of central Nepal (Table 2). In NE North America, epiphytic lichens were sampled between summer 1990 and 1994 along a north-south transect in the boreal forest of Québec between Hudson Bay and Montréal (Table 2). Sampling areas of lichens are the same as the ones for precipitation samples (Table 1).

3. Analytical Techniques

3.1. Precipitation Waters

[10] Boron concentrations were measured using a Dionex 4500i ion chromatography with an ICE-AS1 column separation [Rose, 1999]. B concentration measurements are reproducible within $\pm 12\%$ for standard solutions having B concentration of 10 $\mu\text{g/L}$ and within $\pm 4\%$ for solutions with higher concentrations ranging from 25 to 100 $\mu\text{g/L}$ [Rose, 1999]. ICP-MS was used to analyze samples with lower concentration. After filtering (0.45 μm), samples are directly flushed into the ICP-MS (Perkin Elmer ELAN 6000). The B concentration is determined by comparison with a

standard 10 $\mu\text{g/L}$ solution. A blank and a calibration are done after every three samples in order to correct for a possible instrumental drift. Matrix effects are negligible for solutions containing < 20 mg/L K, Na, and Ca, which is the case for the present sample set. The overall uncertainty ($\pm 1\sigma$) of the method for a standard solution of 1 $\mu\text{g/L}$ is $\pm 6\%$ and $\pm 3\%$ for a standard solution of 10 $\mu\text{g/L}$. Samples with very low B concentrations were duplicated over a 3 month period to find the same results within the error bars. This shows the adequacy of this analytical method for ultratrace boron concentration measurements (snow samples with 0.1–1.5 $\mu\text{g/L}$ B).

3.2. Lichens

[11] Boron concentrations (and chlorine for Nepal samples) were determined by spectrophotometry. Each lichen sample (200 mg) was mixed with an equal amount of CaO in a platinum beaker and step heated at 250°C, 350°C, and 450°C for ~ 1 hour for each step temperature. Then, the residue was mixed with 2.5 g of NaCO₃ and fused at 950°C for 15 min. The fusion product was redis-

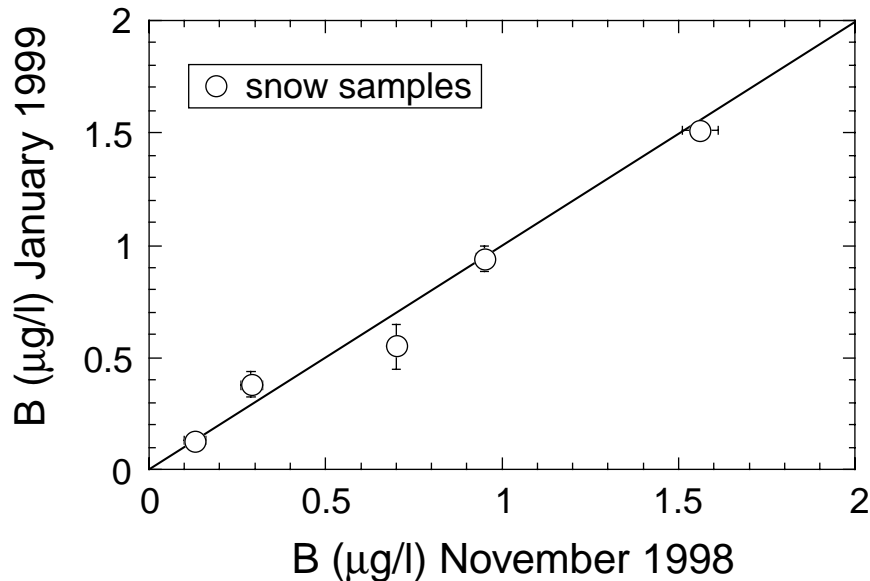


Figure 1. Reproducibility of low B concentration (between 0.1 and 1.5 ppb B) measurements by inductively coupled plasma-mass spectrometry (ICP-MS) in snow samples over a period of three months. The reproducibility of the measurements is within the error bars. Sample pollution/deterioration during storage is negligible.

solved in 50 mL of water, 25 mL of which was used for B analysis after its separation on Amberlite IRA 743 resin and the addition of H_2SO_4 + carmin 40. Depending on Cl concentrations, between 1 and 5 mL of water sample were used for analysis. Nitric acid, $\text{FeNH}_3(\text{SO}_4)_2$ (ferric alun), and mercuric thiocyanate are added to the water. The method is based on the displacement by chloride ions of thiocyanate ions from mercuric thiocyanate and subsequent spectrophotometric determination of thiocyanate as ferric thiocyanate [Vermet *et al.*, 1987].

[12] Several tests have been made at the CRPG-CNRS laboratory in Nancy. The heating step of the BCR SRM-482 standard lichen at 105°C during 7 hours produces no loss in either B or Cl concentrations (L. Marin, personal communication, 2000). However, 6% weight loss is observed and corresponds to evaporation of water. B loss during the preparation of the standard in Brussels cannot be

ruled out, but still, the chances of that happening are small considering that they also have heated the lichen up to only 105°C . Moreover, we know that if B volatilization happens during the drying process, it is coupled with water volatilization, especially if the solution is acidic. In our study we have 6% in water loss and no loss of B or Cl. We therefore postulate that we do not lose B or Cl by heating lichen at 105°C . For the step at 450°C we have verified that no B was lost by the “dosed B addition” technique. We add a different quantity of B to the lichen prior to the heating step. For this added quantity the yield during the analysis is considered to be 100%. Therefore by looking at the excess of B, we are looking at the B concentration of the lichen. Using this technique for our study, no B loss has been observed, even at 450°C . The B and Cl yield after chemical preparation is therefore close to 100% (L. Marin, personal communication, 2000). Reproducibilities on international and internal lichen standards are generally better



Figure 2. Picture of evernia lichen (i.e., sample MO-31b) on a tree branch from the Dordi Khola Valley (Nepal) at 1900 m.

than 10% for B and Cl for the range of concentration measured (L. Marin, personal communication, 2000).

4. Results

4.1. Geographic Variations of B and Halogen Concentrations

[13] B concentrations in lichen and snowpack samples from North America decrease as a function of increasing distance to the coast (Figure 3), the decrease being much steeper for lichens ($\sim 85\%$ decrease over ~ 370 km) than for snowpacks ($\sim 70\%$ decrease from $2 \mu\text{g/L}$ to $1.0 \mu\text{g/L}$ over ~ 800 km). Although a systematic B enrichment is observed in *Bryoria* species compared to *Evernia* sp., no significant difference in B decrease is observed between the two species of lichens studied (Table 2): B concentrations decrease by $\sim 85\%$ over ~ 370 km for *Bryoria* sp. (from 25.9 to 4 ppm) and

by $\sim 60\%$ over ~ 300 km for *Evernia* sp. (from 5.9 to 2.4 ppm). Samples of this latter species from Asia (Nepal) have an even lower B concentration of 1 ppm, corresponding to a decrease of $\sim 83\%$ at ~ 700 km. Along the first 200 km away from the ocean, the magnitude of the decrease in B concentration for lichens and snowpacks is similar to that previously described for rains in different locations and ascribed to a decreasing marine influence inland [Carriker and Brezonik, 1978; Meybeck, 1984]. At variance with the systematic tendency shown by lichens and snowpacks, individual rain events (Asian rains sampled over Bangladesh and Nepal over a transect of 700 km) do not show a systematic B decrease with distance from the sea (Figure 3). On the contrary, it seems that there is a large variability in B concentrations of more or less a factor of 2 (and up to a factor of ~ 10 for Kathmandu rains) for any given locality (Figure 3 and Table 1).

[14] Similar to B, halogen (Cl, Br, and I) concentrations in lichens decrease with increasing distance to the ocean (90% decrease for Cl over 410 km, 85 and 83% for Br and I, respectively; Figure 4). Such a decrease has been reported previously for rainwaters over the same distance range [Stallard and Edmond, 1981; Meybeck, 1984] and interpreted as the result of atmospheric settling of sea-salt aerosols of different sizes [Delmas and Servant, 1974], the ocean being the major source of atmospheric halogen.

[15] When normalized to Na, B and halogens display different systematics. All of the ratios, with the exception of the Cl/Na ratio, are different from the equivalent seawater ratio. For instance, lichens located close to the sea are Cl rich (>3000 ppm) and have Cl/Na ratios (of ~ 1.75) close to that of the seawater ratio (~ 1.85). Lichens have Br/Na ($\sim 2.5 \times 10^{-2}$), 4 times higher than seawater ($\sim 6.2 \times 10^{-3}$). The

Table 2. Trace Element Contents in ppm in Lichens

Sample	Altitude, m	Distance From Coast, km	B, ppm	Cl, ^a ppm	Br, ^a ppm	I, ^a ppm	Na, ^a Ppm
<i>North America (Québec)</i>							
Matagami (<i>Bryoria</i> sp.)		410	4	352	13.5	2.6	353
Evans (<i>Evernia</i> sp.)		340	2.4	612	22.9	2.3	392
Opinaca (<i>Evernia</i> sp.)		220	2.5	418	24.3	2.8	276
Chissassibi (<i>Bryoria</i> sp.)		105	10.5	3397	53.4	10.6	2401
Khoury (<i>Evernia</i> sp.)		45	5.9	3219	54.2	4.8	1666
Khoury (<i>Bryoria</i> sp.)		45	25.9	6284	88.9	15.7	3334
<i>Asia (Nepal)</i>							
MO27 (<i>Evernia</i> sp.)	1600	700	1.5	242			
MO31b (<i>Evernia</i> sp.)	1900	700	1.8	182			
MO32 (<i>Evernia</i> sp.)	2700	700	1	212			
MO35 (<i>Usnea</i> sp.)	3020	700	1.6	270			
MO36 (<i>Usnea</i> sp.)	3190	700	1.4	212			
MO42 (<i>Usnea</i> sp.)	3500	700	1.1	170			
MO51 (<i>Evernia</i> sp.)	3600	700	1.1	170			
MO57 (<i>Usnea</i> sp.)	3100	700	1.4	135			
MO75 (<i>Usnea</i> sp.)	2540	700	1.5	185			
MO78 (<i>Evernia</i> sp.)	1800	700	1.5	197			
MO88 (<i>Evernia</i> sp.)	1560	700	2.2	110			

^aNa and halogen elements in lichens from North America were analyzed by INAA at Ecole Polytechnique de Montréal. Total uncertainties on each concentration value do not exceed $\pm 5\%$.

I/Na ratios ($\sim 4 \times 10^{-3}$) are almost 3 orders of magnitude higher than the seawater ratio ($\sim 4.6 \times 10^{-6}$) and in the same range as the previously observed I/Cl enrichment in aerosol relative to seawater (100–1000 [Moyers and Duce, 1972; Duce and Hoffman, 1976]).

4.2. B Concentration Variations Between and Within Single Rain Events

[16] The B/Cl ratios of single rain events are highly variable (scatter of ~ 2 orders of magnitude; Figure 5) compared to those of lichens. They range from 7.2×10^{-4} to 1.3×10^{-1} for the Nepalese rain samples and from 1.2×10^{-3} to 1.3×10^{-2} for rains from Bangladesh. However, the average B/Cl ratio in rains ($\sim 0.008 \pm 0.02$ for Nepal and Bangladesh rain) is similar to the average B/Cl of lichens from Nepal and Quebec ($\sim 0.008 \pm 0.004$ and $\sim 0.005 \pm 0.003$, respectively). This suggests that there is no significant biological fractionation between lichens and rainwaters.

Therefore lichens are appropriate bioindicators of the atmospheric chemistry of B and halogens.

[17] The variations of elemental concentrations B and Cl, as well as total dissolved salt (TDS) within a single rain event, can also be highly variable (e.g., Figure 6). TDS decrease from 16 to 1 mg/L, while Cl decreases from 1700 to 100 $\mu\text{g/L}$, representing 94 and 93% loss, respectively (Figure 6). This result is in good agreement with previous studies that have shown scavenging of elements during single rain events [Georgii and Weber, 1960]. The decrease in Na concentration is similar to that of Cl or TDS, with 93% of Na loss from 1212 to 78 $\mu\text{g/L}$. On the other hand, the B concentration decrease during this same rain event is only 50%. This is most certainly because much of the boron is in the gas phase, which may be scavenged more slowly than the particulate Na and Cl. Consequently, the net

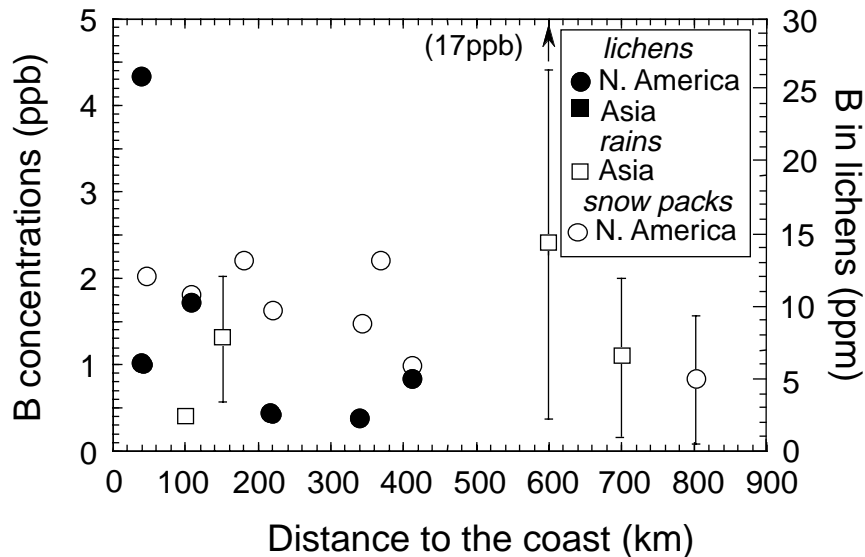


Figure 3. B concentration of rains, snowpacks, and lichens as a function of distance to the sea for NE North America (south from the Hudson Bay) and for Asia (from the coast of Bangladesh to the high Himalayas of Nepal). Samples averaging the signal from a few months to a few years (snowpacks and lichens, respectively) do show a decrease of B concentration with distance to the sea, while individual rain samples do not.

effect on the B/Cl ratio during this particular rain event is an increase from ~ 0.001 to ~ 0.008 .

5. Discussion

5.1. Seawater as a Source of Atmospheric Boron

[18] Despite systematic higher B concentrations observed in coastal areas for rains in Florida [Carriker and Brezonik, 1978], no agreement exists as to whether the ocean is a sink or a source for B in the atmosphere. In addition, it was also shown that the partitioning of gaseous B between sea salts and the atmosphere was strongly dependent on temperature and pH, which controls B speciation [e.g., Duce, 1996].

[19] The fact that lichens sampled the closest to the seashore show the highest B and halogens concentrations (Tables 1 and 2) is a strong

indication that seawater is a source of B for the atmosphere. B distribution in lichens follows that of Cl, whose marine origin is unquestionable: lichens in the most marine locations have, for instance, Cl/Na ratios close to seawater. In addition, there is no observable difference in B concentrations between coastal precipitations from North America and Asia though the average temperature of seawater in Hudson Bay is $\sim 5^\circ\text{C}$, while it is $\sim 23^\circ\text{C}$ in the Indian Ocean. This suggests that the major B release from seawater is not through vapor/sea salt equilibrium since thermodynamic considerations indicate that seawater temperatures $>20^\circ\text{C}$ are necessary for B to be enriched in the vapor phase [Duce, 1996].

5.2. B Transfer From Seawater to the Atmosphere

[20] The lichens, which average rain compositions (both gaseous and particulate species) for

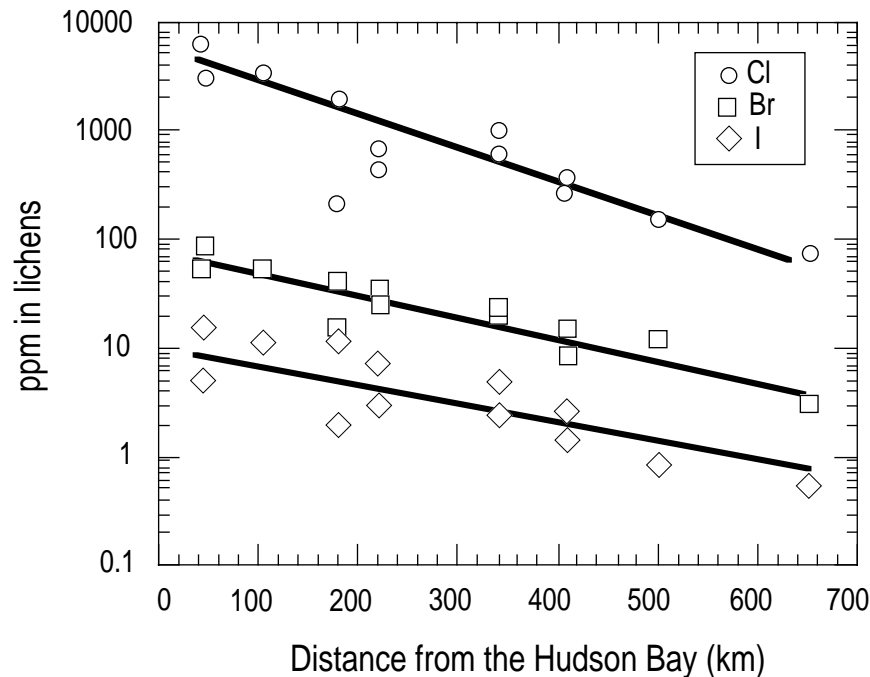


Figure 4. Evolution of halogen concentrations in lichens with increasing distance from Hudson Bay (Québec). Chlorine decreases by two orders of magnitude (90% loss) and bromide and iodine decrease by one order of magnitude (85 and 83%, respectively) over 600 km inland. The ocean is clearly a major source for these elements. Lichens along the transect for which B concentration was not measured are included.

a few years, demonstrate that coastal rains show systematic differences in their Cl/Na, B/Na, Br/Na, and I/Na ratios compared to seawater (Table 3). The magnitude of the difference increases from Cl to Br, B, and I. The elemental ratios (Cl/Na, Br/Na, and I/Na) measured in lichens from coastal areas are in very good agreement with data previously reported for rains sampled in marine environments (Table 3) [Duce and Hoffman, 1976]. However, because previous studies of B concentrations in rain are scarce [Nishimura *et al.*, 1973; Duce and Hoffman, 1976; Martens and Harriss, 1976; Fogg and Duce, 1985; Anderson *et al.*, 1994] and because single rain events can show very variable B concentrations, the B/Na ratio of oceanic precipitation is not yet known accurately. The present data demonstrate that B, normalized to Na, is significantly enriched in

coastal lichens and thus most probably in coastal rains. This would imply that the atmosphere over the oceans is enriched in B compared to seawater composition by a factor of 13.5 ± 7.1 (Table 3).

[21] Two major processes were proposed to explain the enrichments observed for Cl, Br, and I in marine rain relative to seawater: (1) a gaseous release directly from the ocean surface, as proposed for I, and (2) a gaseous release from sea-salt particles, as proposed for Cl and Br. The two processes have fundamental differences in the composition of the aerosol particles which are either depleted relative to seawater, as in the case of Cl and Br, or enriched, as in the case of I because of the rapid adsorption of gas I onto particles. The elemental fractionation taking place during

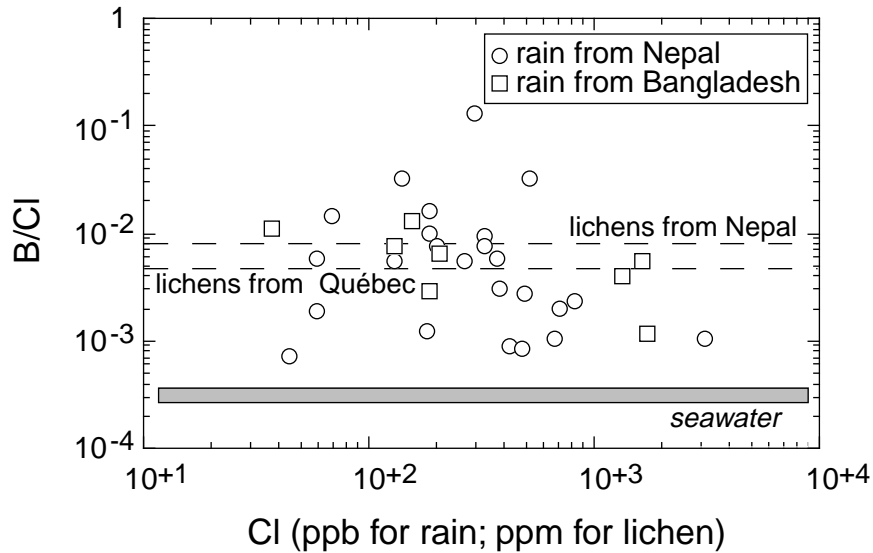


Figure 5. B/Cl variation in lichens (from Nepal and Québec) and rains (from Nepal and Bangladesh) as a function of Cl concentration. The average B/Cl ratio of lichens for each location (dashed line) is similar to the average of the rains, showing that lichens are good monitors of atmospheric deposition. Note that all B/Cl ratios are significantly higher than that of seawater.

these processes can be described by two major parameters. The first one is the fractionation factor of particles relative to seawater, F^X , defined for a given element X by the ratio $(X/Na)_{\text{particle}}/(X/Na)_{\text{seawater}}$, where $(X/Na)_{\text{particle}}$ is the mass ratio of element X to Na in the particles and $(X/Na)_{\text{seawater}}$ is this ratio in bulk (subsurface) seawater. The second one, R^X , describes the fraction of element X in the gas phase relative to the particulate phase ($R^X = [X]_{\text{gas}}/[X]_{\text{particle}}$). Assuming that Na is only present in the atmosphere as particles, the enrichment factors (normalized to Na) predicted for marine air masses relative to seawater are given by

$$(X/Na)_{\text{airmass}}/(X/Na)_{\text{seawater}} = F^X(1 + R^X). \quad (1)$$

[22] Using values previously proposed for F^{Cl} , F^{Br} , and F^{I} from the analysis of sea-salt particles sampled close to the sea surface (0.92 ± 0.04 , 0.33 ± 0.15 , and $\sim 500 \pm 400$, respectively [Duce and Hoffman, 1976]), and for R^{Cl} , R^{Br} , and R^{I} (0.5 , 7 ± 3 , and 3 ± 1 , respectively

[Duce and Hoffman, 1976]), the enrichment factors calculated for Cl, Br, and I (i.e., 1.38 ± 0.06 , 2.64 ± 2.5 , and 2400 ± 2100 , respectively) are consistent with those derived from lichens collected in coastal areas (1.07 ± 0.02 , 4.71 ± 0.7 , and 814 ± 300 ; Table 3). In fact, lichens might better represent the average of atmospheric deposition because data on rains are scarce and highly variable. These values imply very different atmospheric residence times for gaseous and particulate species, their ratio being given by

$$\tau_{\text{gas}}^X/\tau_{\text{particle}}^X = R^X[(1 - F^X)/F^X]. \quad (2)$$

[23] These residence time ratios calculated from the previous literature data are 5.7 for Cl and 3.4 for Br, while it is nearly 0 for I, gaseous I being scavenged very rapidly by particles [Duce and Hoffman, 1976]. Applying such a formalism to B, the lichen data (enrichment factor of 13.5 ± 7.1 ; Table 3) imply a value of 0.177 for F^{B} , assuming a value of 74 for R^{B} (for marine and coastal locations [Fogg and

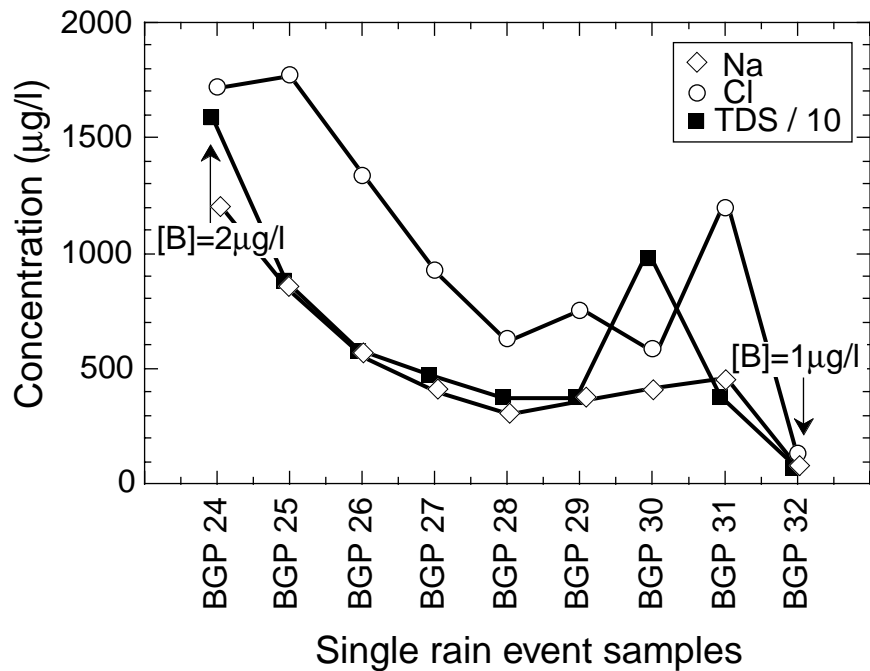


Figure 6. Variation as a function of sampling time of the total dissolved salts (TDS concentration divided by 10) Na and Cl concentrations for nine samples taken successively during a single rain event in Kathmandu, Nepal. The first and the last sample from this event were analyzed for B concentration.

Duce, 1985]). The atmospheric residence time of gaseous B is then calculated to be 15.9-fold that of particulate B in order to match a value of 74 for R^B (as compared to a maximum of 2.6-fold according to Fogg and Duce [1985]). This value of 0.177 for F^B implies that B transfer from the ocean to the atmosphere occurs mostly via the degassing of sea-salt particles, similar to Cl and Br and at variance with I. It also implies that the average B/Na ratio of degassed atmo-

spheric particles of marine origin is 0.177 times that of seawater, i.e., 7.4×10^{-5} .

5.3. Evolution of the Atmospheric B Over Continents

[24] Although lichens and snowpacks show a general decrease in their B concentrations inward to continents, rains sampled over Bangladesh yield more than 1 order of magnitude

Table 3. Comparison of the Ratios of Cl, Br, B, and I Normalized to Sodium Between Lichen and Seawater With That Between Oceanic Atmosphere and Seawater

R	Lichen	Seawater	$R_{\text{lichens}}/R_{\text{seawater}}$	$R_{\text{atmosphere}}/R_{\text{seawater}}^a$
Cl/Na	1.91	1.80	1.07 ± 0.02	1.38 ± 0.06
B/Na	5.6×10^{-3}	4.2×10^{-4}	13.5 ± 7.1	-
Br/Na	2.9×10^{-2}	6.2×10^{-3}	4.71 ± 0.7	2.6 ± 2.5
I/Na	3.8×10^{-3}	4.6×10^{-6}	814 ± 300	2400 ± 2100

^aData from Duce and Hoffman [1976].

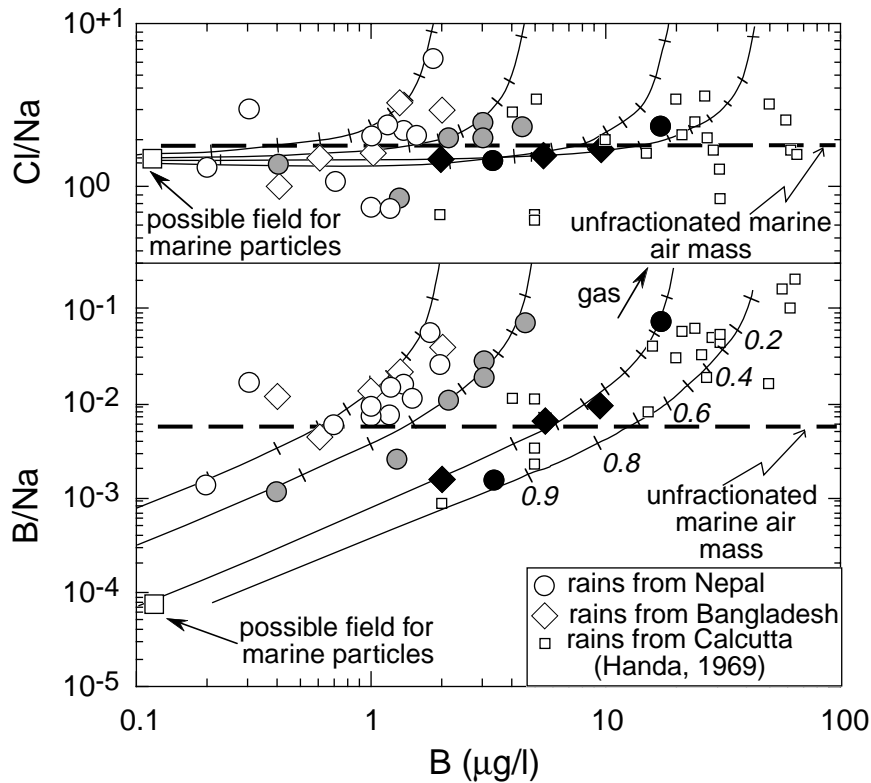


Figure 7. Model of the evolution of B/Na and Cl/Na ratios in rains as function of B concentration, assuming that the selective removal of either gaseous B or particulate B is the dominant control on the B variability of rain. In such a model each rain corresponds to a mixing in various proportions of gaseous B (assumed to contain no Na) and partially degassed marine sea salts (with B/Na ratio of $\sim 7.4 \times 10^{-5}$). The graduations on each mixing curve represent fractions of particulate B . The dashed lines represent the unfractionated marine air mass with constant average B enrichment factors relative to seawater ($\text{B}/\text{Na} = 5.6 \times 10^{-3}$, as suggested by lichen data; see text for details) but variable bulk B concentrations. The present rains, sampled from the coast of Bangladesh to the high elevations of Nepal, and previous samples taken at Calcutta [Handa, 1969] can be separated into different groups (shown by color shade) on the basis of their B/Na ratio and B contents. Circles are for Nepal rains, diamonds are for Bangladesh rains, and small open squares are for Calcutta rains. The good fit of the model to the data suggests that unfractionated marine air masses can be very variable in B concentration (i.e., from $\sim 20 \mu\text{g/L}$ to $\sim 0.2 \mu\text{g/L}$) when reaching the continents.

variation in B concentration (i.e., from ~ 10 to 0.3 ppb; Table 1). Such variable B contents most likely reflect different degrees of exchanges between seawater and marine air masses via sea-salt production and degassing. This “source effect” is obviously a first cause of variability for B in rains over the continents, but the scatter in B concentration of single rain events suggests other important controlling factors.

[25] Since B is present in the atmosphere both as gaseous species and particles (degassed sea salts), a preferential removal of one of these phases from the atmosphere could be the source of a large variability of B in rains. Such a process, if occurring, would lead to peculiar relationships between the B concentrations and the B/Na ratio of rains. In fact, the B concentrations and the B/Na ratio of rains should follow mixing relationships between degassed

marine salts and pure gaseous B. Taking, for instance, a marine air mass having a bulk B concentration of 10 ppb, the gas/particulate ratio for B ($R^B = 74$) implies that 0.13 ppb of B in the air mass must reside in particles whose B/Na ratio is 7.4×10^{-5} . Thus the preferential removal of B, either as particles or as gas, must result in the distribution of rains along a mixing line between two end-members defined by rains bearing exclusively either particle B or gaseous B. This model is in agreement with the present rains which define three major clusters, each of them having possibly originated from unfractionated marine air masses with different initial B concentrations (Figure 7). The whole range of B/Na ratios and B concentrations observed in each cluster can be explained by a variation of the fraction of particle B from $\sim 20\%$ for the rains having the highest B/Na to $\sim 90\%$ for those having B/Na approaching 7.4×10^{-5} . Note that the variability in composition of rains from Bangladesh previously analyzed [Handa, 1969] is also easily explained by this model, despite these rains having much higher B concentrations than the present ones.

[26] The systematics of the Cl/Na ratio of rains are at first order in accordance with the previous model for the fractionation of B in the air mass during the formation of rain. In fact, using the same line of reasoning as for B, most of the present Cl/Na ratio can be explained for each of the three clusters of rains by the uptake of particles of marine origin (having a Cl/Na of 1.6; see section 5.2) in the same proportions as derived from the B/Na systematics. However, the situation appears to be more complex for Cl, which is more chemically reactive than B in the atmosphere, since a number of rains have a Cl/Na ratio lower than that of degassed sea salts (below the mixing lines in Figure 7). In addition, the processes controlling short-term compositional variations of rains are obviously more complicated than described by the present first-order model. This is shown, for instance,

by the change in B concentration and in B/Na ratio of monsoon rains sampled over Kathmandu (Figure 6) in which higher B concentrations are associated to lower B/Na ratios.

[27] Finally, the fact that all of the rains can be modeled by a fractionation in the air mass between degassed sea salts and gas indicates that no significant contribution of continental detrital B can be detected from this data set. This is in accordance with previous estimates of the flux of B to the atmosphere via crustal weathering which represents between 0.8 and 8% of the flux of B particles and is negligible compared to the total flux (particles + gas).

6. Conclusion

[28] The study of lichens, which average atmospheric deposition over periods of several years, allows us to demonstrate that seawater is a source of B to the atmosphere because lichens situated in coastal areas are systematically enriched in B compared to lichens situated inland (enrichment by $\sim 80\%$). Using the B composition of coastal lichens, it can be shown that boron transfer from seawater to the atmosphere is driven mostly by sea salts which, when in suspension in the atmosphere, are partially degassed. This results in atmospheric B being mostly gaseous: assuming a bulk atmospheric ratio of gaseous to particulate B of ~ 74 [Fogg and Duce, 1985], the partially evaporated marine aerosol particles are characterized by a B/Na ratio of $\sim 7.4 \times 10^{-5}$.

[29] Though the sea is a source of B to the atmosphere, marine air masses appear to have highly variable B concentrations when entering over the continents, between ~ 0.2 and ~ 20 ppb in the case of Asian monsoon precipitations sampled in Bangladesh and Nepal. B removal from the atmosphere is associated with severe chemical fractionations, resulting in variations of several orders of magnitude of the B

concentrations and B/Na ratio of rains. If particles are removed preferentially, as suggested by the longer residence time of gaseous B compared to particulate B, then the first rains produced from an unfractionated marine air mass should be B poor, while successive rains formed from the same cloud will be enriched in B. The relationship between the B concentration and the B/Na ratio appears to be a potentially powerful indicator of the origin of a given air mass (fractionated or unfractionated marine air mass), of the amount of marine particles in suspension, and of the fractionation processes taking place during precipitations.

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