Boron in Coastal North Florida Rainfall

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Boron concentrations of coastal North Florida rainfall averaged 8.3, 12, and 7.0 $\mu g\ l^{-1}$ for summer showers, winter frontal activity, and samples collected sequentially during tropical storm Becky, respectively. B/Na ratios were 11×10^{-3} and 5×10^{-3} in summer and winter samples, respectively. Mean calculated B enrichments $E_{Na}(B)$ for summer and winter sample sets were 32 and 11, respectively. A surprisingly constant concentration of 'excess' B above that expected from direct seawater injection of approximately 6 $\mu g\ l^{-1}$ was observed in the sequential Becky samples. The lower winter B/Na ratios, and thus the calculated $E_{Na}(B)$ values, appear related to higher Na concentrations; however, several alternative hypotheses can be advanced to explain the results, including greater particulate sea-salt injection during winter months, incorporation of soil materials with a B/Na ratio above the seawater value, and possible influences of temperature variation on gaseous B incorporation in rain and evaporation from the sea surface.

INTRODUCTION

Dissolved boron and sodium concentrations were determined in rainfall collected on the Gulf Coast of northern Florida in order to investigate chemical and physical processes influencing natural concentration levels in the coastal marine atmosphere. Rainfall samples were collected during summer showers, during drizzle and heavy downpours associated with winter frontal activities, and sequentially during tropical storm Becky.

Boron is not among the elements commonly studied in atmospheric precipitation, aerosols, or gases probably because of the lack of sensitive instrumental analytical techniques; however, several studies of rainwater by *Sugawara* [1948] and *Muto* [1952, 1956] indicate B concentrations averaging approximately 10 $\mu g\ l^{-1}$ [*Livingstone*, 1963; *Turekian*, 1971]. The important role of precipitation composition in geochemical cycling and river composition has been clearly demonstrated in previous work [e.g., *Eriksson*, 1959, 1960; *Turekian*, 1971; *Beck et al.*, 1974; and others]. The similar mean rain and river water boron concentrations suggest that atmospheric precipitation is the major input of B to rivers and plays an important role in the geochemical cycle of this element. Furthermore, river input is thought to be the major source of boron for the oceans [*Harriss*, 1969].

The studies of rainwater composition also revealed B/Cl ratios ten to hundreds of times greater than the seawater ratio of 4.1×10^{-4}. Several hypotheses advanced to account for the observed B enrichment, including B in fine dust and sea spray, volcanic activity, industrial pollution, and evaporation from plants, were reviewed by *Gast and Thompson* [1959]. Based on laboratory evaporation experiments with seawater and boric acid containing distilled water solutions yielding B-enriched condensates, they concluded that the enrichment resulted mainly from evaporation of boric acid from the sea surface. Variations observed in the B enrichment of the condensates proportional to B concentration in both the seawater and the distilled water solutions and temperature of the cooling condensers suggested that the B concentrations of rains or snows should be a function of the temperature of condensation and precipitation.

Measurements of atmospheric gaseous B were attempted by *Creac'h and Point* [1966] at Cap Ferret on the coast of France. They used a 'bubbling cylinder' filled with 600 ml of aqueous solution containing 2 $g\ l^{-1}$ of mannitol to collect a composite sample of aerosol ('spray') plus gases. They found remarkably high concentrations ranging from 29.7 to 93.6 $\mu g\ m^{-3}$ and B/Cl ratios 100 times above the seawater ratio. Highest B concentrations were associated with air masses originating over the Atlantic ocean and coming ashore from SW to NW directions. The B enrichment was attributed to boric acid evaporating from the sea surface. Approximately 1% of the B observed was attributed to aerosol sources (spray) assumed to have the seawater B/Cl ratio.

The experiments of *Gast and Thompson* [1959] were repeated by *Nishimura and Tanaka* [1972] using seawater solutions spiked with boric acid to raise their B concentrations 20–60 times above the seawater level. Extrapolating their results to normal seawater B concentrations, they observed less B enrichment in condensates than were observed in oceanic precipitation and concluded that the ocean is a sink for boron rather than a source.

As was pointed out recently by *Duce and Hoffman* [1976], the investigations above did not consider chemical fractionation on sea-salt particles produced during bubble bursting at the air-sea interface.

The B and Na data presented in this paper yield calculated B enrichments in agreement with previous rainfall measurements; however, several alternative hypotheses can be advanced to explain both the enrichment and the seasonal patterns observed in B/Na ratios.

SAMPLING AND ANALYTICAL PROCEDURES

Rainwater samplers were located on a wooden platform on the seaward side roof of the Florida State University Marine Laboratory near Carabelle, Florida. Rain samples were collected by an automatic rain sampler equipped with a polyethylene bucket (Wong Laboratories) opening only during rainfall (and thus protected from dry fallout) or by 53-cm-diameter plastic funnels suspended 2 m above the platform and leading into 1-l polyethylene sample bottles. Evaporation

from sample bottles was prevented by a rainwater-filled loop in the tubing from funnel to sample bottle and a distilled water bottle through which air from the sample bottle was displaced. Sample contact during both collection and analysis was restricted to polyethylene materials as recommended by *Uppström* [1968].

Samples reported here were collected prior to installation of meteorological instrumentation at the laboratory, and no attempt was made to determine trajectories of air masses from which rain samples were obtained. Generally, summer shower activity along the Gulf Coast during the study period was associated with southwesterly flow off the Gulf of Mexico, while winter frontal systems generally moved in from a westerly or northwesterly overland direction. Tropical storm Becky (average winds just below hurricane force) moved onshore from the Gulf of Mexico, centering to the west of Carabelle, Florida; consequently, observed winds were mostly onshore throughout the storm.

All rainwater samples were collected between July 5, 1970, and April 5, 1971. Ten of the rainwater samples were collected sequentially during Becky, which dumped approximately 20 cm of rain on the sampling site during the early morning hours of July 22, 1970. Sixteen of the remaining 27 rain samples were collected during summer showers, while the other 11 were collected during drizzles and heavy downpours associated with cold front activity.

A sensitive colorimetric method for the determination of low levels of total dissolved boron with curcumin [*Uppström,*

TABLE 1. Boron and Na Concentrations and B/Na Ratios of Gulf Coast Rain Samples for 1970 and 1971

Sample	Date	B,* $\mu g\ l^{-1}$	Na,† $mg\ l^{-1}$	B/Na $\times 10^3$	Rainfall, cm	Remarks
1	July 5	24.2	1.54	15.7	0.6	samples 1 and 2, same summer shower, different collectors
2	July 5	18.7	1.23	15.2	0.6	
3	July 16	10.0	0.56	17.9	5.0	samples 3–5, same summer shower, different collectors
4	July 16	9.4	0.50	18.8	5.0	
5	July 16	10.7	0.54	19.8	5.0	
6	July 22	28.0	16.1	1.71	20 ± 2‡	samples 6–15, tropical storm, sequential samples taken every 30–60 min during Becky
7	July 22	7.7	4.4	1.77		
8	July 22	7.0	0.87	8.07		
9	July 22	9.7	7.37	1.32		
10	July 22	7.0	4.45	1.57		
11	July 22	6.3	0.80	7.85		
12	July 22	2.8	0.15	19.0		
13	July 22	7.7	0.14	55.5		
14	July 22	6.0	1.09	5.52		
15	July 22	8.5	1.56	5.44		
16	July 23	9.3	3.08	3.02	0.9	sample 16, shower, morning after Becky
17	Aug. 10	5.8	...	...	1.1	samples 17–20, individual summer showers
18	Aug. 11	9.2	...	...	6.1	
19	Aug. 12	6.8	...	...	3.7	
20	Aug. 13	3.8	...	...	12.7	
22	Aug. 24	2.9	0.20	14.5	0.6	samples 22 and 23, same summer shower, different collectors
23	Aug. 24	2.9	0.22	13.2	0.6	
24	Aug. 25	3.3	0.57	5.8	0.7	sample 24, individual summer shower
25	Aug. 26	2.5	0.81	3.1	4.1	samples 25 and 26, different summer showers, same day
26	Aug. 26	15.4	1.23	12.5	0.2	
28	Aug. 28	7.6	0.55	13.8	0.4	sample 28, individual summer shower
32	Oct. 6	5.3	2.27	2.30	2.9	samples 32–35, overcast; beginnings of winter frontal activity
33	Oct. 24	6.3	1.95	3.20	1.3	
34	Oct. 28	3.8	1.65	2.30	1.7	
35	Oct. 30	1.1	0.10	11.0	0.7	
38	Nov. 20	13.2	3.4	3.9	0.3	samples 38–45, frontal activity, cold air front generally coming from west or northwest
39	Dec. 12	13.2	5.1	6.8	0.2	
40	Dec. 16	34.2	2.45	3.6	1.7	
41	Dec. 29	8.8	2.05	3.6	3.2	
42	Feb 22	7.3	1.25	1.9	2.0	
43	March 26	24.3	5.0	3.1	1.7	
45	April 5	15.5	0.75	12.0	2.5	

*Accuracy of boron measurements is approximately ±5% (see text).
†Precision of sodium measurements is approximately ±0.05 mg liter^{-1} (see text).
‡Total; each sample (6–15) for July 22 represents 1–3 cm of rainfall.

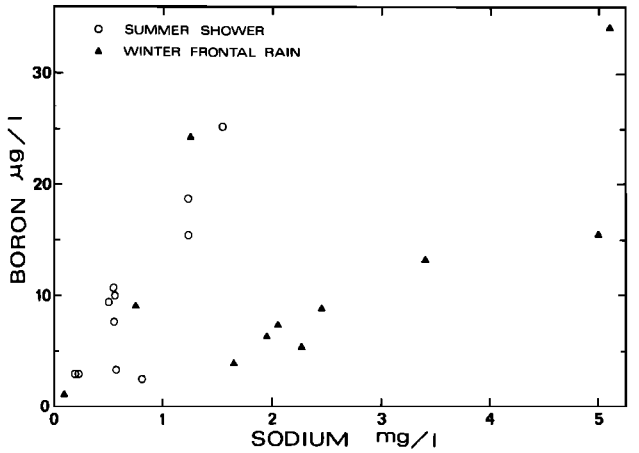

Fig. 1. Boron concentrations plotted versus Na concentrations for rain samples collected during summer showers and winter frontal activity in coastal north Florida. Lower winter B/Na ratios appear associated with higher Na concentrations (see text).

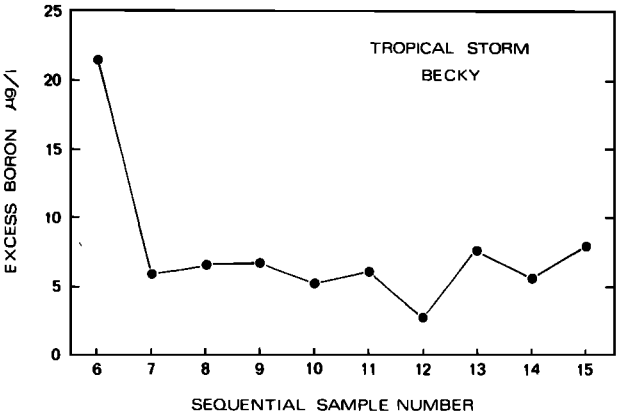

Fig. 2. Excess B in sequential rain samples collected during tropical storm Becky. Each sample represents approximately 1–3 cm of rainfall.

1968], in combination with a low-temperature (<60°C) evaporation preconcentration step, was used to analyze rainwater samples. Recoveries of boron from the evaporation procedure from distilled water samples spiked with boric acid ranged from 95 to 110%. The procedure proved suitable for determining B concentrations as low as 1 $\mu g\ l^{-1}$ with approximately ±5% accuracy (1 σ). Concentration differences between rain samples from the same shower by different collectors ranged from 0 to ±13%, in agreement with this estimated error. Generally, 500- to 1000-ml rain samples were evaporated to 25 ml in disposable polyethylene beakers with IR heat lamps. Thirty-three of the 37 samples analyzed for B were also analyzed for Na by flame emission and atomic absorption spectroscopy prior to sample preconcentration. Estimated precision for Na measurements was ±0.05 mg l^{-1}, with instrumental 'noise' acting as the primary cause of uncertainty.

Results and Discussion

Results of the B and Na analyses of rain samples are summarized in Table 1. B concentrations range from 1.1 to 34.2 $\mu g\ l^{-1}$, with a median concentration of 8.8 $\mu g\ l^{-1}$, excluding the tropical storm Becky data. Sodium concentrations, B/Na ratios, and rainfall totals associated with each sample are also listed, along with general comments concerning meteorological and sampling conditions. A standard rainfall metering gage was utilized for total rainfall measurements.

A plot of B versus Na concentrations (excluding Becky data) appears in Figure 1. B/Na ratios observed in summer and winter samples range from 1.9–19.8 × 10^{-3}, whereas a greater range of 1.32–55.5 × 10^{-3} is observed during Becky. These ratios range from 3.2 to 135 times higher than the seawater value of 4.1 × 10^{-4}. The B/Na ratio is consistently higher in the summer (samples 1–5, 16–28) than during the winter (samples 32–45), as is shown in Table 1; however, the lower winter ratio appears related to higher Na concentrations (see below).

Boron enrichment in atmospheric precipitation has been previously expressed in terms of the 'excess' amount that cannot be explained by direct injection of seawater into the atmosphere [*Nishimura and Tanaka*, 1972] using the equation

$$B_{excess} = B_{rain} - (B/Na)_{seawater} Na_{rain} \quad (1)$$

where B_{rain} is the measured precipitation concentration. This equation assumes that all the Na in rainfall comes from seawater, which is probably not true, particularly in the coastal atmosphere [e.g., *Martens et al.*, 1973]. An alternative expression of enrichment, $E_{Na}(B)$, is defined by the equation [*Duce et al.*, 1972]

$$E_{Na}(B) = \frac{(B/Na)_{rain}}{(B/Na)_{seawater}} - 1 \quad (2)$$

where $(B/Na)_{rain}$ is the ratio of B to Na measured in the sample. Calculated $E_{Na}(B)$ values for our samples are tabulated in Table 3. Summer samples exhibit enrichments ranging from 6.6 to 47, while samples associated with winter frontal activity have enrichments ranging from 3.6 to 28. Mean enrichments for these two sample sets are 32 and 11, respectively (Table 2).

Boron concentrations of the sequential samples collected during Becky range from 2.8 to 28.0 $\mu g\ l^{-1}$, with a mean concentration (excluding initial sample 6) of 7.0 $\mu g\ l^{-1}$ (Table 2) and obvious clustering of values between 6 and 9.7 $\mu g\ l^{-1}$ (Table 1); whereas Na concentrations vary more than 2 orders of magnitude from 0.14 to 16.1 mg l^{-1}. Enrichment values for

TABLE 2. Mean B and Na Concentrations, B/Na Ratio, Excess B, and $E_{Na}(B)$ Values, Associated With Summer and Winter Samples and Tropical Storm Becky

Samples	Mean B, $\mu g\ l^{-1}$	Mean Na, mg l^{-1}	Mean B/Na × 10^3	Mean Excess B, $\mu g\ l^{-1}$	Mean B Enrichment $E_{Na}(B)$
Summer shower activity	8.3	0.78	11	···	32
Winter frontal activity	12	2.4	5.0	···	11
Becky*	7.0	2.3	12	6.3	28

*Excluding initial sample 6 and sample 16 collected hours after storm.

TABLE 3. Calculated Excess B and B Enrichment in Gulf Coast Rain Samples

Summer Shower Activity		Winter Frontal Activity		Tropical Storm Becky		
Sample	Enrichment $E_{Na}(B)$	Sample	Enrichment $E_{Na}(B)$	Sample	Excess B, $\mu g\ l^{-1}$	Enrichment $E_{Na}(B)$
1	37	32	4.6	6	21.4	3.2
2	36	33	6.8	7	5.9	3.3
3	43	34	4.6	8	6.6	19
4	45	35	26	9	6.7	2.2
5	47	38	8.5	10	5.2	2.8
22	34	39	16	11	6.0	18
23	31	40	7.8	12	2.7	45
24	13	41	7.8	13	7.6	134
25	6.6	42	3.6	14	5.6	12
26	29	43	6.6	15	7.9	12
28	33	45	28	16*	8.4	6.4

*From morning shower hours after Becky.

these samples also appear in Table 3. Calculated enrichments vary widely primarily because of Na variations presumably associated with nearby injection of sea-salt aerosols resulting from the high onshore wind stress. Under these conditions it is reasonable to presume that the dominant sodium source is the ocean allowing for a meaningful calculation of the excess boron as described in (1) above. A surprisingly constant excess boron concentration averaging 6.3 $\mu g\ l^{-1}$ is found, although enrichment values $E_{Na}(B)$ calculated for these samples range from 2.2 to 134 (Table 3).

The results from summer and winter sample sets and tropical storm Becky exhibit the following trends.

1. B concentration ranges in summer and winter samples are similar, with median concentrations of 6.8 and 8.8 $\mu g\ l^{-1}$ for the 11 individual summer showers and the 11 winter samples, respectively.

2. The Na concentration range for the winter sample set is greater than the summer concentration range (based on data from seven individual summer showers). Median winter Na concentration is 2.27 mg l^{-1}, whereas the summer value is 0.55 mg l^{-1}.

3. Boron concentrations in sequential Becky samples appear independent of Na concentrations and surprisingly constant throughout the storm.

Variations in the B/Na ratio and thus the calculated enrichment $E_{Na}(B)$ in our samples appear to result primarily from variations in Na concentrations. Possible explanations for the higher median Na concentrations in winter samples include (1) soil-derived Na resulting from probable overland trajectories associated with winter frontal activity and (2) greater sea-salt particulate Na input associated with frontal activity. Particulate Na concentrations of sea-salt origin should be a function of wind speed [*Woodcock*, 1953].

The similar range of B concentrations for both summer and winter sample sets and the relatively constant B concentrations (as well as calculated excess B) in sequential Becky samples independent of widely varying Na concentrations suggest that the B chemistry of the rainwater is not directly controlled by particulate sea salt.

It is interesting to note that the mean B enrichment observed in summer samples is almost 3 times the mean winter sample enrichment (Table 2). *Gast and Thompson* [1959] demonstrated that the seawater vapor pressure of boric acid was directly proportional to temperature, although condensate B enrichment was increased at lower temperatures. We cannot rule out temperature as a possible factor influencing B enrichment in our samples.

Another alternative explanation for seasonal B/Na ratio variations as well as B enrichment is the incorporation in the rain of soil materials with a B/Na ratio above the seawater value. The B/Na ratio of southeastern U.S. soils (e.g., Georgia, Kentucky) appears to be of the order of 10^{-2} according to compiled data from *Connor and Skacklette* [1975]. A few soil samples from the North Florida panhandle area [*Shacklette et al.*, 1971] indicate a mean B concentration near the generally expected 30 ppm; however, Na concentrations appear to be generally less than 3000 ppm, suggesting B/Na ratios greater than 10^{-2}. *Rankama and Sahama* [1950] have previously summarized older data suggesting that coastal soils have 10–50 times as much B as inland soils. If soils are an important contributor to both measured B and Na in our samples, seasonal variations in B/Na ratios and thus calculated B enrichment might be attributable to differences in soil sources with less B-rich inland soils becoming more important in winter samples.

CONCLUSIONS

Our data suggest, in agreement with previous workers, that the B content of coastal rainwater is controlled by a process or processes other than direct seawater injection into the atmosphere. The narrow range of B concentrations observed relative to Na variations and constant excess B observed in tropical storm Becky rainfall suggest that the potential significance of a gaseous B phase in the coastal troposphere should be further investigated through direct measurements of the gas phase as well as the sea-salt particulate B/Na ratio in order to determine the possible significance of conversion of particulate B to a gaseous species in the marine atmosphere. Chemical behavior of a gaseous B phase in the marine atmosphere independent of the sea-salt particulate phase could be the result of a longer residence time for the gas phase.

Other potential explanations for observed B enrichment such as temperature variations, the incorporation of soil materials whose B/Na ratios are above the seawater ratio, or B-enriched surface films [*Szekielda et al.*, 1972] must also be considered. The probable multiple Na sources (i.e., soil and sea salt) in our samples suggest that the B enrichments calculated for our samples should be interpreted with caution.

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