Distribution of Boron in Natural Waters

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Introduction

The distribution of boron in natural waters was reported on some mineral springs[1], thermal springs[2], and irrigation waters[3]. The amounts of boron in the ground waters[4], rains and snows[5] were also reported by several authors. But the discussion on the distribution of boron in these waters has never been made in detail.

The author has reported on the boron content of mineral springs[6], thermal springs[7], river waters[8,9], rains[10], snows[11] and plant

1) T. Tagaya, et al., *Bull. Inst. Phys. Chem. Research* (Tokyo), **21**, 165 (1942).
2) T. Tagaya, et al., *Bull. Inst. Phys. Chem. Research* (Tokyo), **21**, 188 (1942).
3) L. V. Wilcox, *U.S. Dept. Agr. Tech. Bull.* No. 962, 40 (1948).
4) K. Sugihara, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **73**, 359 (1952).
5) K. Sugawara, *Science* (in Japanese), **18**, 485 (1948).
6) S. Muto, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **73**, 108 (1952).
7) S. Muto, ibid. **75**, 407 (1954).
8) S. Muto, ibid. **74**, 576 (1953).
9) S. Muto, ibid. **74**, 640 (1953).
10) S. Muto, ibid, **73**, 446 (1952).
11) S. Muto, ibid, **74**, 420 (1953).

ashes[12]. Although, the analyses were performed mainly with the samples from Kantô District, the author is of the opinion that the following discussion could be extended to the samples from various districts.

As an average content of boron in rains and snows, a value of 0.1 mg. B/l. was obtained. The Watarase River and the Kiriu River in Kantô District are supposed to have no supply of boron from mineral or thermal springs in the upper stream region, and the element seems to be supplied only by rains and snows. The average content of boron in these river waters is as much as 0.20 mg. B/l. Therefore, it is likely that rain and snow play an important role as the supplying source of boron to the rivers. Biological matters and soils are considered to be another supplying source of boron. The present author made the analyses of some plant ashes and obtained a value of 10–1000 p. p. m. B as the average content of the element, while some authors obtained the values of 0.1–1.2 p. p. m. B as the content of boron which exists in water-soluble form in soils[13]. In the main stream of the Tone River, the average content is 0.36 mg. B/l. This value is higher than those of the Watarase River and the Kiriu River. This high value may be due to the supply of boron by mineral and thermal springs, rich in boron, which issue in the upper stream region. The higher boron content is obtained among the mineral springs. For example, Isobe Mineral Spring has an average value of 123.3 mg. B/l. The thermal springs in Gunma Prefecture have an average value of about 10 mg. B/l.; they are supplying a large quantity of water in the upper stream region of the Agatsuma River. The Agatsuma River, which originates from the thermal spring region contains more than 1 mg. B/l. of the element. Numerous springs such as Kawarayu, Shima and Manza Springs etc. are located along the stream of this river.

Boron in Rain and Snow Waters

On the basis of chemical analyses of rain and snow waters which were reported by K. Sugawara and I. Iwasaki, the former author explained that boron was condensed remarkably in rain waters and the gravimetric ratios of boron to chlorine are 4000 times that of sea water[5]. Similar phenomena are for the ratios Ca/Cl and SO_4/Cl in rains and snows. K. Sugawara pointed out that the inorganic constituent of rain water originates from sea water and the rain of the hinterland has the greater value on the ratios Ca/Cl and SO_4/Cl. And he explained that this fact is based on the selective dissolution of the element to the rain.

In this study the present author collected 5 kinds of rain at Kiriu City. The boron content of the samples analysed by L. V. Wilcox's electrometric titration method[14] is summarised in Table I.

Table I

Boron content of rain water

No.	Sampling station	Date	Cl mg./l.	B mg./l.	B/Cl
RKM-1	Kiriu	IX '51	2.9	0.03	0.011
RKM-2	Kiriu	VI '52	5.9	0.13	0.020
RKM-3	Kiriu	VI '52	1.3	0.11	0.084
RKM-4	Kiriu	VI '52	1.8	0.11	0.060
RKM-5	Kiriu	VI '52	0.3	0.11	0.367
Average value			2.44	0.098	0.0403
RAM-1*	8°34′ S 156°53′ E	II '52	176.7	0.13	0.001
Sea water (Western Pacific Ocean)[15]			18760.	4.73	0.00025

The gravimetric ratio of boron to chlorine in rain water is about 200 times that of sea water, but it is not clear whether or not the fact is due to the selective dissolution of boron in rain water. The average value of the element in rain water in Table I is about 0.1 mg. B/l. However, there is a possibility that the value tends to fluctuate according to the sampling station. Still more, the boron content of fresh snow is shown in Table II.

Table II

Boron content of fresh snow

No.	Sampling station	Date	Cl mg./l.	B mg./l.	B/Cl
SKM-1	Kiriu	II '52	2.7	0.04	0.015
SKM-2	Kiriu	II '52	2.2	0.13	0.059
SKM-3	Kiriu	III '52	2.7	0.15	0.056
Average value			2.53	0.107	0.0436
SNY-1	Norikura	VII '52	—	0.002	—
SSM-1	Sennokura	I '55	0.43	0.002	0.004
SAM-1*	64°18′ S 163°16′ E	XI '51	351.9	0.36	0.001

Although there were only a few samples, the boron content in fresh snow was found to be about 0.1 mg. B/l. The gravimetric ratio of boron to chlorine is approximately 0.04. In

12) S. Muto, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, 75, 1028 (1954).

13) J. A. Naftel, *Ind. Eng. Chem. Anal. Ed.*, 11, 407 (1939).

14) L. V. Wilcox, *Ind. Eng. Chem. Anal. Ed.*, 4, 38 (1932).

15) Y. Miyake, This Bulletin, 14, 56 (1939).

* RAM-1 and SAM-1 were given for the reference of boron content of falling waters at the heart of the ocean. They were collected through the kindness of Taiyô Fisheries Co. while on duty, and the author offers his thanks for it.

other words, the boron content in fresh snow is almost equal to the rain water. It is notable that such lower values were obtained for the snow in a mountainous area (SNY–1, SSM–1).

Table III shows the boron content of a series of rains which were collected at different times from the begining of a rainfall.

TABLE III
BORON CONTENT OF RAIN PARTITIONS

Sample No.	Part	pH	Cl mg./l.	B mg./l.	B/Cl
KR–2	1	5.6	2.91	0.03	0.011
	2	—	—	0.03	—
	3	—	0.38	0.02	0.063
KR–5	1	6.7	5.86	0.13	0.022
	2	6.7	4.85	0.12	0.026
	3	6.7	0.50	0.11	0.210
KR–9	1	6.6	6.41	0.06	0.010
	2	6.6	1.95	0.08	0.041

The inorganic constituents of rain water are condensed in the initial stage of rain fall and as was shown in Table III. But when the table is more carefully observed, it is discovered that the rate of decrease in boron content is lower than that of chlorine. Consequently, the ratio of boron to chlorine in the later stage of rain fall is larger than in the initial stage.

Boron in River Waters

According to the above experiments, the water of rain and snow contains about 0.1 mg. B/l. Rains and snows are considered to be the main supplying source of water to the rivers and their tributaries. The boron content of the main stream of the Tone River in Kantô District is shown in Table IV.

TABLE IV
BORON CONTENT OF THE TONE RIVER

Sampling station No.	pH	Cl mg./l.	B mg./l.	B/Cl
St–1	—	6.48	0.38	0.059
St–2	—	6.89	0.40	0.058
St–3	6.9	7.16	0.40	0.056
St–4	6.8	6.89	0.36	0.052
St–5	6.9	6.21	0.40	0.066
St–6	6.9	5.54	0.45	0.081
St–7	6.8	5.27	0.45	0.081
St–8	6.9	5.67	0.28	0.049
St–9	6.8	5.67	0.16	0.028
St–10	6.9	5.94	0.13	0.022
Average		6.162	0.345	0.0560

According to Table IV, the boron content of the Tone River is approximately 3 times those of rain and snow, while the chlorine content is approximately 2.5 times larger than those of rain and snow. Therefore the gravimetric ratio of boron to chlorine is larger than those of rain and snow. As for the chlorine content of river water, for example, about 4 mg. Cl/l. is given by J. Kobayashi, et al.[16] for the Kôryô River at Hiroshima Prefecture, and 5.67 mg. Cl/l. by Clarke[17] as the average content of river waters. Compared to those values, the chlorine content of the Tone River gives rather high value. The social effect of human beings could be considered as one of the important supplying sources of chlorine, but the thermal and mineral springs in the upper stream region seem to be a more important source. The Watarase River and the Kiriu River, the tributaries of the Tone River have no springs in their upper stream region. The composition of those river waters is given in Table V, while the composition of the Agatsuma River and the Okuresawa River to which the spring waters are supplied in the upper stream are given in Table VI.

TABLE V
BORON CONTENT OF THE WATARASE RIVER AND THE KIRIU RIVER

(a) Watarase

Sample no.	pH	Cl mg./l.	B mg./l.	B/Cl
1	7.0	10.1	0.24	0.024
2	7.1	9.4	0.14	0.015
3	7.0	11.7	0.21	0.018
Average value		10.40	0.197	0.0190

(b) Kiriu

Sample no.	pH	Cl mg./l.	B mg./l.	B/Cl
1	6.6	0.16	0.30	1.879
2	6.9	0.17	0.15	0.879
3	7.2	0.11	0.20	1.818
4	7.2	0.14	0.25	1.799
5	7.2	0.16	0.17	1.063
6	7.1	0.21	0.17	0.810
Average value		0.158	0.207	1.310

TABLE VI
BORON CONTENT OF THE AGATSUMA AND THE OKURESAWA

(a) Agatsuma

Sample no.	pH	Cl mg./l.	B mg./l.	B/Cl
1	2.3	167.5	2.25	0.013
2	2.3	140.4	2.25	0.016
3	5.5	18.0	1.88	0.105
4	5.7	10.8	1.50	0.139
Average value		84.2	1.97	0.0234

16) J. Kobayashi, et al., *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **72**, 567 (1951).
17) F.W. Clarke, "Data of Geochemistry", **63**, 119 (1924).

(b) Okuresawa

Sample no.	pH	Cl mg./l.	B mg./l.	B/Cl
1	2.4	3.5	0.75	0.214
2	2.9	0.7	1.88	2.689
3	2.9	1.4	1.23	0.985
4	3.0	3.5	1.25	0.357
Average value		2.28	1.305	0.5724

High boron content is observed for the Agatsuma River and the Okuresawa River which run through the thermal spring region, and have a minimum value of boron content for such rivers are about 1 mg. B/l. But as much as 0.2 mg./l. of boron content is observed for the Watarase River and the Kiriu River which have no supplying source of boron, like thermal springs. This value is almost equal to those of rain and snow. As the result of the social effect on its drainage, the Watarase River has high value of chlorine content, whereas the Kiriu River has no such drainage and the chlorine content is found to be very much lower than that of the former river. Therefore, the gravimetric ratio of boron to chlorine for the former is low, but the corresponding value for the latter is approximately 1. The Agatsuma River contains the larger amounts of boron and chlorine as the water of many thermal springs flows into the river directly. The values of boron and chlorine content of this river are about 2 mg. B/l., and 10–170 mg. Cl/l. respectively. Accordingly the ratio of lower value is observed for the upper stream and the value decreases for the lower stream which has no supplying source of boron, like springs. However, the value for the lower stream is higher than that of the main stream of the Tone River. The Okuresawa River contains no spring in its drainage so that the chlorine content of the river is almost 1–3 mg. Cl/l. It is slightly higher than those of rain and snow. But the boron content of the Okuresawa River is high and some supplying source of boron might be considered beside the spring.

Boron in Spring Waters

In the foregoing chapter, the author discussed one of the supplying sources of boron in river water. However, before we draw a definite conclusion about the source which supplies boron to river waters, the following three facts should be considered. Mineral and thermal springs, geological erosion and communities of human beings will have some effects on the boron content of river waters. And the effect of mineral and thermal springs will be discussed in this chapter.

The author has stated that the water of the Tone River has higher value of boron content owing to the existence of springs in its upper stream region. The springs which have highest boron content are among the alkaline common salt springs such as Isobe and Yashio Mineral Springs, etc. In Table VII some data on the boron content of the mineral springs are shown.

TABLE VII

BORON CONTENT OF ALKALINE COMMON SALT SPRINGS

Name	pH	Cl mg./l.	B mg./l.	B/Cl
Isobe No. 1	8.2	11926.	124.7	0.0105
Isobe No. 2	8.6	12658.	136.9	0.0108
Isobe No. 3	8.4	13642.	156.7	0.0115
Yashio No. 1	7.3	11004.	105.8	0.0096
Yashio No. 2	7.5	8262.	92.8	0.0112
Yashio No. 3	7.6	12989.	122.7	0.0084
Average Value		11747.3	123.33	0.01052

The gravimetric ratio of boron to chlorine for the samples in Table VII is about 0.01, which is lower than that of the Tone River, although the spring water shows the high value of boron and chlorine content. These spring waters are considered to be the petrified marine water similarly to the petroleum salt water. In these springs, the amount of flowings is not very large.

The neutral springs in Table VIII and acid springs in Table IX have large flowing amounts, but these give low boron and chlorine content.

TABLE VIII

BORON CONTENT OF NEUTRAL SPRINGS

Name	pH	Cl mg./l.	B mg./l.	B/Cl
Yunohana	7.3	361.3	5.98	0.0166
Yunokoya	7.5	122.6	4.35	0.0355
Kawarayu	5.8	322.3	8.75	0.0371
Kirizumi	7.1	48.9	0.59	0.0121
Hatonoyu	7.9	683.4	7.01	0.0103
Takaragawa	7.6	246.3	4.44	0.0180
Minakami	7.6	145.9	4.94	0.0340
Sarugakyo	7.4	342.5	14.81	0.0433

TABLE IX

BORON CONTENT OF ACID SPRINGS

Name	pH	Cl mg./l.	B mg./l.	B/Cl
Kusatsu No. 1	2.0	470.5	9.84	0.0210
Kusatsu No. 2	2.0	645.4	3.92	0.0069
Manza No. 1	—	501.8	9.97	0.0199
Manza No. 2	—	123.9	3.98	0.0321
Average value of neutral and acid sprins.		334.61	6.547	0.01964

Generally, the boron and chlorine content of the neutral and acid springs are almost the same and considerably lower than that of the alkaline common salt springs. The

gravimetric ratio of boron to chlorine of the former springs has the higher value than the latter springs. But the average ratio for all springs is lower than that of the main stream of the Tone River.

Summary

On the basis of the data and discussions in the preceding chapters, the distribution and migration of boron in natural waters are summarized in Figure 1. And the data in the figure were confirmed mainly with the samples from Kanto District, whereas the author is of the opinion that the distribution of boron and chlorine in natural waters is generally illustrated as here shown.

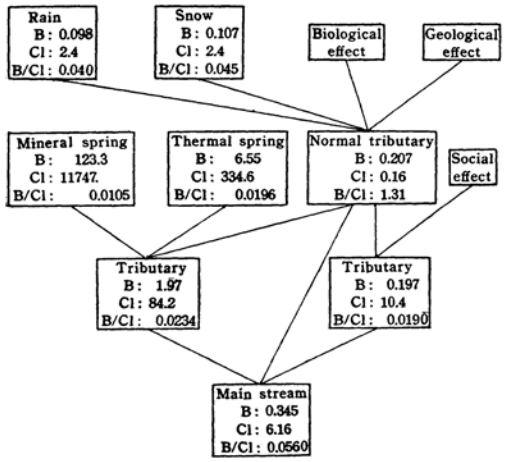

Fig. 1. Boron in natural waters (mg./l.).

The water of rain and snow at Kiriu District contain 0.1 mg. B/l., and 2.4 mg. Cl/l., and the ratio of boron to chlorine is 0.04. (these values might be lower at high mountainous area) Being affected by the biological and geological influences of the drainage, the original water becomes to contain 0.2 mg. B/l. and 0.16 mg. Cl/l. The ratio of boron to chlorine amounts to 1.31 as in the Kiriu River. At this stage, the increase of boron content or decrease of chlorine content are remarkable. When these branches of tributaries are affected by the mineral springs (123.3 mg. B/l., 11747 mg. Cl/l. and 0.0105 of B/Cl) and the thermal springs (6.55 mg. B/l., 334.6 mg. Cl/l. and 0.0196 of B/Cl) the boron and chlorine contont change their value to 1.97 mg. B/l., 84.2 mg. Cl/l. as well as the ratio of boron to chlorine 0.0234 as respectively in the Okuresawa River and the Agatsuma River. And the values of 0.197 mg. B/l., 10.4 mg. Cl/l. and boron to chlorine 0.0190 are obtained for the Watarase River which is affected by communities. Of course the actual condition will not be so simple and many complicated factors may exist before they join the river water. The main stream collects various kinds of tributaries and comes to have the value of 0.345 mg. B/l., 6.16 mg. Cl/l. and the ratio of boron to chlorine 0.0560. Then the stream flows down to the ocean while it is affected by many kinds of things during the way.

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