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Geochemical Investigation in Contaminated River Waters(Part III)
Bromine Contents of River Water in Seoul

by

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汚濁河川水의 地球化學的인 硏究(第Ⅲ報)
서울市內 河川水의 브롬含量

延世大學校 化學科

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(1970. 3. 24 접수)

ABSTRACT

Halogen contents of the river water of Seoul city and of municipal reservoirs were investigated from June in 1969 to February in 1970.

Bromine contents were ranging from 0.006 to 0.048 mg/1 of the reservoirs, 0.021 to 0.048 mg/1 of Han River, 0.051 to 0.540 mg/1 of rivers running through residential areas and 0.083 to 0.920 mg/1 of rivers running through industrial areas.

Bromine contents increased as the river water became contaminated. Most of Br/Cl of Han River and the reservoirs were higher than 3.4×10^{-3} of sea water.

Bromine contents at 17 different places were the largest in November. The contents of chlorine, iodine and COD (chemical oxygen demand) were nearly correlated with that of bromine.

Bromine contents of the river waters in Seoul chiefly originated from consumption of domestic and industrial common salt.

I. INTRODUCTION

Many workers previously reported chlorine contents among halogen quantities. Recently, Whang[1] reported fluorine contents of the river waters and industrial waste waters in Seoul. Behne[2], Heide[3] and Ueno et al[4] investigated bromine contents of the river water in respective countries. No works have yet been published on bromine contents of the river water in this country.

It is well known that river waters of Seoul city have been rapidly contaminated, due to the rapid increase in urban population and industrial facilities.

Accordingly, during the course of investigation on halogen contents the author intended to investigate bromine contents of 31 sites along major streams and 4 reservoirs, and to examine correlation between bromine and other halogen contents, such as fluorine, chlorine, iodine and COD.

II. MATERIALS AND METHOD

1. Geology and Sampling Sites

A. Geology[5]. The upper portion of Han River shows sedimentary rock formation, the middle granite, and the lower schist and

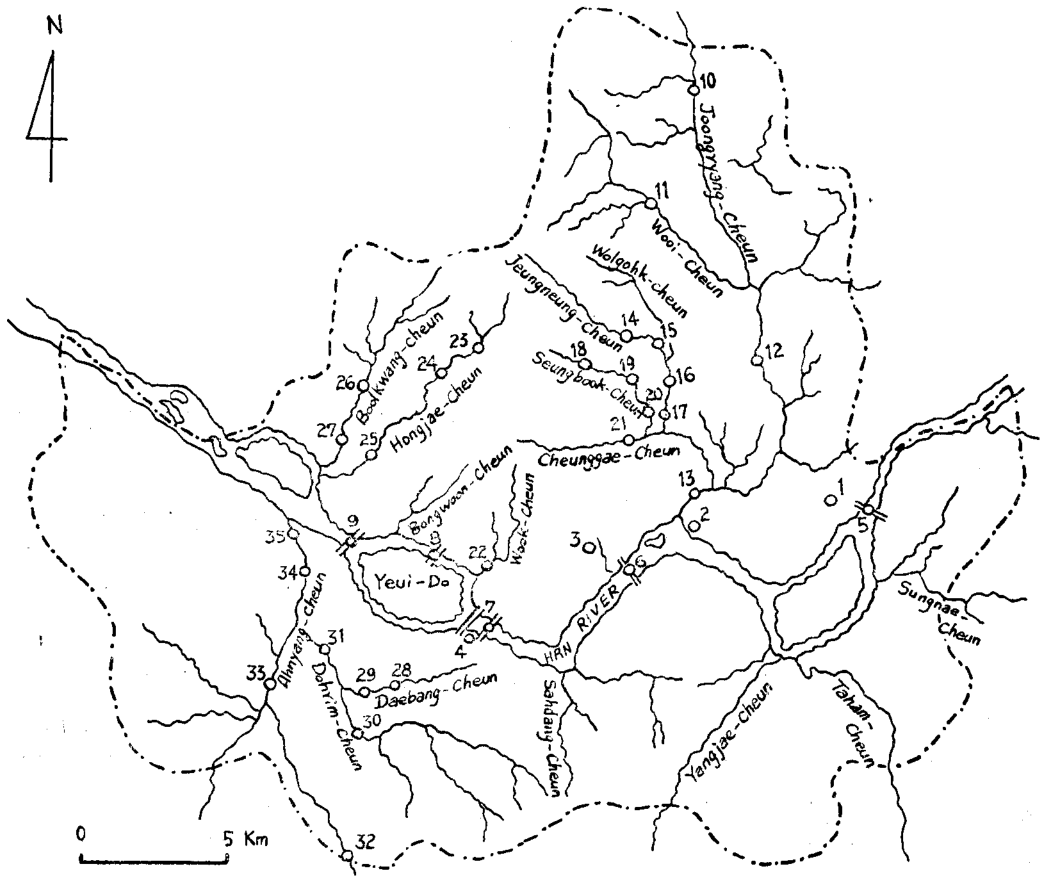

Fig. 1. Places for collection of water sample.

geneiss which are transformation of granite. The geological composition of Seoul area is of granite, geneiss and schist. The soil is sandy. The bottom of the river is mainly covered by sandy gravel. The lower portion of Han River, the residential areas and the river side are formed by alluvial deposit composing of sand, gravel and mud.

B. Sampling Sites. It required quite large scale and mobility for long term sampling to cover the wide areas of Seoul. Because of the difficulty of sampling, the auther selected the definite sites for easier sampling. Five sites along Han River, 4 sites of reservoirs, 18 sites in the northern residential area and another 8 sites in the southern industrial area, namely totally 35 sites were selected for sampling. Each sampling sites are marked with a circle in Fig. 1.

2. Sampling and Methods of Analysis

A. Sampling of Water. Samples were taken at 35 sites on the 21st and 22nd of June in 1969. Samples were also taken every season at 17 sites including Kwangjang-Gyo from June of 1969 to February of 1970. Especially, at Jungneung-Gyo and Chongahm-Daegyo, samples were taken every hour between 8:00 A. M. and 7:00 P.M. on the 18th of November in 1969.

Clear polyethylene bottles were used for collection of samples. In most cases, waters were taken at middle of stream about 10—20 cm deep. Samples were taken several meters away from edge of stream, if impossible as a manner mentioned above.

B. Methods of Analysis. In order to eliminate floating materials, the water was filtered through a Toyo filter paper-5C and was further filtered through Amberlite IR-120 cation exchange resin. For the analysis of bromine, filtered water was determined by means of contact reaction of Shioda et al[6]. The scheme of this analysis is shown in Fig. 2.

Besides this method, the analysis of fluorine and chlorine was followed by colorimetry with alizarin complexone[7] and $Hg(SCN)_2$[8], respec-

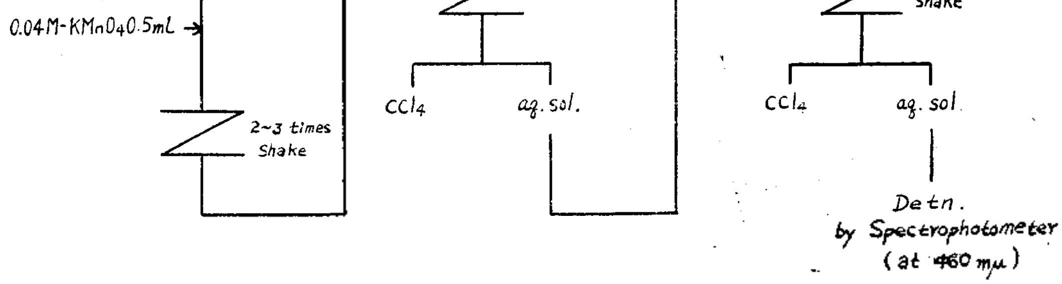

Fig. 2. Scheme for Analysis of Br.

TABLE 1. **Br-contents in reservoir**

Sample No.	Sampled at		Date of sampling	Cl(mg/l)	Br(mg/l)	Br/Cl($\times 10^3$)
1.	Kooui	※(N)	1969. 6. 21	3. 0	0. 019	6. 3
		※(F)	〃	3. 0	0. 017	5. 7
		(N)	1969. 9. 22	3. 0	0. 018	6. 0
		(F)	〃	3. 0	0. 019	6. 3
		(N)	1969. 11. 22	3. 9	0. 016	4. 1
		(F)	〃	4. 0	0. 016	4. 0
		(N)	1970. 2. 23	3. 2	0. 020	6. 3
		(F)	〃	3. 1	0. 018	5. 8
2.	Dookseum	(N)	1969. 6. 21	4. 1	0. 007	1. 7
		(F)	〃	4. 5	0. 006	1. 8
		(N)	1969. 9. 22	3. 3	0. 008	2. 4
		(F)	〃	3. 0	0. 006	2. 0
		(N)	1969. 11. 22	3. 3	0. 007	1. 3
		(F)	〃	4. 9	0. 006	1. 2
		(N)	1970. 2. 23	4. 3	0. 008	1. 9
		(F)	〃	3. 4	0. 008	2. 4
3.	Bohkwang-Dong	(N)	1969. 6. 21	7. 5	0. 048	6. 4
		(F)	〃	6. 7	0. 041	6. 1
		(N)	1969. 9. 22	5. 9	0. 031	5. 3
		(F)	〃	5. 0	0. 028	5. 6
		(N)	1969. 11. 22	12	0. 045	3. 8
		(F)	〃	9	0. 033	3. 7
		(N)	1970. 2. 23	5. 5	0. 031	5. 6
		(F)	〃	4. 8	0. 027	5. 6
4.	Noryangjin	(N)	1969. 6. 21	4. 5	0. 026	5. 8
		(F)	〃	3. 7	0. 017	4. 6
		(N)	1969. 9. 22	3. 9	0. 025	6. 4
		(F)	〃	3. 7	0. 018	4. 9
		(N)	1969. 11. 22	12	0. 026	2. 2
		(F)	〃	11	0. 019	1. 7
		(N)	1970. 2. 23	5. 2	0. 028	5. 4
		(F)	〃	4. 7	0. 020	4. 3
	Potable water (Yonsei Univ)		1969. 7. 5	8. 2	0. 019	2. 3

※(N) Natural water
※(F) Filtered water

tively. Iodine analysis followed contact reaction method[9] and COD followed JIS[10] method with $KMnO_4$.

III. RESULTS AND DISCUSSION

1. Bromine Contents of Reservoirs

Raw water is taken from Han River and treated water supplied throughout Seoul city. Bromine contents are listed in Table 1. The sampling commenced in June of 1969 and ended in February of 1970.

In the Water sampled from Kooui and Dookseum Reservoirs, bromine contents of natural water did not differ from those of filtered water. There was, however, a slight difference between natural and filtered water at Bohkwang-Dong and Noryangjin Reservoirs located at the lower stream of Han River, that is, bromine contents of natural water was larger than those of filtered water. Bromine contents of Bohkwang-Dong and Noryangjin Reservoirs located at the lower stream were larger than those of Kooui and Dookseum Reservoirs located at the upper stream of Han River. Bohkwang-Dong Reservoir contained the largest bromine contents among 4 reservoirs. Those results suggest that large bromine content of Bohkwang-Dong Reservoir seems to be due to locational conditions, for the reservoir is located at the lower stream to the mouth of Joongryang-Cheun to which sewage of Cheunggae-Cheun is added.

Br/Cl of Dookseum Reservoir ranged from 1.2×10^{-3} to 2.4×10^{-3} and only this value except other reservoirs were fairly low when compared to 3.4×10^{-3} of sea water (sea water contains 18,979.9 ppm of Cl and 64.6 ppm of Br[11]).

Bromine content of city water available on the campus of Yonsei University was 0.019 mg/l, which was nearly similar to that of filtered water of Noryangjin Reservoirs. Br/Cl of city water available on the campus was 2.3×10^{-3}.

Kooui and Dookseum Reservoirs located at upper stream of Han River showed little variation of chlorine contents during this experiment. But chlorine contents of Bohkwang-Dong and Noryangjin Reservoirs in November, which were mainly influenced by domestic sewage, were very large. This chlorine contents may be related to large use of salt necessary for the pickling (Kimchi). On the other hand, bromine contents in November showed no variation during this experiment. Due to large amount of salt used in pickling season, Br/Cl in Bohkwang-Dong and Noryan gjin Reservoirs of November became much lower than that of June, September in 1969 and February in 1970.

2. Bromine Contents of River Water

Bromine contents of the water sampled on the 21st and 22nd of June in 1969 were listed in Table 2 and Fig. 3.

TABLE 2. Br-contents in river water (June, 1969)

Regional group	Sample No.	Sampled at	Cl (mg/l)	Br (mg/l)	I (mg/l)	Br/Cl ($\times10^{-3}$)	COD (O_2mg/l)
		Han River main stream					
	5	Kwangjang-Gyo	3.2	0.021	0.0005	6.6	1.5
Han River area	6	The 3rd Han River Bridge	6.9	0.035	0.0016	5.1	8.9
	7	The 1st Han River Bridge	4.8	0.036	0.0025	7.5	10.6

	8	Seoul-Daegyo	5.6	0.033	0.0014	5.9	12.1
	9	The 2nd Han River Bridge	6.8	0.036	0.0019	5.3	15.7
		Joongryang-Cheun					
	10	Keumjeung-Dahri	19	0.055	0.0070	2.9	13.1
	11	Wooi-Gyo	47	0.051	0.0054	1.1	7.0
	12	Joongryang-Gyo	58	0.080	0.0200	1.4	34.2
	13	Seungdong-Gyo	108	0.216	0.0154	2.0	60.3
		Jeungneung-Cheun					
	14	Jeungneung-Gyo	113	0.160	0.0087	1.4	32.7
	15	Wolahm-Gyo	138	0.152	0.0087	1.1	48.2
	16	Chongahm-Daegyo	126	0.232		1.8	78.4
	17	Yongdoo-Gyo	290	0.400	0.0384	1.4	54.3
		Seungbook-cheun					
	18	Samseun-Gyo	103	0.160	0.0079	1.6	40.2
Residential area	19	Donahm-Gyo	104	0.190	0.0110	1.8	47.2
	20	Ahnam-Gyo	113	0.318	0.0075	2.8	70.4
		Cheunggae-Cheun					
	21	Cheunggae-Jehigyo	99	0.348	0.0109	3.5	76.4
		Wook-Cheun					
	22	Wonhyo-Gyo	145	0.330	0.0194	2.3	70.4
		Hongjae-Cheun					
	23	Saekeum-Gyo	54	0.064	0.0052	1.2	16.1
	24	Hongjae-Gyo	98	0.176	0.0107	1.8	21.1
	25	Sah cheun-Gyo	126	0.280	0.0340	2.2	36.2
		Boolkwang-Cheun					
	26	Wahsan-Gyo	120	0.120	0.0134	1.0	20.1
	27	Jungsan-Gyo	189	0.320	0.0212	1.7	24.1
		Daebahng-Cheun					
	28	Daebahng-Gyo	113	0.180	0.0138	1.6	62.3
	29	Singil-Gyo	113	0.160	0.0131	1.4	57.3
		Dohrim-Cheun					
	30	Mahjahng-Gyo	61	0.083	0.0050	1.4	30.2
Industrial area	31	Dohrim-Gyo	142	0.920	0.0382	1.4	129.6
		Ahnyang-Cheun					
	32	Sihoong-Gyo	45	0.182	0.0077	4.0	27.6
	33	Gojeuk-Gyo	84	0.338	0.0390	4.0	236.2
	34	Annyang-Cheun-Gyo	220	0.200	0.0350	0.9	137.7
	35	Yanghwa-Gyo	137	0.238	0.0156	1.7	68.3

Except the main stream of Han River and a few sites of the upper streams, the water contained over 20 mg/l of COD and 0.120—0.400 mg/l of bromine contents. These values mean high contamination of waters.

Bromine contents of Han River were 0.021—0.036 mg/l and Br/Cl was 5.1×10^{-3}—7.5×10^{-3}, which was higher than that of sea water. Bromine contents of both residential and industrial areas showed 0.051—0.400 mg/l and 0.083—0.920 mg/l, respectively. Br/Cl was 0.9×10^{-3}—2.9×10^{-3} in most river. This Br/Cl was lower than that of sea water.

Except the main stream of Han River, bromine contents of the rivers in the residential and industrial areas generally increased at the lower stream.

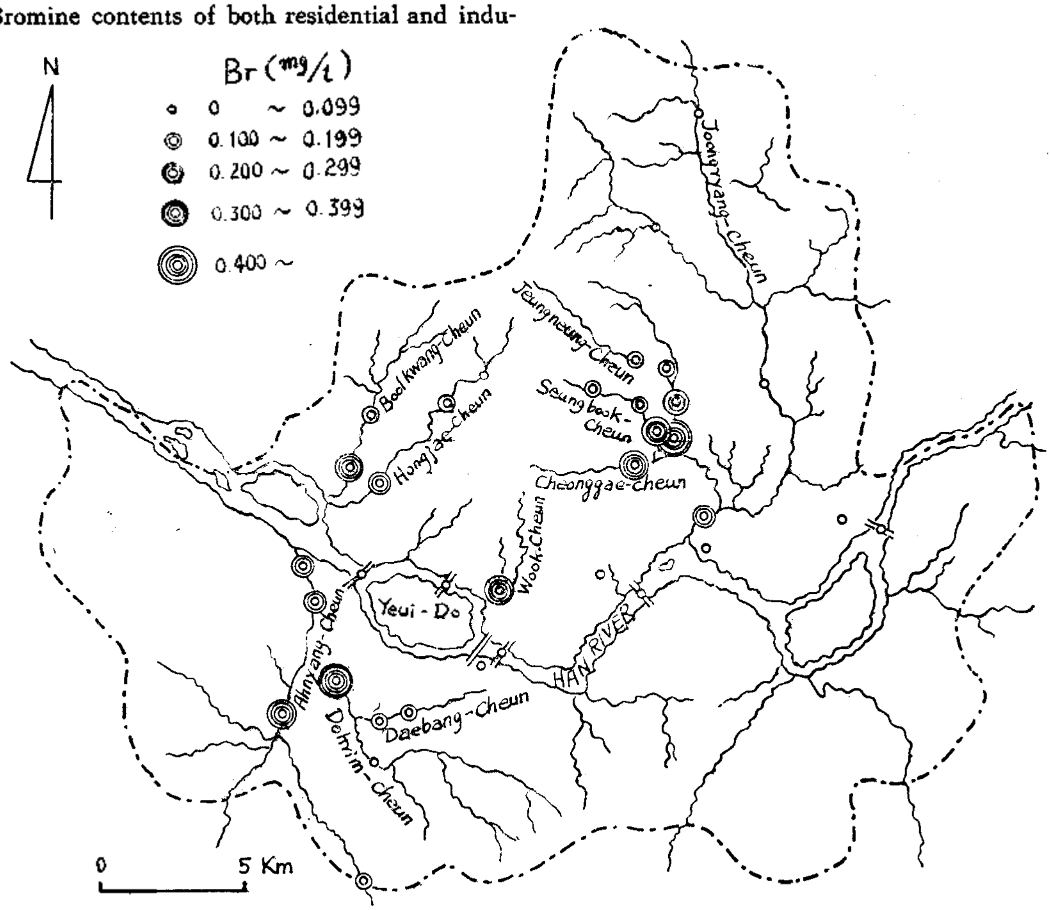

Fig. 3. Distribution of Br in river water.

Table 3 showed average bromine contents of sampling waters obtained at different areas.

Han River, residential and industrial area listed in the order of bromine contents. It seems that large bromine contents in the residential area result from daily uses of salt (salt from brine contains about 0.474% of bromine[12]) and sewage. Bromine in the industrial area seemed attributable to food, brewery, textile, pharmaceutical and other chemical factories which cast their wastes into sewage in the process of manufacturing. The contents of

TABLE 3. Range and mean values of Br-contents in river water

Regional group	Cl(mg/l)	Br(mg/l)	I(mg/l)	Br/Cl($\times 10^{-3}$)	COD(O^2mg/l)
Han River area	3.2~6.9	0.021~0.036	0.0005~0.0029	5.1~7.5	1.5~15.7
	5.5	0.032	0.0018	6.1	9.8
Residential area	19~290	0.051~0.400	0.0052~0.0384	1.0~3.5	1.5~78.4
	114	0.203	0.0156	1.8	41.7
Industrial area	4.5~642	0.083~0.920	0.0050~0.0390	0.9~4.0	27.6~236.2
	177	0.288	0.0209	2.1	168.6

chlorine, iodine and COD showed the same tendency as bromine contents.

3. Seasonal and Hourly Variation of Bromine Contents

Seasonal and hourly variation of bromine contents was examined 17 sites including Kwangjang-Gyo. June, September, and November in 1969 and February in 1970 were selected as a representative month of each corrsponding seasons. Results are shown in Table 4.

TABLE 4. Seasonal variation of Br-contents in river water

Regional group	Sample No.	Sampled at	Date of Sampling	Cl (mg/l)	Br (mg/l)	Br/Cl ($\times 10^{-3}$)	COD (0. mg/l)
	5.	Kwangjang-Gyo	1969. 6.21	3.2	0.021	6.6	1.5
			〃 9.22	3.3	0.023	7.0	1.7
			〃 11.22	5.0	0.034	6.9	2.5
			1970. 2.23	3.5	0.025	7.1	1.9
	6.	The 3rd Han River Bridge	1969. 6.21	6.9	0.035	5.1	8.9
			〃 9.22	7.7	0.034	4.4	4.9
			〃 11.22	9.0	0.036	4.0	6.5
			1970. 2.23	5.8	0.032	5.6	6.0
	7.	The 1st Han River Bridge	1966. 6.21	4.8	0.036	7.5	10.6
Han River area			9.22	4.5	0.034	7.6	6.4
			11.22	13	0.048	3.7	11.3
			1970. 2.23	4.9	0.038	7.7	8.5
	8.	Seoul-Daegyo	1969. 6.21	5.6	0.033	5.9	12.1
			9.22	5.1	0.031	6.1	8.1
			11.22	13	0.036	2.8	12.4
			1970. 2.23	6.0	0.034	5.7	10.2
	9.	The 2nd Han Rive Bridge	1969. 6.21	6.8	0.036	5.3	15.7
			9.22	7.4	0.035	4.7	10.5
			11.22	13	0.039	3.0	14.6
			1970. 2.22	7.8	0.037	4.7	12.8

	11.	Wooi-Gyo	1969. 6.21	47	0.051	1.1	7.0
			〃 9.22	36	0.055	1.5	18.8
			〃 11.22	110	0.110	1.0	76.1
			1970. 2.23				
	12.	Joongryang-Gyo	1969. 6.21	58	0.080	1.4	34.2
			9.22	62	0.096	1.5	50.2
			11.22	95	0.170	1.8	191.4
			1970. 2.23	70	0.120	1.7	63.4
	13.	Seungdong-Gyo	1969. 6.21	108	0.216	2.0	60.3
			〃 9.22	66	0.140	2.1	69.0
			〃 11.22	144	0.250	1.4	116.1
			1970. 2.23	115	0.230	2.0	75.6
	16.	Chongahm-Daegyo	1969. 6.21	126	0.232	1.8	78.4
			〃 9.22	214	0.230	1.1	124.0
			〃 11.22	278	0.501	1.8	
			1970. 2.23	226	0.330	1.3	
	19.	Donahm-Gyo	1969. 6.21	104	0.190	1.8	47.2
			9.22	91	0.180	2.0	20.4
			11.22	376	0.540	1.4	78.1
Residential area			1970. 2.23	120	0.216	1.8	50.6
	20.	Ahnam-Gyo	1969. 6.21	113	0.318	2.8	70.4
			〃 9.22	102	0.276	2.7	43.5
			〃 11.22	430	0.500	1.2	80.0
			1970. 2.23	132	0.336	2.6	69.4
	21.	Cheunggae-jehigyo	1969. 6.21	99	0.348	3.5	76.4
			〃 9.22	93	0.312	3.4	65.9
			〃 11.22	190	0.370	1.7	91.7
			1970. 2.23	122	0.350	2.9	79.3
	22.	Wonhyo-Gyo	1969. 6.21	146	0.330	2.3	70.4
			〃 9.22	116	0.266	2.3	52.2
			〃 11.22	202	0.350	1.5	148.4
			1970. 2.23	153	0.320	2.1	75.5
	24.	Hongjae-Gyo	1969. 6.21	98	0.176	1.8	21.1
			〃 9.22	54	0.054	1.0	23.5
			〃 11.22	396	0.500	1.5	74.0
			1970. 2.23	110	0.194	1.8	41.6
	26.	Wahsan-Gyo	1969. 6.21	120	0.120	1.0	20.1
			〃 9.22	102	0.116	1.1	18.0
			〃 11.22	295	0.360	1.2	43.9
			1970. 2.23	145	0.140	1.0	32.7

	28.	Daebahng-Gyo	1969. 6. 22	113	0. 180	1. 6	62. 3
			〃 9. 22	102	0. 164	1. 6	47. 3
			〃 11. 22	120	0. 244	2. 0	68. 6
			1970. 2. 23	122	0. 193	1. 6	63. 5
Industrial area	35.	Yanghwa-Gyo	1969. 6. 21	137	0. 238	1. 7	68. 3
			〃 9. 22	83	0. 194	2. 3	
			〃 11. 22	162	0. 310	1. 9	118. 1
			1970. 2. 23	125	0. 270	2. 2	87. 6

In rainly June and September, the increased water level resulted in less values of chlorine, COD and bromine contents. On the contrary, the dry season of November, simultaneously with the seasonal pickling, caused bromine, chlorine and COD large in the streams. The seasonal variation was distinct in the residential area where population density is high rather than Han River area.

At Jeungneung-Gyo and Chongahm-Daegyo on Cheungneung-Cheun, bromine and chlorine contents were hourly analyzed between 8:00 A.M. and 7:00 P.M. on the 18th of November in 1969. The results are given in Fig. 4.

At Jeungneung-Gyo chlorine contents varies little but bromine contents varies largely be-

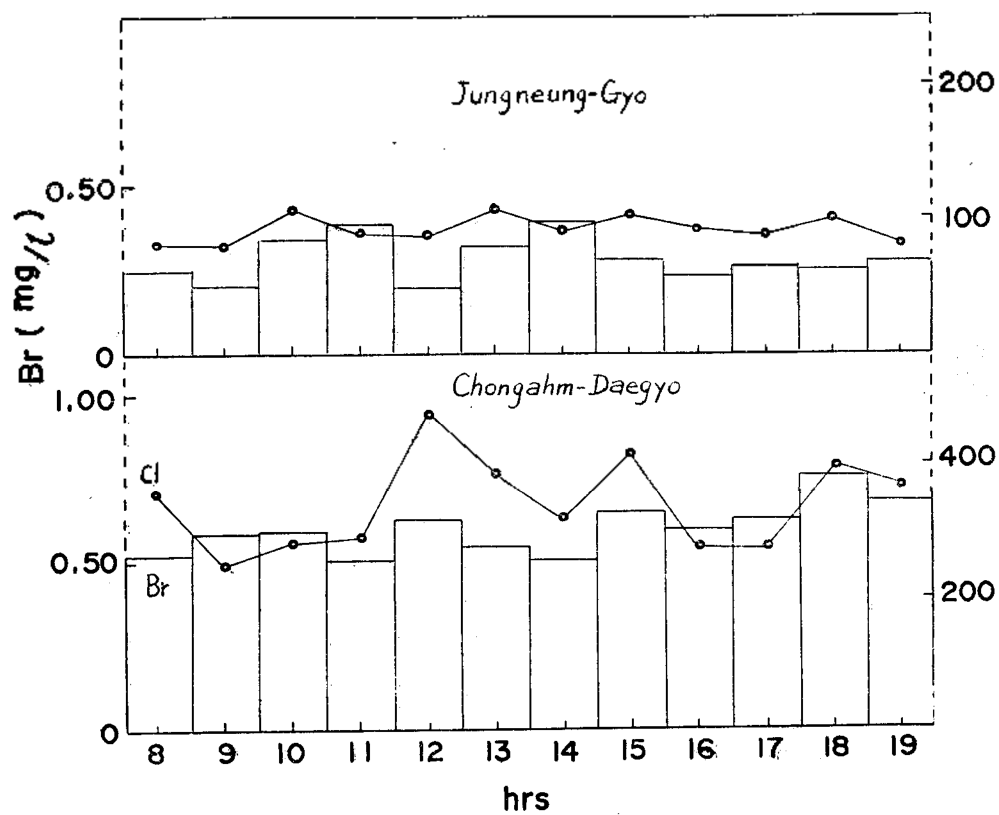

Fig. 4. Hourly variation of Cl and Br.

tween 8:00 A.M., and 3:00 P.M., while at Chongahm-Daegyo, chlorine content was much more variable than bromine content. At Chongahm-Daegyo, between 11:00 A.M. and 7:00 P.M. bromine content seemed to be in proportion to chlorine content but the largest chlorine contents were obtained at noon and 3:00 P.M. and at 10:00 A.M. and 1:00 P.M. at Jeungneung-Gyo. The largest bromine contents were gained between 6:00 P.M. and 7:00 P.M. at Chongahm-Daegyo, at 11:00 A.M. and 2.00 P.M. at Jungneung-Gyo. The above hourly changes of bromine and chlorine contents may be caused by irregular disposal of domestic wastes.

4. Relationship between Bromine and Others

As to the June investigation of bromine and the others, bromine and chlorine contents were related to each other. The correlation coefficient of the two variable was +0.928. The scatter diagram is presented in Fig.5.

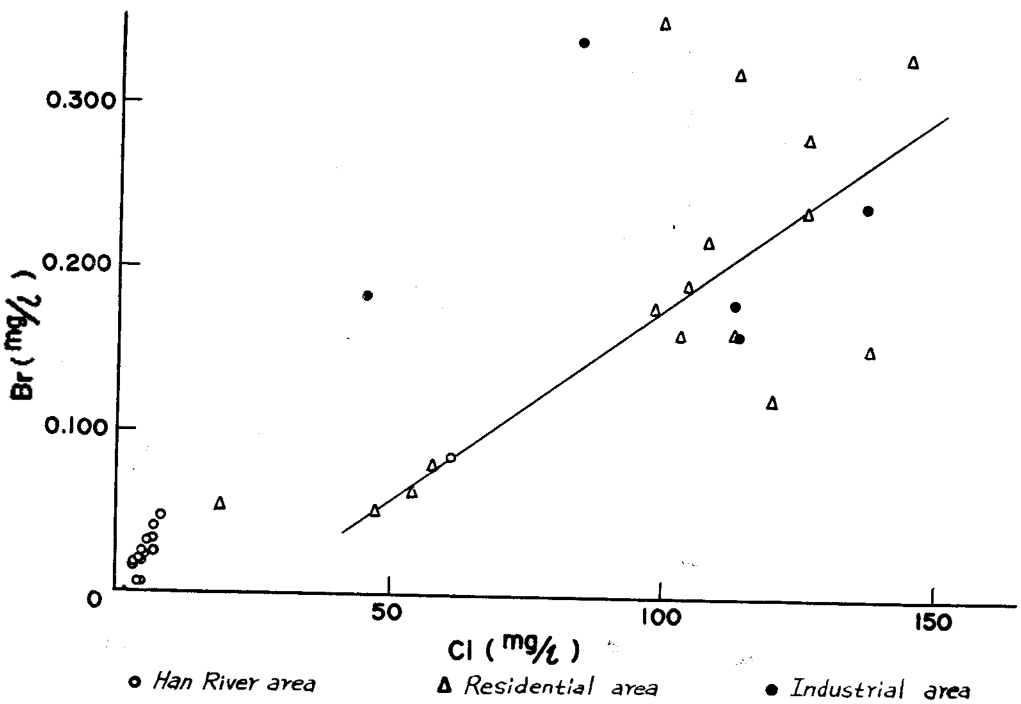

Fig. 5. Relationship between Br and Cl.

Bromine content is also related to iodine content. The correlation coefficient was +0.738. The scatter diagram can be seen in Fig.6.

The correlation coefficient of bromine content and COD was +0.920 as shown in Fig.7.

There was no correlation between fluorine and bromine contents. It is, however, difficult to know the reason why there is no correlation between them as far as this experiment is concerned.

5. Source of Bromine in River Water

Sources of bromine in river water of Seoul are enumerated as follows.

A. Human wastes and excretion form a source of contamination. In this experiments raw salt contained 0.76% and refined one 0.48% of bromine. The average daily intake of salt ranges from 10 to 30 grams per man.

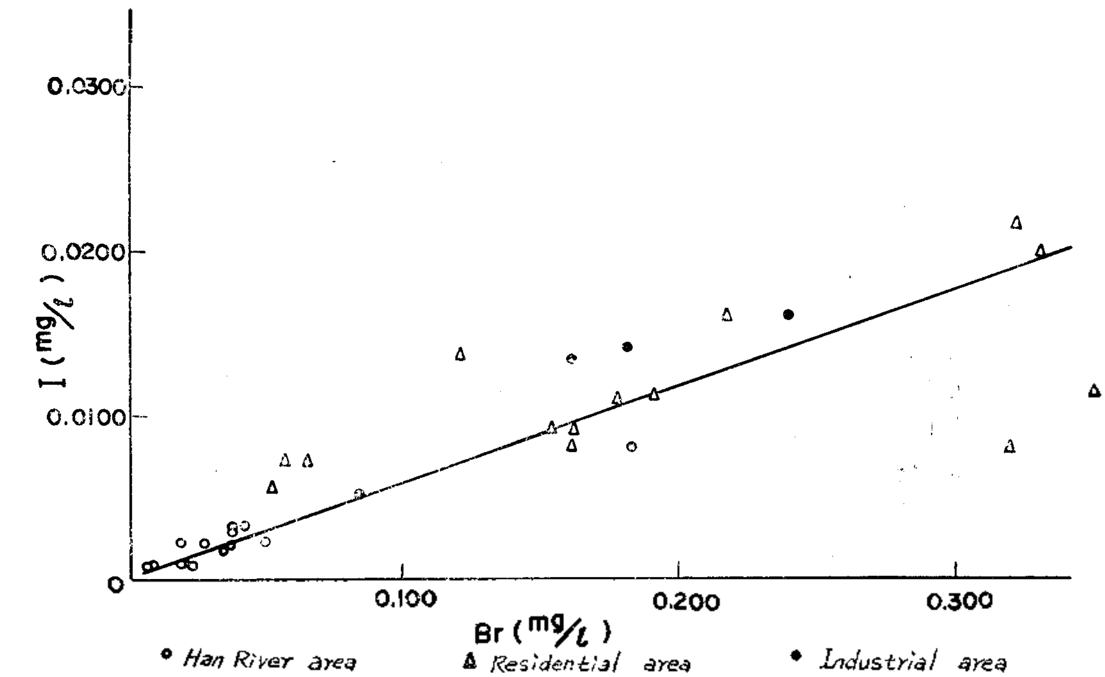

Fig. 6 Relationship between Br and I

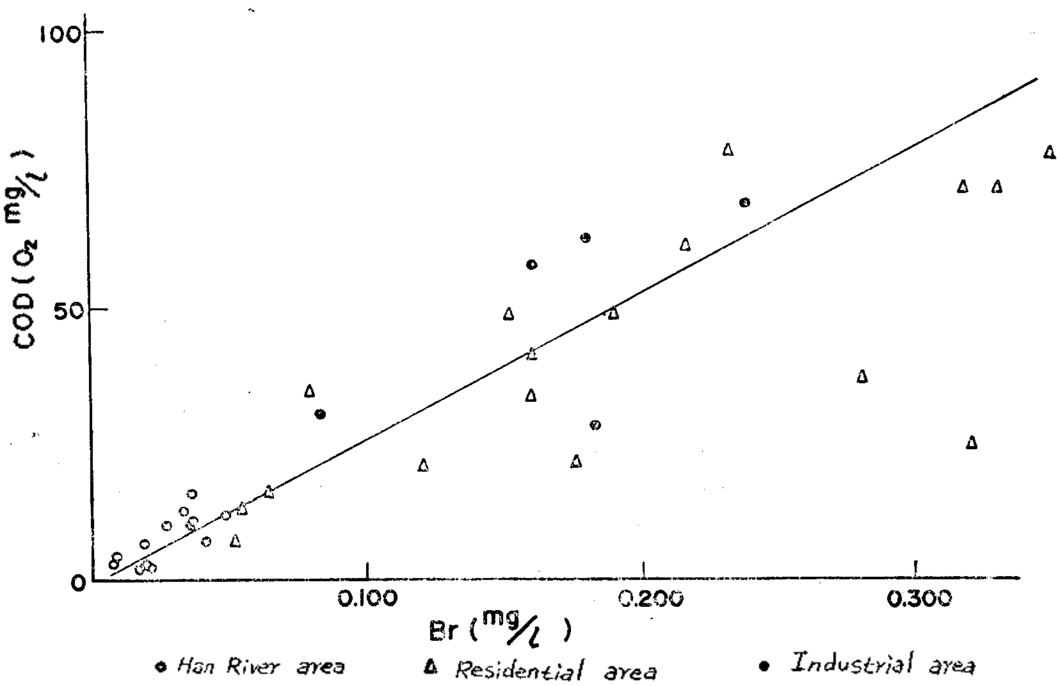

Fig. 7. Relationship between Br and COD.

B. Industrial raw material such as common salt and bromine compounds, which are used as photographic emulsion, sleeping drugs and particular dyes, are a source of contamination of water.

C. Rapid increasing industrial gas and exhaustion gas from automobiles may cause bromine contamination. The average bromine content in petroleum is approximately 2 grams per ton[13]. The gasoline contains 0.3g/l bromine[4]. On the 16th, 26th of July and the 19th of September in 1969, bromine content of rainwater were examined. Bromine contents of rainwater were 0.039,0.030,0.038 mg/l in above corresponding dates. It is apparent that dissolution of bromine in the air into river water should be caused by rainfall.

IV. CONCLUSION

The main results of bromine contents in river water and reservoirs in Seoul, which carried out from in June 1969 to February in 1970, are as follows:

1. Bromine contents of reservoirs ranged from 0.006 to 0.048 mg/l. Less bromine content (0.006—0.020 mg/l) existed at Kooui and Dookseum Reservoirs, and this indicated the better quality of water than the remaining reservoir.
2. Bromine contents in Han River, where comparatively less human wastes were influenced, had values ranging from 0.021 to 0.048 mg/l. Most of Br/Cl was between 3.7×10^{-3} and 7.7×10^{-3}, which was higher than that of sea water.
3. Residential area in high density of population showed bromine contents of 0.051—0.540 mg/l. Br/Cl was between 1.0×10^{-3} and 2.9×10^{-3} which was lower than that of sea water. In June and September, Br/Cl at Cheunggae-Jehigyo was an exception for the above Br/Cl.
4. River flowing through industrial area, where industrial wastes were prevalent, showed bromine content of 0.083—0.920 mg/l. Most of Br/Cl was between 0.9×10^{-3} and 2.3×10^{-3}, which was lower than that of sea water.
5. Bromine content of river water gradually increased from the upper to the lower streams, and so chlorine, iodine and COD.
6. It was found in November that bromine content of river water arrived at peak in terms of seasonal variation. This peak was more clear in the case of residential area.
7. Bromine content during a day considerably changes with subsequent hours at one place and conversely at another.
8. Bromine content of river water in Seoul were partially influenced by industrial wastes but mainly by domestic salt.

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