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汚濁河川水의 地球化學的인 硏究(第IV報)
서울市內 河川水의 플루오르含量

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Geochemical Investigation of Contaminated River Waters (Part IV) Fluorine Contents of River Water in Seoul

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Abstract Geochemical investigation of river waters and reservoirs in Seoul city on fluorine contents were conducted between June in 1969 and February in 1970.

Fluorine contents of most river waters and reservoirs in Seoul city were between 0.09 and 0.32 mg/l.

It was found that fluorine contents of Han River and rivers running through the outskirt of the city were relatively less than those of the river waters running through the residential areas and the industrial areas.

Fluorine contents were less seasonaly variable than chlorine ones.

Some implications of those results were discussed in detail.

Introduction

Fluorine contents of drinking water[1] in Seoul city, domestic salt[2] and food[3] were analyzed. In 1968, Whang[4] reported fluorine contents of 0.07 to 0.29 mg/l of river water and industrial waste water in Seoul city.

This study was carried out to investigate the content and the distribution of fluorine of the river water in Seoul city and to serve as a basic material for the fluoridation to the authorities concerned.

Materials and Methods

1. Sampling Sites Five sites along Han River, 4 of reservoirs, 18 in the northern residential area, and 8 in the southern industrial area were selected for sampling.

The places and the names of sampling sites can be seen in *Fig.* 1, *Table* 1 and 2.

2. Sampling and Methods of Analysis

A. Sampling of Water On the 21st and 22nd of June in 1969, sample waters were taken at 35 sites. At 23 sites including Kwangjang-Gyo sample waters were seasonaly taken from June in 1969 to February in 1970.

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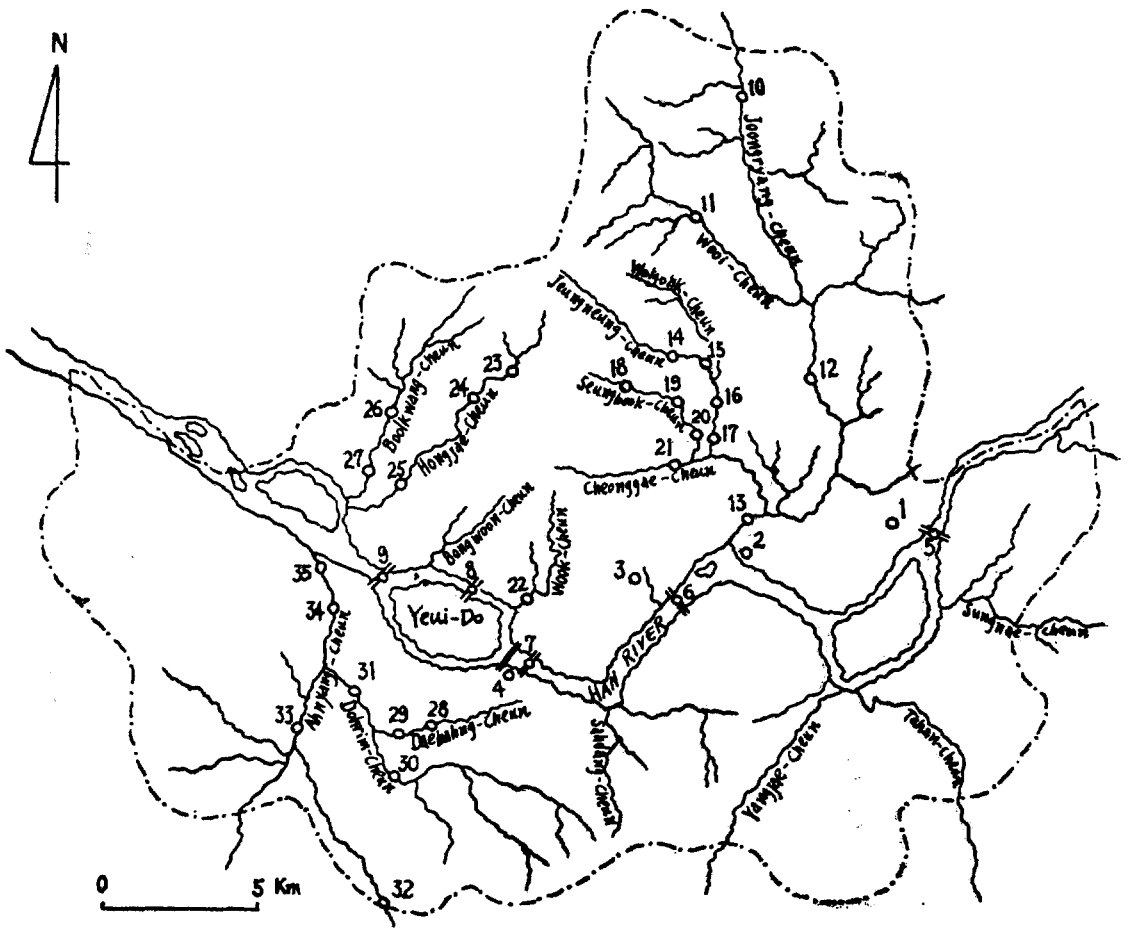

Fig. 1. Places for collection of sample water in Seoul

The detailed procedure of sampling water was previously described[5].

B. Methods of Analysis For the analysis, pre-treatment of sample waters followed the manner of a previous report[5].

Fluorine was analyzed by means of extraction spectrophotometry with ALC (Alizarin complexone)[6]. After transfering sample waters of 20 to 25 ml to a separating funnel, ALC-La solution and N, N-diethylaniline-isoamylalcohol were added, and shaked for extraction of ALC-La-F complex. Subsequently, pH 4.4 buffer solution was added to the newly formed organic layer. Aqueous layer was casted off after shaking the mixed solution. The absorbance of organic layer was measured at 580 mμ by using N, N-diethyl-aniline-isoamylalcohol as a reference.

Silica was analyzed by means of colorimetry with molybdenum yellow reaction.

Results and Discussion

1. Fluorine Contents of Reservoirs Results for fluorine contents of reservoirs, are shown in *Table* 1.

Little difference of fluorine contents not only between natural and filtered water, but also among all the reservoirs were observed.

However, the chlorine contents of reservoirs

Table 1. F-contents in reservoir

Sample No.	Sampled at		Date of Sampling	Water temp. (°C)	pH	Cl (mg/*l*)	F (mg/*l*)	F/Cl ($\times 10^{-2}$)
1	Kooui	(N)*	1969. 6. 21.	21.5	6.8	3.0	0.13	4.33
		(F)**	〃	21	6.8	3.0	0.12	4.00
		(N)	1969. 9. 22.	21	7.4	3.0	0.09	3.00
		(F)	〃	22	7.7	3.0	0.09	3.00
		(N)	1969. 11. 22.	12	7.2	3.9	0.13	3.33
		(F)	〃	12	7.2	4.0	0.13	3.25
		(N)	1970. 2. 23.	7	7.1	3.2	0.14	4.38
		(F)	〃	6	7.1	3.1	0.11	3.55
2	Dookseum	(N)	1969. 6. 21.	22.5	6.8	4.1	0.18	4.39
		(F)	〃	21.5	6.8	4.3	0.14	4.24
		(N)	1969. 9. 22.	21.5	7.7	3.3	0.11	3.33
		(F)	〃	21.5	7.5	3.0	0.11	3.67
		(N)	1969. 11. 22.	12	7.2	5.3	0.13	2.45
		(F)	〃	12	7.2	4.9	0.13	2.65
		(N)	1970. 2. 23.	7	7.2	4.3	0.13	3.02
		(F)	〃	9	7.3	3.4	0.13	3.82
3	Bohkwang-Dong	(N)	1969. 6. 21.	25	6.8	7.5	0.13	1.73
		(F)	〃	24	6.8	6.7	0.11	1.64
		(N)	1969. 9. 22.	21.5	7.5	5.9	0.09	1.53
		(F)	〃	21.5	7.4	5.0	0.09	1.80
		(N)	1969. 11. 22.	13.5	6.9	12.0	0.11	0.92
		(F)	〃	8.8	6.9	9.0	0.11	1.22
		(N)	1970. 2. 23.	7	6.8	5.5	0.09	1.64
		(F)	〃	6	6.8	4.8	0.09	1.88
4	Noryangjin	(N)	1969. 6. 21.	23	7.2	4.5	0.12	2.67
		(F)	〃	22	6.8	3.7	0.13	3.51
		(N)	1969. 9. 22.	21	7.4	3.9	0.15	3.85
		(F)	〃	22	7.4	3.7	0.11	3.00
		(N)	1969. 11. 22.	7	7.1	12	0.14	1.17
		(F)	〃	6.5	7.1	11	0.12	1.09
		(N)	1970. 2. 23.	7	7.0	5.2	0.11	2.12
		(F)	〃	6	6.8	4.7	0.10	2.13
	Potable water (Yonsei Univ.)		1969. 7. 5.	21	6.9	8.2	0.09	1.10

* (N) Natural water ** (F) Filtered water

at the upper stream of Han River were considerably different from those at the lower. This suggest that the lower stream has high density of chlorine contents of the water, owing to the disposal of city sewage into the stream. In November, reservoirs except Kooui reservoir which is located at the upper stream showed distinct increase in chlorine contents. This may be related to pickling season (Kimchi). In the case of fluorine contents, there were neither seasonal variations nor locational differences.

Fluorine content of city water available on the campus of Yonsei University was 0.09 mg/l. Fluorine content on the campus did not differ from that of sample water of reservoirs.

This suggest that fluoridation of city water has not yet taken place.

2. Fluorine Contents of River Water *Table* 2 shows fluorine contents of river waters in Seoul. The period of sampling covers the 21st

Table 2. F-contents in river water

Regional group	Sample No.	Sampled at	Water temp. (°C)	pH	Cl (mg/l)	F (mg/l)	F/Cl ($\times 10^{-2}$)
		Han River main stream					
Han River area	5	Kwangjang-Gyo	22.5	6.8	3.2	0.12	3.75
	6	The 3rd Han River Bridge	26	6.8	6.9	0.10	1.45
	7	The lst Han River Bridge	24	7.2	4.8	0.14	2.92
	8	Seoul-Daegyo	24	7.0	5.6	0.14	1.50
	9	The 2nd Han River Bridge	23	6.8	6.8	0.12	1.76
		Joongryang-Cheun					
	10	Keumjeung-Dahri	22.6	6.8	19	0.12	0.63
	11	Wooi-Gyo	25	7.0	47	0.09	0.20
	12	Joongryang Gyo	23.5	7.0	58	0.14	0.24
	13	Seungdong-Gyo	22	7.0	108	0.19	0.18
		Jeungneung-Cheun					
	14	Jeungneung-Gyo	26	6.6	113	0.25	0.22
	15	Wolahm-Gyo	27	7.0	138	0.26	0.19
	16	Chongahm-Daegyo	25.5	7.4	126	0.23	0.19
	17	Yongdoo-Gyo	28	7.4	290	0.50	0.17
		Seungbook-Cheun					
Residential area	18	Samseun-Gyo	24.5	6.9	103	0.20	0.20
	19	Donahm-Gyo	22.2	6.9	104	0.27	0.26
	20	Ahnam-Gyo	24	7.4	113	0.23	0.21
		Cheunggae-Cheun					
	21	Cheunggae-Jehigyo	22	6.8	99	0.22	0.23
		Wook-Cheun					
	22	Wonhyo-Gyo	24	6.7	145	0.24	0.16
		Hongjae-Cheun					
	23	Saekeum-Gyo	24	6.8	54	0.19	0.34
	24	Hongjae-Gyo	23	6.8	98	0.21	0.22
	25	Sahcheun-Gyo	25.5	7.0	126	0.20	0.16
		Boolkwang-Cheun					
	26	Wahsan-Gyo	27.5	6.9	120	0.22	0.19
	27	Jungsan-Gyo	27.5	7.4	189	0.19	0.10
		Daebahng-Cheun					
	28	Daebahng-Gyo	29.5	6.8	113	0.26	0.23
	29	Singil-Gyo	30	6.8	113	0.38	0.33
		Dohrim-Cheun					
Industrial area	30	Mahjahng-Gyo	31	6.8	61	0.29	0.45
	31	Dohrim-Gyo	30	5.4	142	0.31	0.05
		Ahnyang-Cheun					
	32	Sihoong-Gyo	30	5.4	45	0.05	0.11
	33	Gojeuk-Gyo	28	6.8	84	0.21	0.26
	34	Ahnyang-Cheun-Gyo	30.5	6.9	220	0.31	0.14
	35	Yanghwa-Gyo	25	6.6	137	0.24	0.18

Table 3. Range and mean values of F-contents in river water

Regional group	pH	Cl (mg/l)	F (mg/l)	F/Cl ($\times 10^{-2}$)
Han River area	6.8～7.2 6.9	3.2～6.9 5.5	0.10～0.14 0.12	1.45～3.75 2.10
Residential area	6.6～7.4 7.0	19～290 114	0.09～0.50 0.20	0.10～0.63 0.23
Industrial area	5.4～6.9 6.5	45～642 177	0.05～0.38 0.26	0.05～0.48 0.22

and 22nd of June 1969.

Average fluorine contents of regional groups are given in *Table* 3.

Fluorine content was the lowest in Han River and became larger from residential to industrial area. It is suggested that Han River is diluted with many tributary waters. The same tendency was confirmed in COD, contents of chlorine, bromine [5], and copper[7].

Major sources of fluorine contamination in residential area are considered to be attributable to human waste which chiefly contains salt (domestic crude salt contains 3.8–15 ppm, refined salt 2.5–7.1 ppm of fluorine[2]), and partially tooth paste and rodenticide.

Fluorine sources of river water running through the industrial area are considered to be partially attributable to wastes of pharmaceutical, chemical, food processing, leather tanning, plants and paper mills[1] etc, besides domestic sewage of the city. The average fluorine contents in the industrial area was not much larger than that in the residential area. Judging from the above results, there would be no large scale manufacturing plant using phosphate rock, quartzite, and fluoro apatite as raw materials. However, there would be small scaled plants manufacturing tooth paste, electric bulb, and rodenticide using fluorine compounds as a raw materials.

Detailed sources of fluorine in river water were previously described by Whang[4].

Fig. 2 shows the results of samples on June in 1969 and its distribution of fluorine contents.

Fluorine contents of 4 reservoirs and Han River were between 0.10 and 0.14 mg/l (except the June sample of 0.18mg/l at Dooksuem Reservoir). No significant differences in fluorine contents was found among them. This indicates that at the lower stream along Han River the fluorine contents are not influenced by sea water (sea water contains 18,980 mg/l of chlorine and 1.3 mg/l of fluorine[8]).

Fluorine contents of 0.19 to 0.27 mg/l in the most residential area were larger than those of Han River.

Values of all the rivers are as follows.

Joongryang-Cheun contained from 0.09 to 0.19 mg/l of fluorine contents, Jeungneung-Cheun 0.23 to 0.26 mg/l (except Yongdoo-Gyo), Seungbook-Cheun 0.20 to 0.27 mg/l, and Cheunggae-Cheun 0.22 mg/l. Of those rivers Seungdong-Gyo was lower contents of 0.19 mg/l. This suggest that it is because less contaminated Joongryang-Cheun flows into Seungdong-Gyo and much water lessen the relative density of fluorine contents. Besides these rivers, Wook-Cheun contains 0.24 mg/l, Hongjae-Cheun from 0.19 to 0.21mg/l, and Boolkwang-Cheun 0.19 to 0.22 mg/l. In the case of Joongryang-Cheun running through the suburb, fluorine contents increased as it flowed from the upper stream to the populated lower stream. There were little variations in other rivers. In

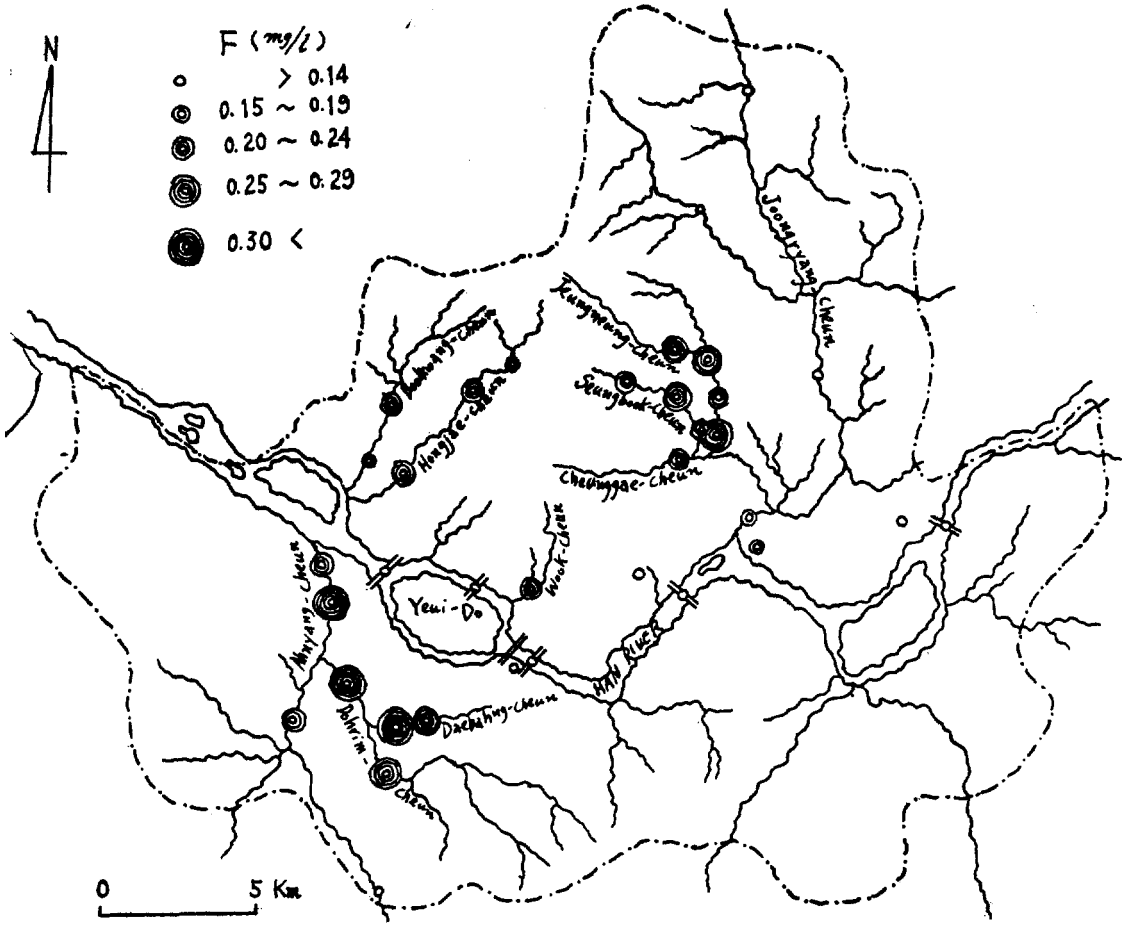

Fig. 2. Distribution of F in river water

the case of chlorine, the contents increased as the rivers flowed from upper to lower stream.

In the industrial area, the fluorine contents ranged from about 0.21 to 0.38 mg/l. Daebahng-Cheun contained fluorine ranging from 0.26 to 0.38 mg/l, Dohrim-Cheun 0.29 to 0.31 mg/l, Ahnyang-Cheun excluding Sihoong-Gyo 0.21 to 0.31 mg/l. The industrial area showed slightly larger contents than the residential area.

3. Seasonal and Hourly Variation of Fluorine Contents Fluorine contents of samples taken at 19 sites including Kwangjang-Gyo in June, September, November of 1969 and February of 1970 are listed in *Table* 4.

Owing to the rainny June and September, relatively much water caused chlorine contents and COD[5] low. On the latter of November chlorine contents and COD reached the peak due to pickling season concomitantly with dry season. For the reasons indicated above, chlorine contents and COD were larger in November. This seasonal variation occurred more intensively in the residential area than in Han River. Fluorine contents were less variable than chlorine contents and COD.

Fluorine contents were hourly analyzed for 12 hours at Chongahm-Daegyo and Jeungneung-Gyo on Jeungneung-Cheun from 8:00 A.M. through 7:00 P.M. on the 18th of November in 1969. For comparison, both hourly chlorine

Table 4. Seasonal variation of F-contents in river water

Regional group	Sample No.	Sampled at	Date of Sampling	Water temp. (°C)	pH	Cl (mg/l)	F (mg/l)	F/Cl ($\times 10^{-2}$)
	5	Kwangjang-Gyo	1969. 6. 21	22.5	6.8	3.2	0.12	3.75
			〃 9. 22	22	7.6	3.3	0.14	4.24
			〃 11. 22	8.5	7.2	5.0	0.13	2.60
			1970. 2. 23	6	7.1	3.5	0.11	3.14
	6	The 3rd Han River	1969. 6. 21	26	6.8	6.9	0.10	1.45
		Bridge	〃 9. 22	24	7.5	7.7	0.09	1.17
			〃 11. 22	8	7.2	9.0	0.12	1.33
			1970. 2. 23	7	6.8	5.8	0.10	1.72
	7	The 1st Han River	1969. 6. 21	24	7.2	4.8	0.14	2.92
Han River		Bridge	〃 9. 22	21.5	7.7	4.5	0.15	3.33
area			〃 11. 22	7.5	7.0	13	0.13	1.00
			1970. 2. 23	6	7.1	4.9	0.11	2.24
	8	Seoul-Daegyo	1969. 6. 21	24	7.0	5.6	0.14	2.50
			〃 9. 22	21.5	7.7	5.1	0.11	2.16
			〃 11. 22	6	7.2	13	0.12	0.92
			1970. 2. 23	6	7.2	6	0.09	1.50
	9	The 2nd Han River	1969. 6. 21	23	6.8	6.8	0.12	1.76
		Bridge	〃 9. 22	21.5	7.4	10.4	0.15	2.03
			〃 11. 22	8	7.2	13	0.13	1.00
			1970. 2. 23	9	6.7	7.8	0.11	1.41
	11	Wooi-Gyo	1969. 6. 21	25	7.0	47	0.09	0.20
			〃 9. 22	24	7.4	36	0.13	0.36
			〃 11. 22	11	6.9	110	0.19	0.17
			1970. 2. 23	—	—	—	—	—
	12	Joongryang-Gyo	1969. 6. 21	23.5	7.0	58	0.14	0.24
			〃 9. 22	24.5	7.2	62	0.13	0.20
			〃 11. 22	10	6.9	95	0.11	0.12
			1970. 2. 23	8	6.6	70	0.15	0.21
	13	Seungdong-Gyo	1969. 6. 21	22	7.0	108	0.19	0.18
			〃 9. 22	23	7.1	66	0.10	0.15
			〃 11. 22	9	7.0	144	0.14	0.10
Residential			1970. 2. 23	8	6.9	115	0.20	0.17
area	16	Chongahm-Daegyo	1969. 6. 21	25.5	7.4	126	0.23	0.19
			〃 9. 22	23	7.5	214	0.23	0.11
			〃 11. 22	9	6.9	278	0.25	0.09
			1970. 2. 23	15	7.5	226	0.25	0.11
	19	Donahm-Gyo	1969. 6. 21	22.2	6.9	104	0.27	0.26
			〃 9. 22	21	7.4	91	0.21	0.23
			〃 11. 22	12	7.2	376	0.20	0.05
			1970. 2. 23	12	7.0	120	0.27	0.23

	20	Ahnam-Gyo	1969. 6. 21	24	7.4	113	0.23	0.21
			〃 9. 22	22	7.1	102	0.22	0.21
			〃 11. 22	13	7.0	430	0.20	0.05
			1970. 2. 23	5	7.0	132	0.29	0.22
	21	Cheunggae-Jehigyo	1969. 6. 21	22	6.8	99	0.22	0.23
			〃 9. 22	23	7.0	93	0.18	0.19
			〃 11. 22	11.5	7.2	190	0.21	0.11
			1970. 2. 23	9	6.9	122	0.24	0.20
	22	Wonhyo-Gyo	1969. 6. 21	24	6.7	146	0.24	0.16
			〃 9. 22	21	7.3	116	0.20	0.17
			〃 11. 22	10.5	6.9	202	0.16	0.08
			1970. 2. 23	5	6.9	153	0.16	0.10
	24	Hongjae-Gyo	1969. 6. 21	23	6.8	98	0.21	0.22
			〃 9. 22	21	6.9	54	0.19	0.35
			〃 11. 22	14	7.0	396	0.19	0.05
			1970. 2. 23	8	7.0	110	0.19	0.19
	26	Wahsan-Gyo	1969. 6. 21	27.5	6.9	120	0.22	0.19
			〃 9. 22	21	7.2	102	0.20	0.20
			〃 11. 22	11	6.8	295	0.19	0.06
			1970. 2. 23	10	6.7	145	0.22	0.15
	28	Daebahng-Gyo	1969. 6. 22	29.5	6.8	113	0.26	0.23
			〃 9. 22	20	7.2	102	0.25	0.25
			〃 11. 22	10	6.7	120	0.19	0.16
			1970. 2. 23	10	6.5	122	0.32	0.26
	31	Dohrim-Gyo	1969. 6. 22	30	5.4	642	0.31	0.05
			〃 9. 22	23	7.3	93	0.30	0.32
			〃 11. 22	9	6.8	259	0.25	0.09
Industrial			1970. 2. 23	14	5.3	173	0.21	0.12
area	33	Gojeuk-Gyo	1969. 6. 22	28	6.8	84	0.21	0.26
			〃 9. 22	22	7.0	29	0.22	0.76
			〃 11. 22	8	6.7	67	0.15	0.22
			1970. 2. 23	10	7.2	68	0.17	0.25
	35	Yanghwa-Gyo	1969. 6. 21	25	6.6	137	0.24	0.18
			〃 9. 22	24	6.9	83	0.32	0.39
			〃 11. 22	10	6.8	162	0.18	0.11
			1970. 2. 23	16	6.8	125	0.15	0.12

and fluorine contents are shown in *Fig.* 3.

More variation of chlorine and fluoine contents at Chongahm-Daegyo was observed than that of Jeungneung-Gyo. That is, large contents of chlorine at Chongahm-Daegyo were analyzed at noon, 3:00 P.M., and 6:00 P.M. but a little increase in fluorine contents were noted between 11:00 A.M. and 2:00 P.M. The hourly variation of fluorine contents was slight when compared with that of chlorine contents. Hourly

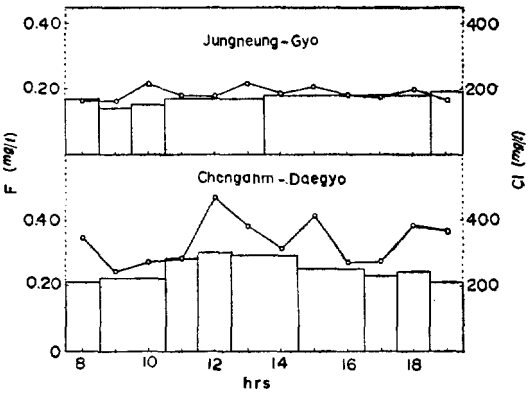

Fig. 3. Hourly variation of Cl and F

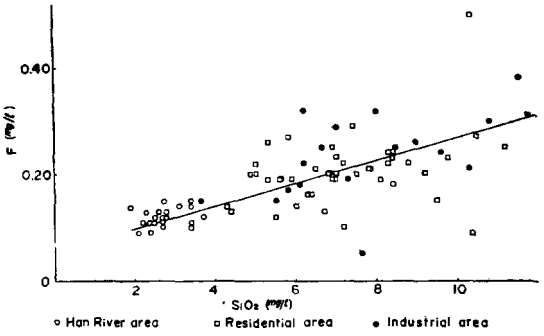

Fig. 5. Relationship between F and SiO_2

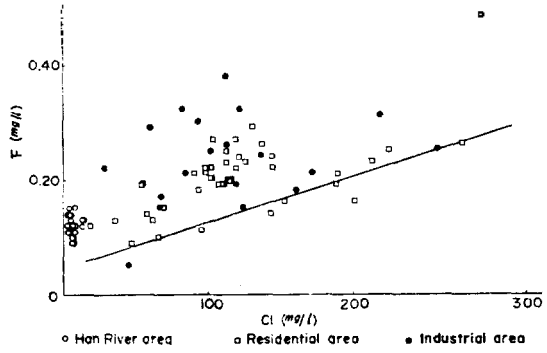

Fig. 4. Relationship between F and Cl

variation of chlorine contents was very variable, causing by hourly irregularity of disposal of wastes. But, fluorine contents in river water seems not to be influenced by hourly change in the disposal of wastes.

4. Relationship between Fluorine and Others The correlation coefficient of fluorine and chlorine contents was computed as +0.507 (*Fig.* 4). Chlorine content was significantly correlated with fluorine content in both residential and industrial areas, but in Han River there was no correlation.

Fig. 5 shows the relationship between fluorine and silica. The correlation coefficient was +0.617.

There was no correlation between fluorine, and bromine, iodine, sulfate ion and COD.

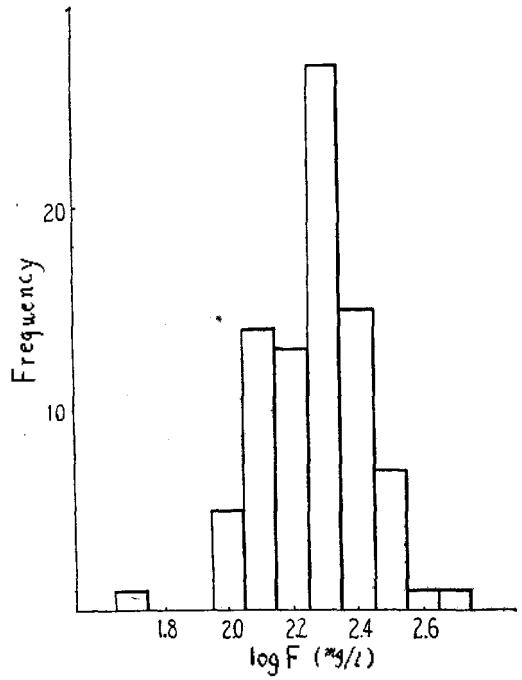

Fig. 6. Histogram of fluorine

5. Frequency of Fluorine Frequency of fluorine contents is shown in *Table* 5. Seventy five per cent of sample waters contained from 0.11 to 0.25 mg/l of fluorine. *Table* 5 also showed normal distribution as shown in *Fig.* 6.

Table 5. Frequency of F-contents in river water

F (mg/l)	Freq.	F (mg/l)	Freq.
<0.10	8	0.21~0.25	20
0.11~0.15	24	0.26~0.30	8
0.16~0.20	21	>0.50	6

Conclusion

The following results were obtained in analyzing the fluorine contents of reservoirs and river waters in Seoul for the period between June in 1969 and February in 1970.

1. Reservoirs of Seoul city contained from 0.09 to 0.15 mg/1 of fluorine contents (except the June measurement of natural water at Dookseum Reservoir). There was no difference in fluorine contents between natural and filtered waters.

2. Han River contained from 0.09 to 0.15 mg/1 of fluorine contents. The fluorine contents at Kwangjang-Gyo located at upper stream of Han River showed the range from 0.11 to 0.14 mg/1. At the 2nd Han River Bridge located at lower stream, the content was from 0.11 to 0.15 mg/1. Therefore locational difference along the river does not reflect significant variation of fluorine content.

3. River running through the residential area were chiefly influenced by city sewage. Joongryang-Cheun contained from 0.09 to 0.20 mg/1 of fluorine contents, Jeungneung-Cheun 0.23 to 0.26 mg/1 (except Yongdoo-Gyo), Seungbook-Cheun 0.20 to 0.29 mg/1, Cheunggae-Cheun 0.18 to 0.24 mg/1, Wook-Cheun 0.16 to 0.24 mg/1, Hongjae-Cheun 0.19 to 0.21 mg/1, and Boolkwang-Cheun 0.19 to 0.22 mg/1.

4. Rivers running through the industrial area showed slightly large contents of fluorine than those through the residential area. The range between 0.19 and 0.38 mg/1 of fluorine contents was obtained in Daebahng-Cheun, 0.25 and 0.31 mg/1 in Dohrim-Cheun, 0.15 and 0.32 mg/1 in Ahnyang-Cheun (except Sihoong-Gyo).

5. Seasonal and hourly variations of fluorine contents in the river water were less than those of chlorine contents.

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