Distribution of Heavy Metals in Bottom Mud of Rivers IX.

—Distribution of Total and Acid-soluble Cu—

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Abstract

The total and 0.5N-HCl soluble Cu contents in the bottom mud of major rivers in Japan were determined. The base-line levels of total and acid-soluble Cu were 23 ppm and 7 ppm, respectively. Rivers are divided into three types based on the distributions of total and acid-soluble Cu contents in mud as follows: 1) Non-polluted rivers: Total and acid-soluble Cu contents show the value near the base-line level from upper to lower streams. Total Cu contents are affected by the parent materials of the sampling station, however, and the amount of acid-soluble Cu is less than 30 per cent of total Cu. 2) Urban rivers: Total and acid-soluble Cu contents increase remarkably downstream, and the amount of acid-soluble Cu is more than 60 per cent of total Cu. 3) Mining rivers: Total and acid-soluble Cu contents are remarkably high upstream where the waste water from mines is received, and decrease during transport.

1. Introduction

Copper is a natural constituent of bottom mud. However, the anthropogenic input of Cu caused by copper refinery, electroplating of metals, and mining results in widespread environmental damage. A large part of the anthropogenic copper discharged into the aquatic environment becomes part of the suspended particles and this fraction settles into the riverbed. Moreover, Cu ion easily forms CuS under anaerobic conditions because copper has a strong affinity with sulfur and it is taken into bottom mud. It was reported that humic acids were excellent scavengers for copper (NRIAGU and COKER, 1980; NRIAGU *et al.*, 1981) and that heavy metals in sediment were related to organic matter (BURTON and LISS, 1976). Such compounds may be contained in the mud of urban rivers which received domestic sewage.

Previously, the present authors reported that the amount of 0.5N-HCl soluble metals was associated with the anthropogenic input of heavy metals (TADA *et al.*, 1976). The technique of leaching the sample with cold 0.5N-HCl was used for the assessment of trace metal pollution by CHESTER and VOUSTINOU (1981). Moreover, LUOMA and BRYAN (1981) also

showed that the method of extraction with 1N-HCl could be useful to define the chemical and biological interaction of trace metals.

The object of the present study is to describe the base-line levels of total and 0.5N-HCl soluble Cu and the progress of copper pollution in the bottom mud of Japanese rivers. The base-line levels were obtained from the bottom mud collected upstream of a river unaffected by waste water drainage. The progress of the copper pollution in the rivers was compared with these base-line levels. Moreover, the copper distribution patterns from the different type rivers were researched.

2. Experiments

1. Materials

One hundred and seventy-eight (178) mud samples were collected 1 km upstream from the estuary in 91 rivers in August and September, 1973. One hundred and ninety-three (193) mud samples were collected at an upstream station located near a mountain and where there was no discharge of waste water from 77 rivers in August and September, 1976. Two samples were collected from each of the upper and lower stream stations.

The samples from rivers which were

studied in further detail were collected at 8 to 10 stations between the upper and lower streams of 10 rivers, i.e., the Sagami, Oi, Toyo, Yahagi, Tama, Tsurumi, Syonai, Watarase, Hazama, and Yone-shiro Rivers. The mud samples of 10 to 20 were collected from upper, middle, and lower streams of three stations and one sample from another station.

2. Methods

Total and 0.5N-HCl soluble Cu in bottom mud were determined using the same method as mentioned in the earlier paper (TADA *et al.*, 1976).

3. Results and Discussion

1. Base-line level of Cu in Japanese rivers

Figures 1 and 2 show the histogram of the total and 0.5N-HCl soluble Cu, respectively, in the upper and lower streams of major rivers in Japan. Table 1 shows the averages of total and 0.5N-HCl soluble Cu in these rivers.

The upstream bottom mud, which was not expected to suffer from copper pollution, contained total Cu in the range of 4 to 113 ppm, and ca. 90% of samples contained less than 50 ppm. The average value was

Fig. 1. Distribution of total Cu in bottom mud of Japanese rivers.

Fig. 2. Distribution of 0.5N-HCl soluble Cu in bottom mud of Japanese rivers.

23 ppm. The amount of acid-soluble Cu was below 20 ppm in 95% of the rivers and the average was ca. 7 ppm, which corresponded to 30% of total Cu. It was reported by SWAINE (1969) that soils normally contained 2 to 100 ppm of total Cu; the average was 20 ppm, and up to ca. 1 ppm might be extracted by H₂O or HCl (pH 2). The average of 0.1M-HCl soluble Cu in paddy fields was 9.08 ppm (KANKYO-CHO, 1973). Consequently, Cu content was similar to those of normal soils. Then the values in the upstream bottom mud can be evaluated as the base-line level of the bottom mud in Japanese rivers.

To investigate the effect of the parent materials on the base-line levels, Japan was divided into the following three zones based on the parent rock: 1) basic volcanic zone, 2) metamorphic zone, and 3) other rock zone. Table 2 shows the averages of total and acid-soluble Cu in the bottom mud of rivers running through these three zones. It was observed that the bottom mud derived from basic volcanic and

Table 1. Averages of total and 0.5N-HCl soluble Cu in Japanese rivers.

Sampling station	$\bar{x}$ (ppm)	Total s (ppm)	n	$\bar{x}$ (ppm)	HCl s (ppm)	n
Upstream	23	17	193	7.1	5.9	183
Downstream	47	48	179	22.4	43.8	149
IL* < 5.03%	28	21	118	7.6	7.7	90
IL* > 5.03%	61	52	55	36.2	35.5	59

*Ignition loss

Table 2. Distinction of total and 0.5N-HCl soluble Cu contents based upon parent rock and geological zone.

	Total			HCl		
	$\bar{x}$ (ppm)	s (ppm)	n	$\bar{x}$ (ppm)	s (ppm)	n
Parent Rock						
Basic volcanic R.	33	20	23	11.3	9.5	23
Metamorphic R.	33	24	23	9.4	6.9	30
Other R.	17	15	127	5.1	3.3	118
Geological Zone						
Hokkaido	17	10	16	4.4	2.5	16
Tohoku	20	10	31	6.9	5.1	20
Outer Z.	27	16	51	8.3	6.5	55
Inner Z.	19	16	85	6.5	5.7	92

metamorphic rocks had a high total Cu content. It was reported that the average total Cu content was 149 ppm in basic volcanic rocks, 38 ppm in the intermediate volcanic rocks, and 16 ppm in acidic volcanic rocks (YAMAGATA, 1977). Thus, copper was obtained in high concentrations in the mud of the Sagami and Tenryu Rivers which run through the Fuji volcanic zone. The Kino, Yoshino, and Niyodo Rivers which run through the Sanbagawa metamorphic belt also had high concentrations of total Cu in bottom mud.

The Tonegawa tectonic line divides Japan into four areas, namely, the east area of this line can be divided into Hokkaido and Tohoku, and the west area into the Outer and Inner zones. The average total Cu of the bottom mud in rivers belonging to the Outer zone indicated a higher value than that of the other areas such as shown in Table 2.

The average acid-soluble copper in bottom mud did not differ greatly among these divided areas.

2. Progress of Cu pollution in Japanese rivers

As shown in Fig. 1, the distribution of total Cu ranged from 3 to 1163 ppm in the downstream bottom mud of Japanese rivers. About 10% of the samples indicated over 100 ppm of total Cu. Also, the average acid-soluble Cu was three times

higher than the base-line levels; the maximum value was 400 ppm. Compared with the base-line levels, the bottom mud in the downstream of some rivers is considerably polluted by Cu.

The downstream mud was divided into two groups according to ignition loss (IL), namely, higher or lower than 5.03%, the average value of Japanese rivers (SHIBAHARA *et al.*, 1976). Table 1 shows the averages of total and acid-soluble Cu. The averages of the lower IL group were not significantly different from the base-line levels, whereas those of the higher group were 3 to 4 times higher than the base-line levels. Furthermore, the fraction of acid-soluble Cu was 60% of total Cu. It is suggested from these data that organic matter in rivers may be an important factor controlling copper pollution in bottom mud.

3. Cu distribution pattern

1) Non-polluted rivers

Figure 3 shows the amounts of total and acid-soluble Cu in the Sagami River running through the Fuji volcanic zone, the Oi river running through the Shimanto belt, the Toyo River running through the metamorphic rock belt with its complicated geology, and the Yahagi River belonging to the Inner zone. Drainage from industry and mines has produced little effect on these rivers (KENSETSU-SHO, 1976).

Fig. 3. Total (●—●) and 0.5N-HCl soluble (○---○) Cu in non-polluted rivers.

The bottom mud in the Oi and Yahagi Rivers indicated a narrow range of total Cu distribution between 20 to 25 ppm and 8 to 10 ppm, respectively. These rivers run through a geographically uniform area. The total Cu varied with the sampling stations in the Sagami and Toyo Rivers. The former contained a total of ca. 100 ppm Cu in the upstream bottom mud, and at stations which belong to the Fuji volcanic zone. The latter ranged widely from 15 to 60 ppm total Cu.

The distribution of acid-soluble Cu in these rivers varied only slightly with the sampling station, even if there was a wide variety in total Cu such as in the Sagami or Toyo River. The value was 5 ppm in the Oi River, 2 to 5 ppm in the Yahagi River, 5 to 10 ppm in the Toyo River,

and 10 to 20 ppm in the Sagami River.

Consequently, total Cu seemed to be more affected by parent rock than acid-soluble Cu.

2) Polluted rivers

Urban rivers: Figure 4 shows the distribution of total and acid-soluble Cu in the mud of the Tsurumi, Tama, and Shonai Rivers.

The amounts of total and 0.5N-HCl soluble Cu increased remarkably downstream in these rivers. The amounts of total Cu in the downstream mud of the Tsurumi and Tama Rivers running through the Keihin Industrial Area reached 180 ppm and 120 ppm, respectively. The Shonai River running through the Nagoya Industrial Area evidenced a total Cu of 90 ppm.

Fig. 4. Total (●—●) and 0.5N-HCl soluble (○---○) Cu in urban rivers.

Fig. 5. Total (●—●) and 0.5N-HCl soluble (○---○) Cu in mining rivers.

In these rivers, the amount of acid-soluble Cu indicated a distribution pattern similar to that of total Cu. The extractable fraction was 70-80% of total Cu in downstream bottom mud.

Mining Rivers: Figure 5 shows the distribution of total and acid-soluble Cu in the Watarase, Yoneshiro, and Hazama Rivers running through copper mine areas.

The bottom mud contained 306 ppm total Cu and 30 ppm 0.5N-HCl soluble Cu upstream in the Watarase River which receives the water of the Ashio mine. The Hazama River which receives the drainage

of the Hosokura mine contained high total and acid-soluble Cu in bottom mud. However, these amounts decreased drastically 10 km downstream from the mine. The bottom mud of the Yoneshiro River, which receives waste water from many mines, contained large amounts of total and acid-soluble Cu. Total Cu was 3163 ppm and acid-soluble Cu was 538 ppm at a station near the Hanaoka mine.

It was observed from the above data that Cu contents in the rivers running through the mine were remarkably higher than the base-line level and decreased during transport. Unlike urban rivers, the extractable fraction was only 30%, however.

4. Map of Cu pollution in Japanese rivers

The distribution map of 0.5N-HCl soluble Cu in Japanese rivers is shown in Fig. 6 from the viewpoint of pollution. The concentration of acid-soluble Cu is divided into three categories on the basis of the average $\bar{x}$ and standard deviation s in the upstream mud, namely, 1) $(0) \sim (\bar{x} + s)$, 2) $(\bar{x} + s) \sim (\bar{x} + 3s)$, 3) over $(\bar{x} + 3s)$. The map of acid-soluble Cu is similar in pattern to those of Cd and Zn as reported in the previous study (TADA and SUZUKI, 1981).

4. Conclusion

1) The base-line levels of total and acid-soluble Cu in the bottom mud of Japanese rivers are 23 ppm and 7 ppm, respectively.

2) Total Cu content is generally affected by the parent rock in non-polluted rivers.

3) A large part of Cu occurring in the bottom mud of urban rivers is associated with organic matter and is very soluble in 0.5N-HCl.

4) The content of total Cu is high in bottom mud containing the drainage of mines but decreases drastically downstream.

摘 要

日本の河川底質中の Cu の分析を行なった。その結果、含有量のベースラインは 23 ppm, 0.5N-HCl 可溶態量のベースラインは 7 ppm である。含有量のベースラインは底質中の母岩によって影響を受けやす

Fig. 6. Distribution map of Cu extracted with 0.5N-HCl.

- 0~13.0 ppm
- 13.1~24.8 ppm
- 24.9 ppm~

く、塩基性火山岩帯を流れる河川は比較的 Cu 含有量が高い。一方、酸可溶態量は母岩による影響は少ない。また、非汚染河川では、上流から下流まで、含有量および酸可溶態量共にベースラインに近い値を示す。これに対して、都市型河川では含有量がベースラインより数倍高く、そのうち 70~80% までが 0.5N-HCl で溶出される。鉱山型河川では上流の排水受水部で含有量が異常に高いが、0.5N-HCl で抽出される Cu は 20~30% であり、流下するに従って減少する。

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