Recent Heavy Metal Concentrations in Watarase Basin around Ashio Mine

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Pollution in the Watarase River caused by mineral wastewater containing high levels of copper discharged during the development of the Ashio Copper Mine is one of the most well-known environmental pollution problems in Japan, and has been called the "Starting line of environmental pollution problems in Japan." In this study, we conducted follow-up investigations on the conditions of pollution in the Watarase River since 1991, and measured the heavy-metal levels in water in other rivers near the Watarase River and in soils around them. In addition, we compared the results in this study with previous results, *i.e.* pollution conditions in the Watarase River, other rivers and soils. Six points in upstream sites of the Watarase were chosen for sampling. Six samples from river water, five samples from soils around the respective points, and three samples from tap water distributed there were collected for the analysis. Heavy metal levels in rivers and soils around the Ashio Copper Mine were significantly lower than the environmental standards for them. When compared with our previous investigations, the levels of polluting heavy metals around the closed refinery at the Ashio Mine were gradually but clearly reduced. In conclusion, the environment around the Watarase River has been steadily improved so that safety in the living environment is assured.

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INTRODUCTION

Pollution in the Watarase River caused by mineral wastewater containing high levels of copper discharged during the development of the Ashio Copper Mine has drawn attention as one of the most well-known environmental pollution problems in Japan, and has been called the "Starting line of environmental pollution problems in Japan."[1)] A copper vein was found there in 1610, and especially since 1868, when Japan opened its country, mining accelerated to support the rapid industrial development of Japan to catch up with industrialized Western countries. In the late 19th century, dead fish in the river, which was contaminated with the water discharged from the refinery, were observed. This drew our attention as the first sign of a series of disastrous impacts. Around 1894, the latest refining method was introduced, and the valleys around the refineries were filled with sulfur oxide gas exhausted from the refurbished refinery. The results were empty valleys without any trace of life. Then, Kozai pointed out this pollution issue and found high copper levels in farmland soil in the area.[2)]

Poisonous metals, including copper and arsenic, were discovered in the waters of the Watarase River when the amount of water had increased due to heavy rains. The Ashio refinery was surrounded by 14 very large slag-pile accumulation basins and these are a constant menace to the natural river system, for any one of them might collapse into the river if there were heavy rains or an earthquake.[1)]

Mining operations at the Ashio Mine were abandoned in February 1973, but the copper refinery business, which apparently caused heavy metal contamination, was not discontinued until 1988. Thus, there is no possibility of new pollution.[3)] After the termination of refining operations at the Ashio Mine, we conducted a series of investigations on the heavy metal levels in rivers around the Ashio Mine beginning in 1991, for the purpose of determining pollutants. In our previous investigations[4–7)] for the rivers around the Ashio Mine, a slight degree of pollution by heavy metals had already been confirmed. In this study, we conducted a follow-up investigation to confirm the degree of improvement of environmental circumstances around the basin of the Watarase River

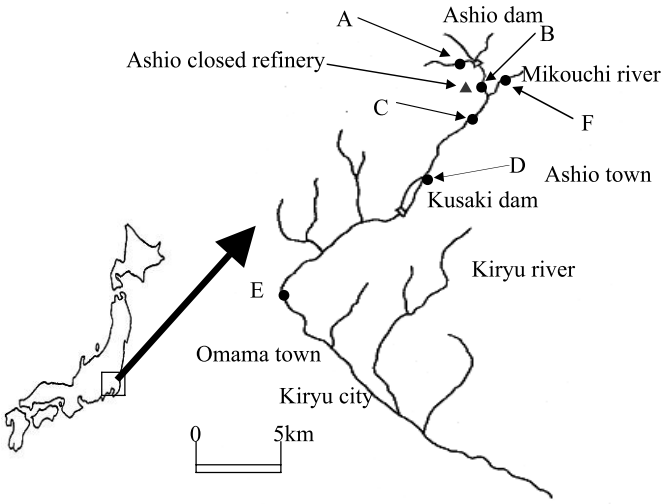

Fig. 1. Map of Ashio Area with Sampling Sites

in comparing with our previous data. Therefore, we focused on measuring the levels of several kinds of heavy metals in the river water and soils sampled around the Watarase River, and compared them to the environmental regulation standard in Japan.

Ashio is a small town located about 150 km north of Tokyo. The Watarase River runs down from the mountains in the Ashio area and flows into the Kanto Plain, which includes the main source of tap water for human activities in Kanto area. This is also an important reason for researching the current status of the Ashio area.

MATERIALS AND METHODS

In this study, six points in upstream sites of the Watarase River [A: Upstream of the Ashio Dam, B: Around the closed refinery, C: Around the Ashio Town Office, D: The Souri area at the Kusaki Dam, E: Under the Takatsudo Bridge in Omama Town, and F: Around the Mikouchi River (tributary of the Watarase River)] were chosen for sampling. Sampling site is showed in Fig. 1. On May 4, 2005, six samples from river water, five samples from soils around the respective points, and three samples from tap water distributed there were collected for the analysis. Each sample was analyzed according to the Japanese Industrial Standards and the Notification of Ministry of Health, Labour and Welfare, Japan. In the analysis, heavy metal levels were simultaneously measured by inductively-coupled plasma spectrometry (ICP, using the absolute calibration method) and ICP-mass spectrometry (ICP-MS, using the internal standard method) for metals, where the measurement conditions were optimized for each metal.

RESULTS AND DISCUSSION

The concentrations of elements found in water samples and soil are shown in Tables 1 and 2. As for the six samples from river water, the copper level, levels of heavy metals (arsenic, cadmium, lead, hexavalent chromium, mercury, selenium and boron) regulated under Japanese environmental standards by the Japanese Basic Environment Law, as well as nickel and antimony are shown in Table 1. In the case of soils, none of the levels of heavy-metals (cadmium, lead, hexavalent chromium, arsenic, total mercury, alkyl mercury, selenium and boron) regulated under the Soil Contamination Countermeasures Law exceeded the environmental standards for soils. Therefore, the copper and arsenic levels in particular are shown in Table 2. All the samples from tap water conformed the quality standards for heavy metals in tap water under the Water Works Law. In this study, heavy metal levels in rivers and soils around the Ashio Copper Mine were significantly lower than the environmental standards for them.

The copper levels in the area around the closed refinery and the downstream areas were higher than those in the upstream area of the sampling points

Table 1. The Concentrations of Elements Found in Water at Each Sampling Point A–F

(μg/l)

element	A	B	C	D	E	F	MRL[a)]
copper	0.3	6.1	1.6	1.6	1.5	0.9	—
arsenic	2.9	3.8	3.9	1.8	1.5	1.4	10
cadmium	0.02	0.34	0.04	0.04	0.07	< 0.02	10
lead	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	10
hexavalent chromium	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	50
total- mercury	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.5
selenium	< 0.2	0.2	0.3	0.4	0.3	< 0.2	10
boron	3.3	4.3	12.7	6.7	20.9	3.6	1000
nickel	0.8	1.1	0.5	0.7	0.5	0.9	—
antimony	0.13	0.16	0.28	0.15	0.17	0.09	—

a) Maximum Residue Limit; Japanese environmental regulated standards in river water by the Japanese basic environment law.

Table 2. The Concentrations of Elements Found in Soil at Each Sampling Point A–F

(mg/kg)

element	A	B	C	D	E	F	MRL[a)]
copper	0.02	0.45	0.44	not measured	0.02	0.01	125 mg/kg in farmland
arsenic	0.001	< 0.001	0.012	not measured	< 0.001	< 0.001	15 mg/kg in farmland

a) Maximum Residue Limit; Japanese soil standards by the Japanese soil contamination countermeasures law.

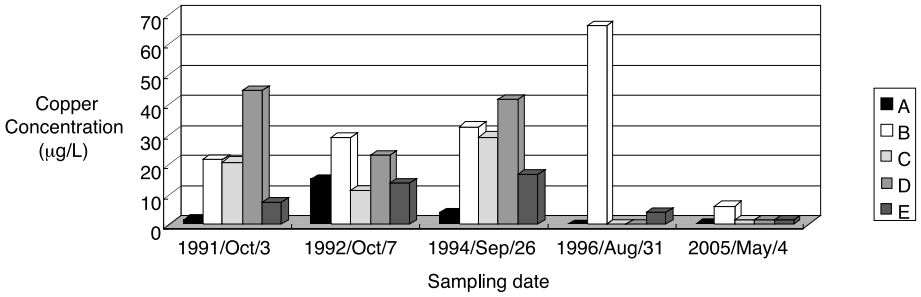

Fig. 2. Annual Changes of Copper Concentration in River Water at Each Sampling Point A–F

(Table 1). Residual copper was detected in the samples from the areas around the refinery and the downstream areas, suggesting the actual conditions of pollution there. Results for soils indicated that the copper level around the refinery was the highest when compared with upstream and downstream areas, and the level was relatively low at the downstream areas, showing the same tendency as that in the river water analysis (Table 2). These results suggested that the refinery was the source of copper pollution and the environmental conditions have not recovered completely. In addition, the copper level in soils in these areas was very much lower than the environmental standards for soils, and their effect on the environment was reconfirmed to be negligible.

On the other hand, the arsenic levels in river water in all the areas were detectable but lower than the environmental standards, and the same result was obtained from soils. However, the arsenic level in water around the closed Ashio Copper Mine was approximately three times higher than that around the Mikouchi River, a tributary of the Watarase River. Furthermore, the arsenic levels in river water in these areas were generally higher than those in the other areas. Therefore, it was suggested that mining at the Ashio Mine had also affected the arsenic levels in these areas.

The annual and spatial distribution of copper and arsenic concentration in the river water of five sampling points (A–E) is shown in Figs. 2 and 3. Comparing current data to collected data from 1991,[7)] we have found that the copper and arsenic concen-

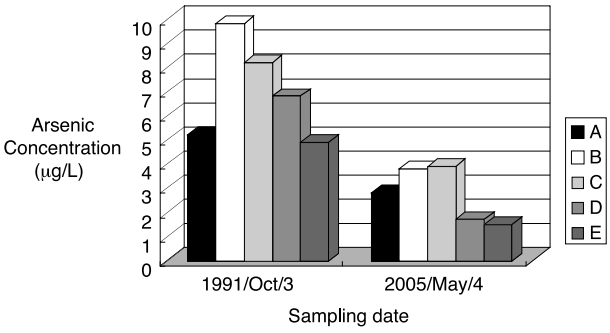

Fig. 3. Annual Changes of Arsenic Concentration in River Water at Each Sampling Point A–F

trations have decreased. However, we found a relatively high concentration on sampling site B in 1996. Morishita and Tsukigi stated that heavy contamination of suspended copper and arsenate was detected during flooding.[8] There is a possibility that measured concentration depends on the running water quantity of the river. But, this study has not established a relationship between measured concentrations and running water quantity. It might be concluded from this study that the current status of the Ashio area provided better conditions than in the past.

When compared with our previous investigations, the levels of polluting heavy-metals around the closed refinery at the Ashio Mine were gradually but clearly reduced. In another report, Kurihara *et al*. reported that copper and arsenic concentrations of river water at the site near sampling point B in this study are 170 and 14 μg/l, respectively, when it was investigated at July 26, 1981.[9] The environment around the Watarase River has been steadily improved so that the safety in the living environment might be enhanced.

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