Zinc contamination in river water and sediments at Taisyu Zn–Pb mine area, Tsushima Island, Japan

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Abstract

Tsushima Island is one of the oldest zinc-lead mining areas in Japan. River water and sediment samples were collected mainly from Taishu area to determine the contamination level of Zn and to clarify its behaviour in the natural system. Among the water samples analysed, 64% exceeded the standard environmental limit of 0.03 $\mu g\ ml^{-1}$ for Zn. In most cases, Zn concentration in sediment samples also exceeded the standard value, and the concentration varied from 86.75–7490.07 $\mu g\ g^{-1}$. The mineralogical constituents in sediments were almost similar and quartz had the strongest peak, but the interior part of the ores had many minerals, with galena having the highest proportion. Considering the enrichment factor values (EFc), 12 samples have values of more than 50, indicating a high pollution load for Zn. This study revealed that the sulphide ores, and contaminated sediments, are the possible contamination sources of Shiine River, and Zn dissolution occurred by reactions, such as desorption and ion exchange.

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1. Introduction

The environment of mineralised areas is rich with high concentrations of metals that can have toxic effects on plants, animals and human beings. In Japan, there exist variable human damage caused by mine wastewaters, such as copper (Cu) poisoning in the Ashio Cu mine area, and the Itai-itai disease induced by cadmium (Cd) in the Kamioka mine area. Therefore, in the Basic Environment Law of Japan (MOE, 2004a), there are severe restrictions for Cu and Cd in the environmental standard for the protection of human health. Also, the chemical behaviours of base metals in mine wastewater and treatment methods have been established for Japanese rivers through many studies to satisfy the environmental standard. Since, zinc

(Zn) has not been considered poisonous, in terms of human health protection, it was regulated only inside the standard for the conservation of the living environment. The 1971 Emission Standard of Zn was 5 $\mu g\ g^{-1}$ for mine wastewater and 1 $\mu g\ g^{-1}$ for the waterworks department, but there was no restriction that covered all river areas, except for limits set voluntarily by the local government units. But Zn is present everywhere in nature with wide variation in concentrations. For example, 1.2% of Zn, initially present in river sediment, is released to the environment after 15 months, representing an estimated quantity of about 4 kg Zn over an area of 50 m^2 (Isaure et al., 2005).

However, within an environment conservation result review, posted by the Organization for Economic Cooperation and Development (OECD) in January 2002, the adoption of a limit to conserve aquatic life was recommended, and on May 11, 2003 the Zn limit for all river areas in Japan was set to 0.03 $\mu g\ g^{-1}$ (MOE, 2004b). Following this, the Ministry of the Environment of Japan conducted a field survey on Zn emission, and found that about 50 rivers across the nation of Japan exceeded the limit, and the main cause are the mines (MOE, 2004b). In order to improve

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this situation, the identification of contamination sources of Zn and its behaviour on the natural system are necessary. But, the regulation was set quite recently, and adequate research has not been carried out yet, especially on river water and sediments lying on the river bottom.

Rivers in the Tsushima Island, southern part of Japan were investigated in this study for the following reasons. Tsushima is famous for one of Japan's oldest Zn–lead (Pb) mines, and the distance between the mine and the sea is very short. In this study, the samples were collected from Taishu area (mainly from Shiine River), the length of which is short. There are many tributaries and mine entrances/exits in this area, and the river crosses outcrops of several ore veins. The objective of this study was to determine the contamination level of Zn, and to clarify the mechanisms of adsorption on and desorption from the sediments. An attempt was made to find the answer of the question: are only the mining activities responsible for Zn pollution in this area or not?

2. Materials and methods

2.1. General description of Tsushima Island and study area

Tsushima Island is located in the western part of the Japanese islands with a length of 12 km east–west and 25 km north-south. It is the largest island of the Nagasaki Prefecture, which is situated in the Tsushima Strait at 34°25′N and 129°20′E. Differential erosion of geological structures is one of the characteristics of the island's landscape. The island mainly consists of Tertiary sedimentary rocks (shale and sandstone), which are intruded by Miocene granitic rocks. Contact metamorphism has affected the sedimentary rocks near the granitic body. Lead–Zn veins (Taishu mine) occur in the granitic body and sedimentary

rocks (Ishihara, 1971; Ishihara et al., 1992; Takagi, 2004). The main ore minerals are galena, sphalerite, pyrrhotite and pyrite (Sihimada and Hirowatari, 1972).

The Akusuidani River is the main stream of the Shiine River, and the Onigasai River is a tributary (Fig. 1). The Sasu River is situated to the north of the Onigasai River. The mine entrance is on the bank of Akusuidani River, the mine pollution control plant on the bank of Onigasai River, and the mining plant on the bank of Sasu River.

2.2. Sampling

River water was collected from 25 sites, and tap water from 1 location. Twenty-four water samples were collected from Shiine River and its two tributaries (Onigasai and Akusuidani), and one sample from Sasu River. Sediment samples were taken from 18 sites where water was also sampled. At the same location, two types of sediments were collected from 11 sites (bottom sediment (bt) and bank sediment (bk)) while from another 7 sites only bottom sediment was collected, making a total of 29 samples. One sediment sample was collected from a single site, and used for analysis. In addition, ores and rocks were collected from some sites for study. All sediment samples, including ores and rocks, were collected from Shiine River.

2.3. Sample preparation and analysis of water and sediment samples

The pH, electrical conductivity (EC), oxidation-reduction potential (ORP), temperature and CO_2 concentration of river water samples were measured just after sampling at the site using a Towa DKK HM-20P pH meter, a Towa DKK CM-21P
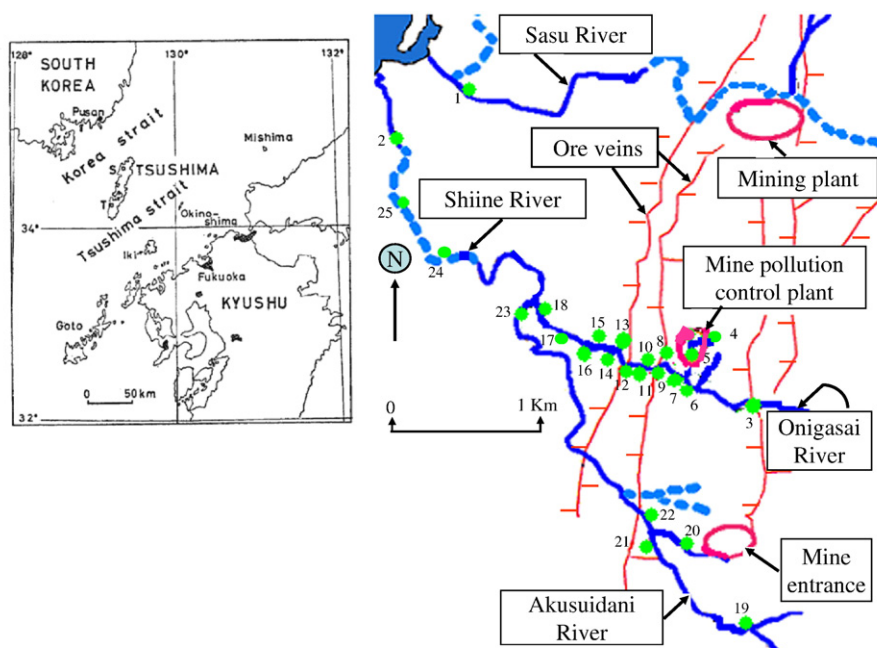

Fig. 1. Tsushima Island, Japan (inset). Locations of the mining plant, mine entrance, mine pollution control plant, ore veins and sampling sites.

EC meter, a Towa DKK RM-20P ORP meter and a CO_2 gas meter (Ti-9004 by Toko Chemical Lab.), respectively. The sediment sample mass collected in each case was about 500 g. Sub-samples of the material were oven dried at 45 °C for 48 h, disaggregated in a porcelain mortar with a pestle, and sieved through a 63 μm stainless steel screen. For chemical analysis, they were subsequently pulverized into powder using an agate ball mill (200 rpm, 30 min). Metal concentrations of sediments were determined by a Hitachi Z-6100 Polarized Zeeman Atomic Absorption Spectrophotometer (AAS), while the concentrations of Zn and Cd, both in water and sediments, were determined by a Hewlett-Packard 4500 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The detection limit for Zn and Cd were 10 ng l^{-1} and 7.5 ng l^{-1}, respectively. A Geochemical Standard Lake Sediment, JLk - 1 (provided by the Geological Survey of Japan, 1-1-3 Higashi, Yatabe, Ibaraki, Japan) was also analysed, using the same procedure as a check, and reached 98% recovery of Zn. A Bruker AXS: D-8 Advance (Berlin, Germany) X-ray diffractometer (XRD) was employed for XRD analysis.

2.4. Dissolution–desorption experiment

2.4.1. Samples

Three types of solid samples were chosen for the dissolution–desorption experiment: (a) surface of ore collected near sampling site 4, (b) interior part of sulphide ore, and (c) bank sediment sample collected from sampling site 11 (bk). To prepare the ore sample, the surface was scraped off with a flat-blade screwdriver, and the material collected into a polythene bag. Then it was pulverized to powder in an agate ball mill (200 rpm, 30 min) and placed into a glass container for chemical analyses. After removing the surface part, the ore was crushed with a hammer, and only the interior particles were collected carefully and milled as mentioned above. River water from sampling site 11 was collected to study possible reactions, since the sediments collected from this site had the highest Zn content (Table 2).

2.4.2. Experimental procedure

There were 8 different reaction times, i.e., 5 min, 1, 8 and 24 h, 3, 7, 14 and 28 days. Exactly, 0.3 g of solid sample and 3 cm^3 of water were placed in a 5 cm^3 HDPE container for reaction, and temperature was maintained at 25 °C during the experiments. After reaction, sample solutions were filtered by suction through a 0.22 μm Millipore filter. The filtrate was collected into a polyester container for analysis. The residue left after filtration was dried at a temperature of 48 °C for 24 h. Then 50 mg of each dried sample was acidified with a strong acid mixture (1 ml HF, 0.8 ml $HClO_4$, 1 ml HCl and 1 ml HNO_3), and digested on a hot plate at 120 °C for 24 h for complete dissolution of minerals. Then the solutions were prepared for ICP-MS measurement following the manufacturer's recommendations. Geochemical standard ore sample, JZn-1 (provided by the Geological Survey of Japan, 1-1-3 Higashi, Yatabe, Ibaraki, Japan) was also analyzed using the same procedure as a check and found 98–106% and 104–110% recovery of Zn and Cd, respectively.

2.5. Sequential extraction experiment

2.5.1. Sediment samples

Three types of sediment samples were chosen for the sequential extraction experiment on the basis of their Zn concentration: (a) bank sediment sample from site 11 (bk), which was also used in the dissolution–desorption experiment, and is extremely Zn rich (7490 μg g^{-1}), (b) bottom sediment sample from site 17 (bt) containing an intermediate concentration of Zn (2587 μg g^{-1}), and (c) bottom sediment sample from site 21 (bt), having the lowest concentration of Zn among the sediment samples collected (159 μg g^{-1}).

2.5.2. Experimental procedure

For this experiment a 4-step extraction procedure was adapted from a 9-step sequential extraction method introduced by Miller et al. (1986). The sequential extraction procedure and the extractants employed to solubilise 0.5 g sediment sample is described below:

Step 1 (Exchangeable): 20 cm^3 of 0.5 M $Ca(NO_3)_2$ are added and then stirred for 16 h.

↓

Step 2 (Acid soluble): 10 cm^3 of 0.88 M CH_3COOH + 10 cm^3 of 0.2 M $Ca(NO_3)_2$ are added to the residue left from Step 1 and then stirred for 8 h.

↓

Step 3 (Mn Oxide-occluded): 10 cm^3 of 0.02 M $NH_2OH·HCl$ + 10 cm^3 of 0.2 M HNO_3 are added to the residue left from Step 2 and then stirred for 0.5 h.

↓

Step 4 (Organically bound): 20 cm^3 of 0.1 M $K_4P_2O_7$ are added to the residue left from Step 3 and then stirred for 24 h.

After each step, the solution was filtered by suction through a 0.22 μm Millipore filter, and the filtrate collected in a polyester container. Then the solutions for each step were prepared accordingly for ICP-MS measurement following the manufacturer's recommendations.

3. Results and discussions

3.1. Extent of Zn contamination in water

The physico-chemical properties and Zn concentrations in river water samples are presented in Table 1. Among the physico-chemical properties, pH and EC were comparatively higher (8.28 and 62.8 mS m^{-1}) in water collected from Sasu River. Whereas, water samples collected from Shiine River and its two tributaries did not vary significantly in pH and EC, but the CO_2 and Zn concentrations varied greatly from 6.7 to 20.2 mg l^{-1} and 0.61 to 447.45 μg l^{-1}, respectively (Table 1). The Ministry of Environment in Japan accepts a guideline limit of 30 μg l^{-1} for Zn to conserve aquatic life (MOE, 2004b), whereas Wedepohl (1969–1979) set the standard limit at 15 μg l^{-1} for surface water quality. Typical Zn concentrations in river water are about 10 to 50 μg l^{-1} (Hem, 1992). If the Japanese standard for Zn is considered, 64% of the river water samples exceed it, and are mostly found in the Onigasai River. The other samples from the Akusuidani River and the other parts of Shiine River had only one sample with a value exceeding the standard limit.

Table 1
Physico-chemical properties and Zn concentration of water samples collected from Taisyu Zn–Pb mine area, Tsushima Island, Japan

Sampling site	Distance from river mouth (m)	pH	EC (mS m^{-1})	ORP (mV)	Temperature (°C)	CO$_2$ (mg l^{-1})	Zn (µg l^{-1})	Cd (µg l^{-1})
1	–	8.28	62.80	166	13.4	12.9	37.96	0.87
2	500	7.23	11.79	180	17.4	20.1	25.85	2.40
3	5400	6.92	12.76	159	13.1	18.6	172.40	1.96
4	–	6.75	10.38	198	11.2	12.3	46.31	1.08
5	–	6.92	12.53	208	8.4	10.2	447.45	0.87
6	4780	7.07	12.34	209	8.6	20.2	27.88	8.69
7	4710	7.10	12.30	200	8.7	18.3	53.45	0.49
8	4640	6.75	12.27	220	8.0	18.6	55.22	0.96
9	4570	6.79	12.27	158	8.1	19.0	67.75	1.12
10	4570	6.71	12.22	103	8.1	18.4	77.77	1.35
11	4500	6.72	12.38	141	8.5	19.7	65.61	1.48
12	4430	6.75	12.46	164	8.6	18.6	69.88	1.20
13	4310	7.06	12.48	173	8.7	17.9	69.82	1.22
14	4240	7.00	12.47	210	8.8	18.4	86.58	1.21
15	4170	7.04	12.48	205	8.9	20.2	86.32	1.46
16	4100	7.25	12.48	191	8.9	17.8	124.24	1.46
17	3610	7.25	12.56	211	8.7	18.4	133.34	1.88
18	3560	7.35	11.70	201	8.3	19.2	28.84	2.23
19	6440	7.23	7.80	238	7.8	8.8	1.49	0.28
20	5250	7.41	10.51	205	8.1	12.6	0.61	0.01
21	5090	7.33	8.92	165	8.0	6.7	6.56	0.01
22	4940	7.38	9.80	151	8.2	10.6	2.46	0.03
23	3720	7.40	11.24	128	7.8	12.3	12.19	0.02
24	1900	7.07	11.71	130	10.2	10.7	96.87	0.06
25	1000	6.79	11.80	139	15.2	13.1	17.44	2.31
26	–	7.65	6.12	202	18.8	4.6	6.60	2.36

Sample site 1 was at the mouth of Sasu River. Sample sties 4–5 were on a tributary of Onigasai River. Sample 26 was tap water.

The confluence point of the Onigasai and Akusuidani Rivers is approximately 3600 m upstream from the mouth of the Shiine River. The only water sample on the Shiine River with a high Zn content is 24 (97 µg l^{-1}), and is situated about 1600 m below the confluence point (Fig. 1). The Zn concentration in the water samples of the Akusuidani River does not exceed the Japanese guideline limit, indicating that there is no sign of Zn contamination. It should be mentioned that the Zn concentration was above the guideline limit near to sites where the Onigasai River crosses outcrops of ore veins (Fig. 1). Also at site 5, near the mine entrance of the pollution control plant, water sample exceeds the Zn limit significantly (447.5 µg l^{-1}). Therefore, it can be inferred that the ore veins and entrance of mine pollution control plant may have a direct influence on Zn contamination of river water.

3.2. Metal concentration of sediment and extent of Zn contamination

Metal concentrations in sediment samples are presented in Table 2. At most sites, the Zn concentration in sediment samples exceeds the average Zn concentration of shale and uncontaminated Japanese soil at 95 and 96 µg g^{-1}, respectively (Turekian and Wedepohl, 1961; Herawati et al., 2000), and the concentration varied greatly with a range from 86.75–7490.07 µg g^{-1}. It is apparent from Table 2 and Fig. 1 that the Zn concentrations were low in all sediment samples from the Akusuidani River (86.75–158.94 µg g^{-1}), which are in agreement with the low levels in water samples. But in the case of Onigasai River there is no relationship between the data of the sediment and water samples. The same pattern is also observed for mine entrances and plants.

The XRD data on sediment samples showed similarities in terms of major minerals (Table 3). Quartz has the strongest peak in all samples, with a relative intensity of 100. The second strongest peak was for chlorite in all samples, with relative intensity between 5 and 21. Mica, illite, feldspar, kaolinite and chamosite were found in many samples, but the intensity of their peaks was mostly under 10. A small amount of sphalerite was found only in the samples collected from Onigasai and Shiine Rivers (after the confluence point), and none from Akusuidani River. This may be and the reason for the high Zn concentration in sediments. The samples from the Onigasai River, where a high Zn concentration was detected had especially high peaks for chamosite and chlorite (10–20). It should be noted that there were a few inconsistencies in mineral constituents between the bottom and the bank side sediments, since their origin is different.

Fig. 2 shows the strong correlation between Zn and Cd concentrations in river water samples. Cadmium is geochemically similar to Zn, and occurs in sphalerite together with Zn. These two elements also showed significantly positive correlation in sediment samples (Fig. 3a and b). This result is of course in agreement with the known geochemical relationship between the two elements, which is supported by Fassett (1980) and Ullrich et al. (1999), who reported that Cd and Zn are always found together in nature and their concentrations are closely correlated.

Table 3 shows the major minerals in ore and sediment samples used in the dissolution–desorption experiment. The core sulphide part of the ore consists of many minerals, and it was the only sample with the highest peak intensity for galena, followed by sphalerite, magnesium calcite, montmorillonite and other

Table 2
Metal concentration ($\mu g\ g^{-1}$) in the fine fraction (<63 μm) in sediments collected from Shiine River, Tsushima Island, Japan

Sampling point	Na	K	Mg	Ca	P	Al	Mn	Fe	Zn
2 (bt)	3474.46	14,604.50	6528.93	1903.03	420.28	51,607.8	626.26	34,972.1	1350.51
5 (bt)	4093.39	9520.56	4729.33	1009.98	194.18	34,592.6	370.91	23,878.2	954.78
5 (bk)	3952.96	10,994.75	5326.72	1126.80	203.98	40,281.3	421.07	24,830.6	547.97
7 (bt)	3687.35	9389.27	4497.76	899.38	182.93	34,908.3	305.37	22,338.6	533.61
7(bk)	3878.32	9573.93	4523.67	953.00	193.37	34,610.7	364.24	22,503.9	655.99
8 (bt)	3754.77	12,011.13	5891.55	1157.43	221.50	44,075.5	467.66	27,809.6	796.56
9 (bt)	3430.15	10,118.04	4721.24	986.76	210.29	37,338.4	377.44	27,679.3	1343.37
9(bk)	3853.01	9251.16	4371.43	968.45	192.58	34,322.2	363.68	23,693.9	778.37
10 (bt)	3563.10	12,063.29	5415.80	1090.13	225.23	43,133.6	298.56	26,029.2	619.52
10(bk)	4532.40	14,096.76	6561.30	1212.06	229.84	50,349.5	366.52	27,731.2	863.89
11 (bt)	3741.19	11,158.36	5167.15	1034.05	248.92	40,010.2	320.50	31,041.6	2991.72
11(bk)	3091.41	9364.95	4327.34	1011.34	293.35	34,903.9	454.80	36,678.2	7490.07
12 (bt)	3240.25	8291.52	3847.59	916.50	165.13	30,361.7	284.26	32,467.8	1472.47
12(bk)	3132.80	9991.47	4541.91	1112.34	280.34	36,492.7	362.26	40,672.2	2247.10
13 (bt)	2583.60	6774.54	3216.46	867.22	220.69	24,680.5	389.89	44,548.8	4480.57
13(bk)	2371.23	7255.97	3323.46	834.66	183.32	25,751.4	270.38	27,166.5	2210.84
14 (bt)	3837.27	8764.91	4491.94	1413.84	195.13	32,908.9	386.22	21,396.1	891.32
14(bk)	2995.11	8586.65	3823.06	1059.56	229.06	30,715.9	371.52	35,786.2	3241.99
15 (bt)	4118.74	9396.62	4161.94	1087.78	150.89	33,820.4	231.54	23,207.0	3131.81
15(bk)	4184.37	8493.70	3929.02	981.87	187.48	31,902.9	234.74	23,757. 6	1549.07
16 (bt)	4665.17	8992.78	4134.39	1069.58	181.23	32,998.7	250.75	23,142.4	1641.39
16(bk)	4199.67	9076.38	4085.30	1133.73	216.52	33,488.3	290.36	28,708.4	1896.34
17 (bt)	2696.74	9633.60	4192.02	1040.53	203.70	33,701.0	341.16	29,998.4	2587.49
21 (bt)	4788.72	11,791.16	5569.77	2255.54	255.15	44,392.2	363.80	24,097.6	158.94
22 (bt)	3785.19	9489.22	4505.56	1493.35	144.82	36,223.4	434.10	19,478.2	86.75
23 (bt)	3745.37	11,102.59	5475.13	1664.04	156.40	41,911.9	571.37	22,217.9	94.35
24 (bt)	4180.75	10,024.39	5508.99	1786.31	224.40	38,446.0	475.42	25,227.0	1125.28
25 (bt)	4538.02	9037.00	5201.13	1776.92	174.91	34,849.1	386.24	20,040.2	220.66
25(bk)	3874.04	9297.31	4084.22	1283.45	227.05	34,593.8	372.22	21,864.7	635.23

bt=Bottom sediment; bk=Bank side sediment.

minerals. Many clay minerals are also included in the interior part of the ore, which could affect the reactivity. From this data it is evident that the interior sulphide parts of the ores are Zn and Pb rich. The surface part of the ore contains only sphalerite in terms of sulphides. This infers that the ore surface composition is more similar to that of the sediment than to the interior part of the ore, although the intensities of clay minerals were higher than the sediment samples (Table 3). On the other hand, among the sediment samples used in the dissolution–desorption experiment, the feldspar peak was not detected in sample 17 (bt). It is also apparent from Table 3 that the intensity of sphalerite was low for sample 17 (bt) compared to sample 11 (bk), which may be due to its intermediate range of Zn concentration (2587 $\mu g\ g^{-1}$). It contains, however, more chlorite than sample 11 (bk). A similar pattern was also found in sample 21 (bt); sphalerite was not detected, and this is supported by the low Zn concentration (159 $\mu g\ g^{-1}$), and the intensities of clay minerals, which were also relatively low.

3.3. Enrichment factors (EFc)

To evaluate the magnitude of contaminants in the environment, the enrichment factors were computed relative to the abundance of species in source material to that found in the Earth's crust (Huheey, 1983; Loska et al., 1997; Atgin et al., 2000). Atgin et al. (2000) reported that crustal enrichment factors (EFc) of elements are frequently used to determine the

degree of modification in sediment composition. The following equation was used to calculate the EFc:

$$\mathrm{EFc} = (C_{Zn}/C_{Al})_{sample}/(C_{Zn}/C_{Al})_{Earth's\ crust}$$

where, $(C_{Zn}/C_{Al})_{sample}$ is the ratio of concentration of Zn (C_{Zn}) to that of Al (C_{Al}) in the sediment sample, and $(C_{Zn}/C_{Al})_{Earth's\ crust}$ is the same reference ratio in the Earth's crust. The average

Table 3
Mineral constituents of the samples used in adsorption experiment

Minerals	Sampling points and peak intensity of minerals observed by XRD				
	11 (bk)	17 (bt)	21 (bt)	Ore surface	Ore interior
Quartz	100	100	100	100	n.d.
Feldspar	14.4	n.d.	5.9	50a	n.d.
Kaolinite	12.7	8.2	6.3	22	38
Chlorite	7.8	17.6	5.1	22	33
Micas and illite	10.6	9.1	4.9	n.d.	n.d.
Sphalerite	14.4	4.0	n.d.	22a	66a
Magnesium calcite	n.d.	n.d.	n.d.	23	41
Chamosite	10.8	12.0	n.d.	n.d.	n.d.
Maghemite	n.d.	n.d.	n.d.	n.d.	21
Montmorillonite	n.d.	n.d.	n.d.	n.d.	26
Galena	n.d.	n.d.	n.d.	n.d.	100
Zn–Cd sulphide	n.d.	n.d.	n.d.	n.d.	59
Zinc lead oxide (3)	n.d.	n.d.	n.d.	22b	66b
Zinc lead oxide (4)	n.d.	n.d.	n.d.	50b	n.d.

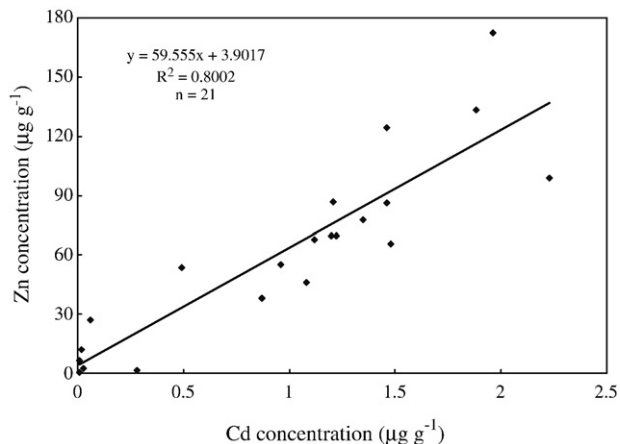n.d.=Not detected; bt=Bottom sediment; bk=Bank sediment.

Fig. 2. Correlation between Zn and Cd concentration in river water samples collected from the Taisyu Zn–Pb mine area, Tsushima Island, Japan.

abundance of Zn (70 µg g^{-1}) in the reference Earth's crust was taken from Huheey (1983), and Al was selected as the reference element, due to its crustal dominance and its high immobility. The reference value of Al is 7.8% (7.5–8.1%).
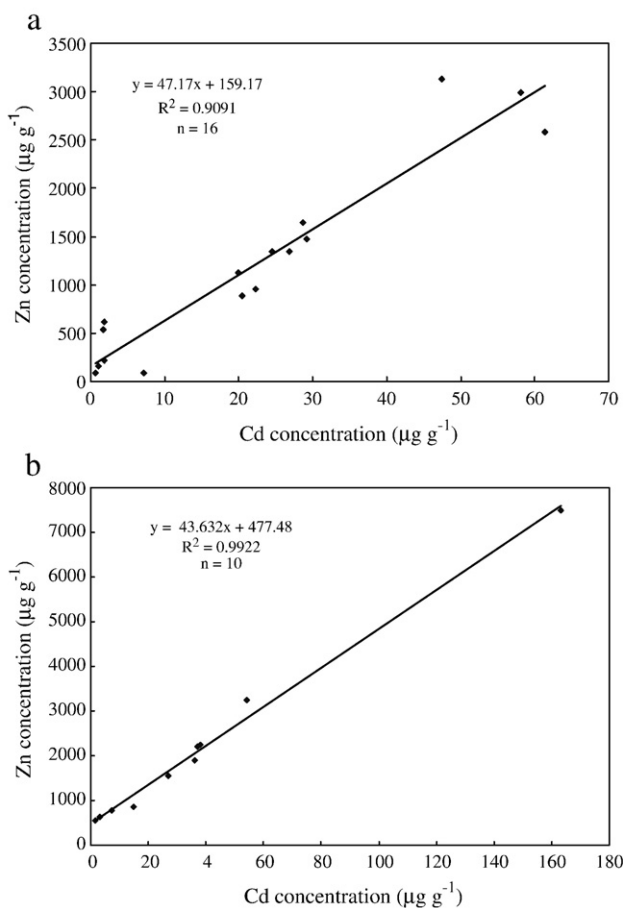

Fig. 3. a. Correlation between Zn and Cd concentration in bottom sediment samples collected from the Taisyu Zn–Pb mine area, Tsushima Island, Japan. b. Correlation between Zn and Cd concentration in bank sediment samples collected from the Taisyu Zn–Pb mine area, Tsushima Island, Japan.

If the EFc value of an element is greater than unity, this indicates that the metal is more abundant in the sample relative to that found in the Earth's crust. Although EFc values less than 5 may not be considered significant, they are indicative of metal accumulation, because such small enrichments may arise from differences in the composition of local sample material with respect to the reference Earth's crust ratio values used in the EFc calculations (Atgin et al., 2000). If the EFc values are greater than 5, samples are considered contaminated. Fig. 4 represents the EFc values of Zn in the sediment samples. It is evident that only 3 samples (21, 22 and 23) have no significant enrichment values (<5.0). The other 12 samples have EFc values more than 50, and the remaining samples have values between 5 and 50. It is presumed that high EFc values indicate an anthropogenic source of Zn, mainly from mining activities in this area. Since, the bioavailability and toxicity of any metals in sediments depends upon the chemical form and concentration of the metals (Kwon et al., 2001), it can be inferred that Zn in sediment samples with the highest EFc values, along with higher labile fractions in sediments have a potential for mobility and bioavailability in the environment.

3.4. Dissolution and desorption behaviour of Zn and Cd

The changes in Zn concentration in solution with time, due to reaction of ores and sediments with river water are shown in Fig. 5. In the case of the interior part of the ore, the Zn concentration in solution increased considerably in the first 24 h, and then slow down continuously with time, may be due to adsorption in clay minerals. The solution reacted with ore surface behaved quite differently; Zn concentration gradually increased with time due to reaction of ore surface and sediment with river water. This may be due to more release of Zn from the altered outside part of the ore consisting with more soluble oxides, and very small or no adsorption due to less amount of clay minerals. The XRD data for the ore surface and sediment samples also support these results as the peaks intensity of clay minerals for both samples were lower than ore interior part (Table 3).

Among the heavy metals analysed, Cd had the highest correlation coefficient with Zn (0.80, 91 and 0.99 in water and
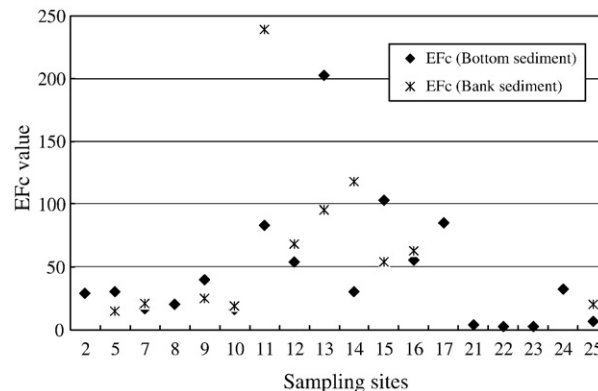

Fig. 4. Enrichment factor (EFc) of Zn at different sampling sites in Taisyu Zn–Pb mine area, Tsushima Island, Japan.
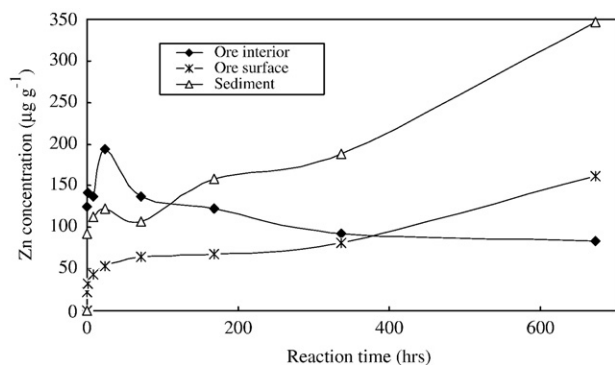
Fig. 5. Dissolution and desorption behaviour of Zn in solution of ore and sediment reacted with river water.

Fig. 7. Zn and Cd ratio in solution of ore and sediment reacted with river water at different reaction time. Horizontal line expresses the Zn:Cd ratio of water sample 11 (bk) used in dissolution and desorption experiment.

sediment (bt and bk), respectively). Fig. 6 shows the Cd concentration changes with time due to reaction of ores and sediments with river water. Higher concentration of Cd in solution reacted with ore surface than ore interior was obtained mainly due to the dissolution of the small amount of secondary Cd minerals like greenockite (CdS) that could not be identified by the XRD and optical observation. However, it is well known that oxidation of sphalerite causes the formation of greenockite in Pb–Zn mines (e.g. Kamioka mine in Japan). Comparing the dissolution patterns of Zn and Cd, it is apparent that the overall behaviour of these two elements is similar. It should be noted that both the Zn and Cd concentrations were higher in the interior part of the ore (25,299.6 and 143.6 $\mu g\ g^{-1}$, respectively) than the ore surface (1573.1 and 23.9 $\mu g\ g^{-1}$, respectively). Fig. 7 shows the change of the Zn:Cd ratio at different reaction times of ore surface, ore interior and sediment sample. The ratio obtained from the analytical results of water sample 11 (river water used in the dissolution–desorption experiment) is employed for the comparison of results. It is evident from Fig. 7 that the ratio showed a sharp rise for the solution reacted with sulphide ore and it exceeds the Zn:Cd ratio of river water within the first 5 min of dissolution. Whereas the Zn:Cd ratio of the solution reacted with ore surface sample rises gently and does not exceed the Zn:Cd ratio of river water. From the above results, it is inferred that the sulphide ores are the possible contamination
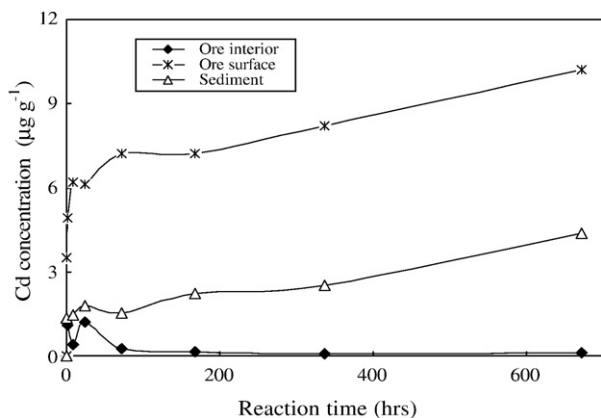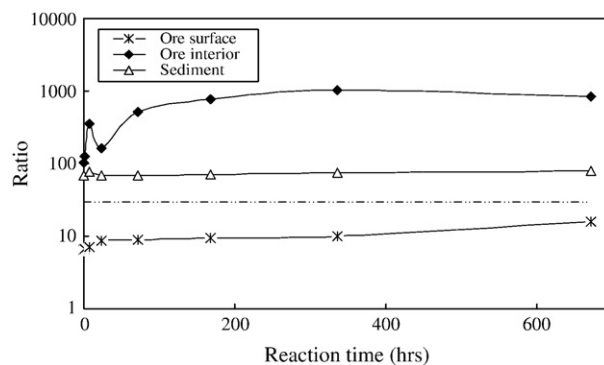
sources of Shiine River. In case of the sediment, it could be said that the effect of sulphide tends to raise the ratio slightly upwards, and adsorption in clay minerals tends to bring the ratio downwards, creating almost a constant value of ratio (Fig. 7). Therefore, the sediment sample is also inferred to be a possible contamination source of the Shiine River.

The results of the dissolution–desorption experiment, inferred that excessive Zn in the river water is most likely derived from the sediments than the sulphide ore. In this case, there are two possible states of Zn dissolution from sediments. These are: (1) sulphide mineral grains in the sediments, and (2) Zn taken into sediments by reactions, such as adsorption and ion exchange. From the XRD analytical results, the sulphide peaks in sediment sample 11 (Zn rich, used in dissolution–desorption experiment) were lower than the combined clay mineral peaks (sulphide intensity was below 15), meaning that the portion of sulphides minerals in sediments is less than that of clay minerals. Therefore, the most possible source of Zn is its dissolution from sediments by reactions like desorption and ion exchange. Conclusively, in the first step of Zn contamination, it is dissolved from sulphide ores and is released in the river water. As a second step, part of the Zn is taken up by sediments by adsorption, and it's subsequently desorbed in river water under suitable pH-Eh conditions.

Zinc dissolved into river water from sulphide ores are inferred to exist in the forms of $ZnOH^+$ and Zn^{2+}. They are taken into sediments in the forms of ZnO and $Zn(OH)_2$. In the sequential extraction experiments on Zn rich sediment, Zn tends to be adsorbed on sediments in an exchangeable state, possibly by adsorption or ion exchange reactions with high CEC clay minerals such as chlorite. Zinc taken up by sediments may be desorbed into river water, raising its concentration. On the other hand, when Zn concentration is low, it tends to exist in an acid soluble form. This means that Zn occurs as sulphide or hydroxide and is stabilised in the sediments. In this case, Zn is relatively insoluble, so not much is desorbed into river water compared to the Zn rich sediments. Throughout the river, it could be said that the Zn concentration increases due to the sources suggested above.

The decrease in concentration could occur through adsorption by sulphides or ion exchange reactions with clay minerals,

Fig. 6. Dissolution and desorption behaviour of Cd in solution of ore and sediment reacted with river water.

joining of tributaries, and dilution by the increase volume of river water, and reduced desorption from the sediments. All these aspects may be responsible for the fluctuation of Zn concentration in Shiine River.

According to this study, Zn is released into river water by desorption from sediments, causing an increase in its concentration. This also means that the Zn concentration in sediments deposited in river areas, changes from high to low due to the rate of desorption. On the other hand, the concentration of Zn in sediments should be high and stable where the water concentration is low. However, the Zn concentrations in sediment samples are about $1.0E+05$ times higher than the concentration in water samples. A little amount of Zn desorbed from sediments could easily raise the Zn concentration of river water as has been observed in the dissolution–desorption experiment. This means that sediments and water could both be Zn rich at the same time, under suitable physico-chemical conditions.

3.5. Sequential extraction experiment

Zinc in bank sediment sample 11 (bk) (also used in the dissolution–desorption experiment) was mostly extracted in step-1 (exchangeable form) among the 4-steps used in the experiment (Fig. 8). This means that Zn in sediment sample 11 (bk) tends to undergo ion-exchange reactions with possibly ferrihydrite and clay minerals. According to XRD data (Table 3), sample 11 (bk) is rich in clay minerals such as chlorite, which supports this assumption. In addition, it is widely known that 2:1 type clay minerals, such as chlorite, have a high CEC compared to 1:1 type clay minerals (Mitchell, 1993). It could be said from this data, that Zn is released into river water by desorption from Zn rich sediments (like sample 11 bk), which is presumed to be exist in sediments by ion exchange reaction and/or adsorption. A similar pattern was also observed for other elements, except for Cu. This means the behaviour of Zn and Cd in sediment sample 11 (bk) are similar and, therefore, the Zn:Cd ratio could be used to deduce the dissolution–desorption mechanism in sediment. From this experimental result, it could be said that Zn is retained in sediments, but it is desorbed under suitable physico-chemical conditions and raises its concentration in river water.
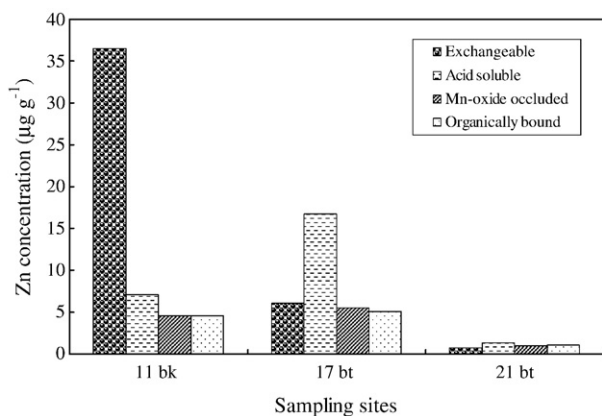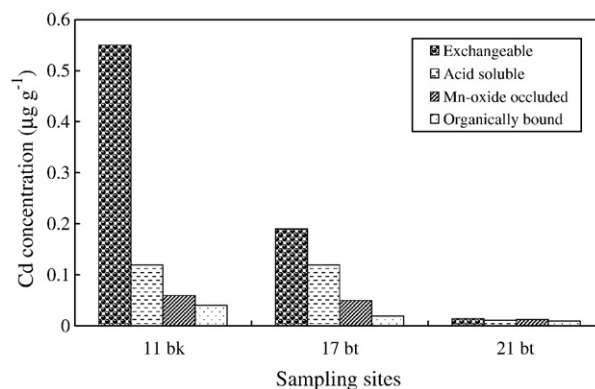
Fig. 9. Cd concentration in sediment samples at different steps of the four stage sequential extraction experiment.

On the other hand, Zn was mostly extracted in step-2 (acid soluble) in samples 17 (bt) and 21 (bt). The peak of step-2 was outstanding in sample 17 (bt), but it was almost similar to other steps in sample 21 (bt). This indicated that Zn in sediment sample 17 (bt) strongly tends to dissolve in acid, suggesting that it may occur as hydroxide in the sediments. Cadmium also shows a similar pattern as sample 11 (bk), and the analytical data proved that Cd dissolution is mostly related to Zn (Fig. 9). Zinc concentration of sample 17 (bt) was in the intermediate range among the sediment samples of this study, so it is inferred that the decrease in Zn concentration causes the behaviour of Cd to differ. Although, Zn concentration was very low in sample 21 (bt), step-2 was the highest in Zn. From the result of this experiment, it can be inferred that low Zn concentration in sediments forms hydroxide or sulphide and fix to sediments. The hydroxide or sulphide inside sediments is poorly soluble and stable, therefore dissolution occurs less in that area of the river.

4. Conclusion

The water samples, collected from Onigasai River and the upper part of Shiine River near to the confluence point, exceeded the environmental limit at most sites for Zn, while all the samples collected from Akusuidani River were below it. At the same time, Zn concentrations in sediments also exceeded the average standard of soil, and according to EFc values all the samples were found as polluted, except 3 sites. Experimental results of this study showed that Zn dissolved considerably from sediments and ores in less than 5 min, and clay minerals were found more in Zn rich sediments than sulphides. When the sediments are Zn rich, it is uptaken in and retained by adsorption to the sulphides in the sediments, or Zn is uptaken into sediments by reactions like adsorption and ion exchange with high CEC clay minerals such as chlorite. On the other hand, when Zn concentration is low in sediments, it is assumed that Zn forms hydroxide or sulphide minerals, and is, thus, stabilised in sediments. In this case, Zn is relatively insoluble and does not desorb into river water. This study infers that Zn contamination in the Taisyu area is not only related to the mining activities, but it is also released from the ores and sediments.

Fig. 8. Zn concentration in sediment samples at different steps of the four stage sequential extraction experiment.

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