

Assessment of metal concentrations in lake sediments of southwest Japan based on sediment quality guidelines

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Abstract Geochemical analysis of the bottom sediments of Lakes Banryoko, Onbe, Hamahara and Kijima in Shimane prefecture of southwest Japan was carried out to determine their metal concentrations, and to assess the potential for ecological harm by comparison with sediment quality guidelines. The work conducted includes water quality measurement, and analyses of trace and major elements and rare earth element (REE) of sediments. Results showed that water quality of the lakes contrasts slightly between their upper and lower parts. Average abundances of As, Pb, Zn, Cu, Ni, and Cr in Banryoko sediments were 27, 33, 90, 27, 25, and 46 ppm, respectively, compared to 31, 52, 175, 44, 44, and 75 ppm at Onbe, 11, 26, 96, 13, 13, and 35 ppm at Hamahara, and 24, 43, 193, 31, 12, and 30 ppm at Kijima. These concentrations exceeded the lowest effect level that has moderate impact on aquatic organisms as proposed by the New York State Department of Environmental conservation. Pb and Cu abundances are comparable to the Coastal Ocean Sediment Database threshold, while As and Zn exceed this value, indicating the concentrations of these metals are potentially toxic. Increases in the abundances of these metals in lake sediments are probably related to the reducing condition of the sediments, anthropogenic sources and surface soil erosion. The REE patterns of sediments in the study areas are broadly comparable to the average upper continental crust, but show some contrast between lakes due to differing source litho type. Significant positive corre-

lations between Fe_2O_3 and As, Pb, Zn, and Cu were found in the sediments, suggesting these metals may be adsorbed on Fe oxides in the lake sediments.

Keywords Lake sediment · Geochemistry · Trace metal · Southwest Japan

Introduction

Heavy metals are among the most persistent of pollutants in the aquatic ecosystem because of their resistance to decomposition in natural conditions (Arnason and Fletcher 2003). Higher concentrations of these metals are released into the aquatic environment as a result of leaching from bedrocks, atmospheric deposition, water drainage, runoff from riverbanks, and discharge of urban and industrial wastewaters (Soares et al. 1999; Yang and Rose 2005). Lake sediments thus provide records of natural watershed conditions and of changes caused by human activities (Arnason and Fletcher 2003). Contamination of aquatic ecosystems by heavy metals can be confirmed in water, sediment and organisms (Albering et al. 1999; Sprenke et al. 2000; Yang et al. 2002). Heavy metals may affect human health if they reach levels such that they constitute toxic pollutants. Over the last few decades, many geochemical studies have been directed at coastal and lake sediments to determine the extent of contamination from heavy metals (e.g. Rosales-Hoz et al. 2000; Evans et al. 2003; Marvin et al. 2004).

Environmental pollution has become a serious problem since the accelerated growth in world population during the 20th century, and Japan is no exception. The modern industrial revolution in Japan

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started in the early 1950s, and continued through the 1970s (Yoshimura et al. 2005). However, the drainage basins of lakes in southwest Japan have been affected by numerous human activities over the last century (Sadakata 1985), and these could have resulted in anthropogenic trace element emissions into the atmosphere and deposition in lake systems (Matsunaga et al. 1999). Moreover, modification of the river drainages (e.g. dams, artificial channels) at specific locations could lead to changes in the chemical composition of detritus. Such modification has occurred in the past, with massive influx of granitoid waste from historic tatara mining (Ortiz and Roser 2004). Ishiga et al. (2000a) reported that the large-scale exploitation of residual iron sands in the catchments of lakes in Shimane prefecture, southwest Japan led to extensive deforestation, and resulted in an increased influx of clastic detritus. Catchment soil erosion is also an important factor for the increased export of terrestrial metal concentrations to aquatic ecosystems (Yang and Rose 2005). The result is transfer of plant debris from surface soils to the drainage waters, which transport them to lacustrine sediments where they finally settle out. Plant debris constitutes an important reservoir for trace metals, which have a high affinity for this naturally accumulating material (Yang et al. 2002).

Many environmental studies have been made of the extent of sediment contamination in coastal and estuarine areas in southwest Japan (e.g. Matsunaga et al. 1999; Ishiga et al. 2003), but few have considered the potential for ecological risk associated with heavy metal concentrations in the sediments. High heavy metal concentrations in sediments may cause adverse biological effects even though water quality criteria are not exceeded (NRC 1989). Recently, comparison with sediment quality guidelines has become a common approach as a first step in assessing environmental impacts (Roach 2005). Two approaches have commonly been used for assessing the significance of metal contamination in bottom sediments as part of the first stage of an overall assessment: (1) comparison of concentrations with those from unimpacted or background sediments; and (2) comparison with effects-based sediment quality guidelines for each contaminant and the cumulative effects of contaminants in sediments (Long et al. 1998).

The present study of the bottom sediments of Lakes Banryoko, Onbe, Hamahara and Kijima in Shimane prefecture of southwest Japan was conducted to determine heavy metal concentrations, and to examine their provenance using rare earth element analyses. The potential toxic effects of the metal concentrations on aquatic biota in the lakes are discussed by com-

parison of abundances in the upper continental crust and by reference to sediment quality guidelines. Present-day water quality was also assessed. The results of this study show that the significant concentrations of heavy metals present in the lake sediments are of potential concern to aquatic organisms.

Materials and methods

The study sites are all within Shimane prefecture of southwest Japan (Fig. 1). Shimane prefecture has a total area of about 6,707 km², and lies between 34°20'N to 35°34'N and 131°42'E to 133°18'E. Bedrock geology consists mainly of Paleogene to Cretaceous granitoids and felsic volcanic rocks (Fig. 1). The sampling area is characterized by humid climate, with average annual temperature of about 15°C, and average annual precipitation of a little more than 2,000 mm.

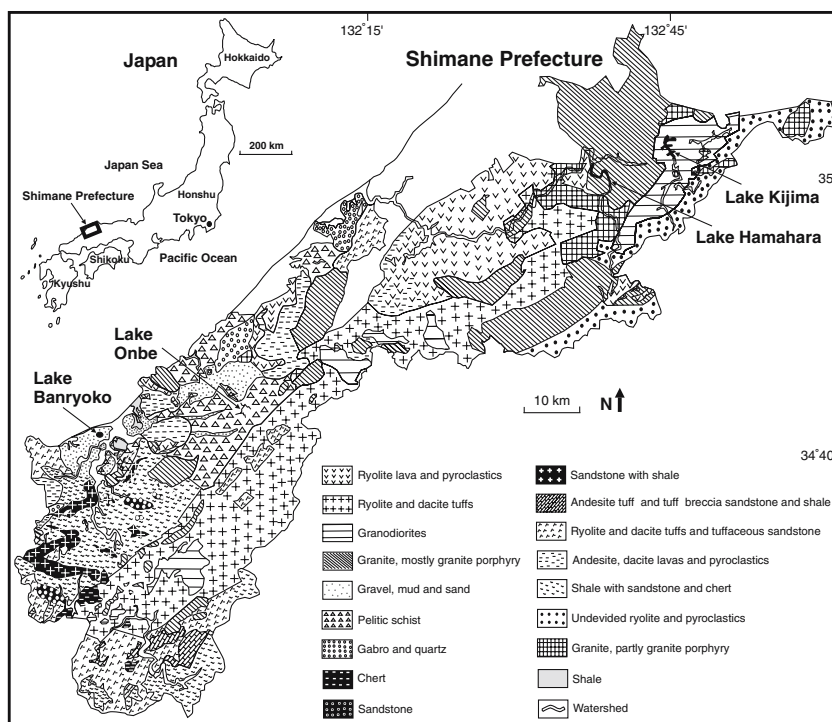
Lake Banryoko is on the outskirts of Masuda City in Shimane prefecture (Fig. 1), at an altitude of 25 m above mean sea level. Maximum water depth is 9 m, and surface area is about 3 km². The lake was originally a brackish-water lagoon, with direct connection to the Sea of Japan, but is now isolated by a sand bar built by long shore drift. The salinity of the lake has declined since it was isolated from the sea. Gravels, muds and sands characterize the geology of the drainage area of the lake.

Lake Onbe is also near Masuda City. It has a surface area of about 102 km² (maximum depth 9 m), and receives inflow from the Misumi River. The rock underlying the lake basin consists predominantly of pelitic schist.

Lake Hamahara is about 15 km from Oda City (Fig. 1), and has a surface area of approximately 300 km² and maximum depth of 9.5 m. The geological basement of the lake consists of granite, mostly granite porphyry and granophyre. The lake lies in the Gouno River watershed, and is retained by the Hamahara dam, which was built for water supply and electricity production in 1973. The Gouno River catchment drains an area of about 3,900 km², and is the largest river in southern Japan. It is the only waterway that discharges from the Lake Hamahara, and finally empties into the Sea of Japan.

Lake Kijima is about 20 km from Oda City (Fig. 1). The surface area of the lake is approximately 140 km² (maximum depth 10 m), and basement rock is granodiorite. The main watershed surrounding the lake is the Kando River system, which has an area of about 448 km² (Ortiz and Roser 2003, 2006). The Tonbara and Akana Rivers feed Lake Kijima.

Fig. 1 Simplified basement geology and the locations of the four lakes in Shimane prefecture. Inset: location in Japan. Geology based on the 1:200,000 geological map of Shimane prefecture (EBGMSP 1997)



Lakes Banryoko and Onbe, and Lakes Hamahara and Kijima are geographically close to each other (Fig. 1), and the levels of all except Lake Banryoko are strongly regulated for hydroelectric power production by artificial dams. The catchment areas of the lakes are mostly forested, with a mixture of native broadleaf species, plantation forests, and bamboo. Flatlands along the rivers are used for paddy cultivation, and the lakes thus receive wastewater from irrigation (Chandrajith et al. 1995). The lakes and their environments serve as recreational areas for the local residents, as well as supporting their aquatic communities.

Analytical procedures

Measurement of water quality

Water parameters including depth, temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) concentration, oxidation-reduction potential (ORP), total dissolved solid (TDS) and turbidity were measured in the field, using a portable Horiba U-22 multi-monitoring system (Horiba Co. Ltd). Data collected from different depths at 46 locations from the four lakes are summarized in Table 1.

Sediment sample collection and preservation

Forty-six sediment samples were collected from Lakes Banryoko, Onbe, Hamahara and Kijima in May 2005

(Fig. 2). All samples (0–12 cm of the bottom sediments) were collected from the deepest parts of the lakes, using an Ekman-Berge Bottom Sampler (Rigo Co. Ltd, Japan). Composite samples were taken from the central portion of the catcher with a plastic spatula to avoid any contamination from the metallic parts of the sampler. Sediments samples weighing about 200 g were packed in zip-lock bags and stored in a cooler box at 4°C for transport to the laboratory. ORP and pH values of each sample were measured in the field at time of sampling, using a Horiba U-23 combined instrument (Rikagaku kenkujo, Japan).

Sediment sample preparation

Approximately 50 g of each sample were dried in an oven at 110°C for 48 h. The dried samples were then ground for 20 min in an automatic agate mortar and pestle grinder. The powdered samples were then compressed into briquettes using a force of 200 KN for 60 s.

X-ray fluorescence (XRF) analysis

Selected major oxide [$Fe_2O_3^*$ (total iron expressed as $Fe_2O_3^*$), TiO_2 , CaO , and P_2O_5], total sulfur (TS) and trace element (As, Pb, Zn, Cu, Ni, Cr, V, and Sr) concentrations were determined by XRF at Shimane University, using a RIX-2000 spectrometer (Rigaku Denki Co. Ltd) equipped with a Rh-anode X-ray tube.

Table 1 Water quality of lakes in southwest Japan

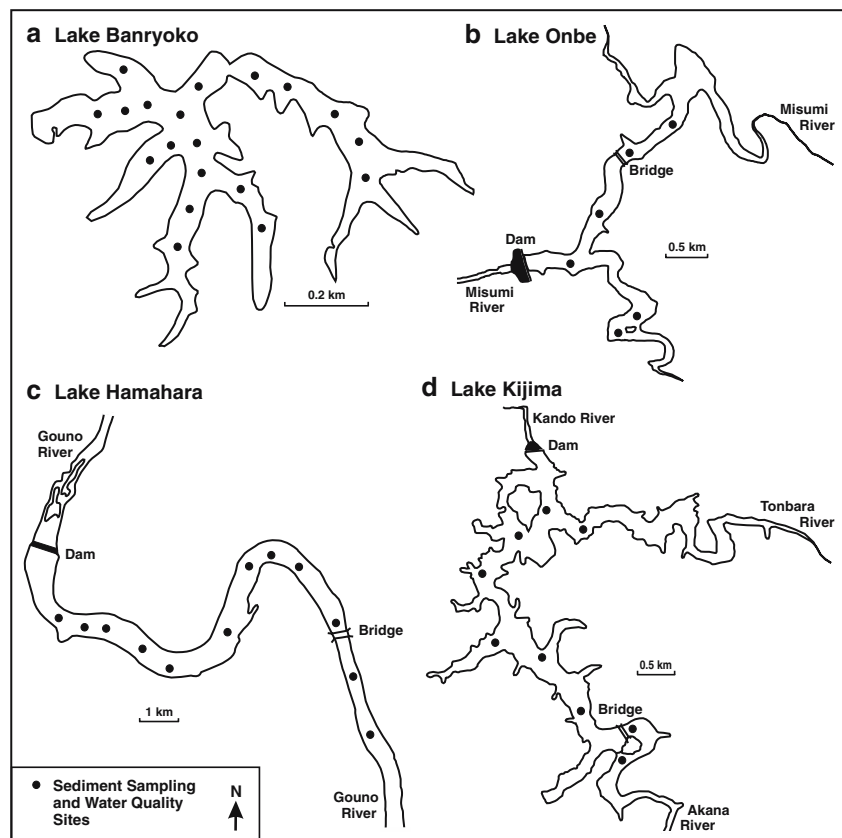
Area		Temperature (°C)	pH	EC (mS/cm)	DO (mg/l)	ORP (mV)	TDS (g/l)	Turbidity (mg/l)
LB (<i>n</i> = 19)	U Range	11.8–14.4	5.8–5.9	11.7–11.8	12.1–13.0	132–157	0.08	30.3–38.9
	L Range	8.3–9.3	5.5–5.8	11.9–12.1	5.9–8.4	171–233	0.08	31.0–178.0
	Mean	11.1	5.8	11.8	10.6	177	0.08	82.5
LO (<i>n</i> = 6)	U Range	11.9–22.2	7.9–8.3	10.4–12.5	15.0–16.9	158–194	0.08	8.7–54.2
	L Range	7.4–9.8	7.5–7.9	10.1–10.7	9.0–13.7	200–225	0.07	71.0–77.5
	Mean	12.1	7.8	11.0	13.3	199	0.08	55.3
LH (<i>n</i> = 12)	U Range	17.0–17.5	7.9–8.9	10.6–11.8	7.7–12.0	185–189	0.07–0.09	nm
	L Range	16.9–17.0	7.4–7.8	9.4–10.1	4.9–7.2	190–196	0.06–0.07	
	Mean	17.1	8.0	10.4	7.7	172	0.06	
LK (<i>n</i> = 9)	U Range	15.3–19.1	8.5–9.1	10.3–11.5	11.6–16.2	116–174	0.07	2.7–8.5
	L Range	13.4–14.7	7.4–8.2	10.8–11.1	6.4–10.3	179–188	0.07	3.6–12.0
	Mean	16.0	8.5	10.7	11.5	155	0.07	5.9

EC Electrical conductivity, DO dissolved oxygen, ORP oxidation reduction potential, TDS total dissolved solid

LB Lake Banryoko, LO Lake Onbe, LH Lake Hamahara, LK Lake Kijima

U Upper; L Lower, nm not measured

Fig. 2 a–d Locations of water quality and sediment sample sites in the lakes in Shimane prefecture



All analyses were made on the pressed powder briquettes, following the method of Ogasawara (1987). Average errors for all elements are less than $\pm 10\%$ relative. Analytical results for United States Geological Survey (USGS) standard SCo-1 (Cody Shale) were acceptable compared to the proposed values of Potts et al. (1992).

Instrumental neutron activation analysis (INAA)

Rare earth element (REE; La, Ce, Sm, Eu, Gd, Tb, Yb, and Lu) and other trace element concentrations (Sc, Hf, Ta, Th, Cs, Sb, and Rb) in fourteen selected samples were determined by INAA at the Research Reactor Institute of Kyoto University. Sample prepa-

Table 2 Geochemical compositions of Kando River and lake sediments in southwest Japan

Area	Source	Trace elements (ppm)										Major oxides and TS (wt%)				
		As	Pb	Zn	Cu	Ni	Cr	V	Sr	TiO ₂	Fe ₂ O ₃	CaO	P ₂ O ₅	TS		
LB (<i>n</i> = 19)	Gravel, mud, sand	Range	16–39	26–39	62–122	16–39	15–35	32–59	61–126	36–71	0.55–0.84	3.99–8.50	0.61–0.80	0.09–0.16	0.09–0.23	
		Mean	26.9	32.6	89.5	26.7	24.9	45.6	100.2	52.6	0.71	6.62	0.66	0.13	0.13	
		SD	6.88 ^{a, d}	4.39 ^d	13.77 ^b	6.09 ^b	4.92 ^c	7.13 ^c	20.19 ^b	8.28 ^c	0.06 ^a	1.28 ^c	0.04 ^c	0.02 ^b	0.03 ^a	
LO (<i>n</i> = 6)	Pelitic schist	Range	29–34	45–65	169–179	39–50	30–57	57–89	142–178	87–114	0.63–0.83	7.27–9.34	1.08–1.43	0.18–0.23	0.09–0.15	
		Mean	31.4	52.3	175.0	44.4	44.3	74.8	158.9	102.0	0.71	8.38	1.16	0.19	0.11	
		SD	1.81 ^a	8.10 ^a	3.85 ^a	4.77 ^a	11.86 ^a	13.82 ^a	16.03 ^a	10.84 ^b	0.08 ^a	1.00 ^a	0.14 ^b	0.02 ^c	0.02 ^a	
LH (<i>n</i> = 12)	Granite (sandy)	Range	5–27	15–47	40–239	4–36	3–62	20–78	28–239	94–147	0.12–0.98	1.51–7.44	1.09–2.25	0.06–0.41	0.03–0.44	
		Mean	10.8	25.9	95.9	13.4	13.4	34.7	89.4	115.4	0.45	3.87	1.37	0.15	0.10	
		SD	8.06 ^c	12.10 ^c	67.99 ^b	11.85 ^c	16.95 ^b	15.04 ^b	57.43 ^b	14.87 ^b	0.23 ^b	1.97 ^b	0.33 ^b	0.12 ^{b, c}	0.12 ^a	
LK (<i>n</i> = 9)	Grano-diorite/ FV	Range	19–33	25–51	90–236	11–38	8–16	18–35	54–160	117–318	0.28–0.61	4.29–10.50	1.12–1.96	0.27–0.46	0.12–0.19	
		Mean	23.8	43.2	193.2	30.6	11.8	30.1	134.8	190.0	0.55	9.00	1.58	0.36	0.15	
		SD	4.91 ^{b, d}	7.59 ^b	43.26 ^a	7.88 ^b	2.38 ^b	5.52 ^b	33.82 ^a	66.65 ^a	0.11 ^b	1.91 ^a	0.32 ^a	0.07 ^a	0.03 ^a	
KR (<i>n</i> = 20)	Granit-oids	Mean	NA	17.3	NA	NA	26	54	148	301	0.88	8.56	2.58	0.23	NA	

LB Lake Banryoko, LO Lake Onbe, LH Lake Hamahara, LK Lake Kijima, FV felsic volcanic, NA not available

^{a, b, c} Means with different superscript letters in a column are significantly different (*P* < 0.05)

Kando River (KR) stream sediment data (<180 μm) from sites above Lake Kijima (Ortiz and Roser 2003)

ration, analytical methods and precision are described by Musashino (1990). Average errors for these elements are less than ±10%, and results for the Geological Survey of Japan standard JA2 were acceptable when compared with values given by Potts et al. (1992). The Eu anomaly (Eu/Eu*) was calculated following the formula given by Condie (1993): $Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{1/2}$; where $Gd = (Sm \times Tb^2)^{1/3}$; and *N* = chondrite normalized concentrations.

Results

Water quality and the water column

Physico-chemical properties (temperature, pH, and DO) of the water bodies of all four lakes contrast slightly between their upper and lower parts. Temperature gradually increases toward the surface. Measured pH values were approximately neutral to alkaline in all layers in Onbe, Hamahara and Kijima, ranging from 7.4 to 9.1, and meet the USEPA criteria (6.5–9.0) for freshwater aquatic life (USEPA 1998). However, Lake Banryoko is more acidic (pH 5.5–5.9) and fails the USEPA criteria. The pH values in all four lakes are higher in the upper layers. This is related to active photosynthesis in the upper layers, making water undersaturated in CO₂ (HCO₃⁻ in water; Das 2005). Dissolved O₂ concentrations in the deeper parts are lower than those in overlying water layers. The reduction in pH and DO values seem to confirm increased respiration rates and reducing conditions in deeper water strata, as reported by Bellanger et al. (2004) for lakes in northwest Venezuela.

The average EC of Lake Banryoko was 11.8 mS/cm, whereas average values for Onbe, Hamahara and Kijima were 11.0, 10.4 and 10.7 mS/cm, respectively. High EC values in all lakes suggest higher ionic concentrations due to leaching from weathering profiles in their catchments. TDS values display almost constant profile in all four lakes. ORP values were higher in the lower layers of the lakes. The bottom water layers were more turbid than the upper parts, and Lake Banryoko showed maximum turbidity of 178 mg/l. The water masses of all lakes thus show slightly stratified conditions with respect to temperature, pH, and DO at around 5–6 m.

Sediment characteristics

In this study, the sediment samples collected from the four lakes were mainly very soft, blackish, slightly silty, fine clays. The fine-grained sediments prevalent in

Banryoko, Onbe and Kijima were enriched in organic matter. These three lakes contained the highest proportion of clay materials. The clay particles often appeared to be coated with Fe(oxy)hydroxides, which can act as carriers of metallic pollutants by adsorption, as observed by Galán et al. (2003) in the river sediments in Spain. However, sand samples were abundant in Lake Hamahara, which also contained higher amounts of plant debris than the other lakes.

Average pH values of the sediments from Lakes Banryoko, Onbe, Hamahara, and Kijima were 7.3, 7.2, 6.8, and 7.1, respectively. ORP ranges were –10 to –74, –150 to –230, –140 to –146, and –110 to –197 mV, respectively, indicating anoxic conditions prevailed in the sediments in all four lakes. Redox conditions in the lake sediments were thus less oxic than in their overlying water columns.

Concentrations of elements in lake sediments

Elemental compositions of the bottom sediments analyzed by XRF are summarized in Table 2. Abundances of As in the Banryoko sediments are relatively high, ranging from 16 to 39 ppm (av. 26.9 ppm), and Pb concentrations average 32.6 ppm, ranging from 26 to 39 ppm. Zn and Cu contents range between 62 and 122 and 16–39 ppm, with averages of 89.5 and 26.7 ppm, respectively, whereas Ni and Cr abundances range from 15 to 35 and 32–59 ppm, respectively. Banryoko sediments contain the least Sr (av. 52.6 ppm; range 36–71 ppm) among the four lakes.

On average the Onbe sediments contain 31.4 ppm As, ranging from 29–34 ppm. Zinc contents show little variation, with a range of only 169–179 ppm (av. 175 ppm). The highest concentrations of Pb (65 ppm), Cu (50 ppm), Cr (89 ppm) were observed at Onbe. Ni abundances range between 30 and 57 ppm, averaging 44.3 ppm. The highest average value of V (158.9 ppm) was also recorded in the Onbe sediments. Average concentrations of TiO₂ and TS are almost identical at Onbe and Banryoko (Table 2). However, Onbe sediments have greater contents of Fe₂O₃ (av. 8.38 wt%), CaO (av. 1.16 wt%), and P₂O₅ (av. 0.19 wt%) compared to Banryoko sediments (av. 6.62, 0.66, and 0.13 wt%, respectively).

Most metals are enriched in the clays relative to the sands in the Lake Hamahara, e.g. As (av. 20.3 ppm in the clays; av. 6.1 ppm in the sands), Pb (av. 40.5 ppm; av. 18.6 ppm), Zn (av. 175 ppm; av. 56.4 ppm), and Cu (av. 27.8 ppm; av. 6.3 ppm). Abundances of Ni show significant variation, with a range of 3–62 ppm. Cr contents vary between 20 and 78 ppm in all lithotypes.

The lowest average value of V (89.4 ppm) was found in Lake Hamahara.

Arsenic concentrations in Kijima sediments range from 19 to 33 ppm (av. 23.8 ppm). Pb contents range from 25–51 ppm and average 43.2 ppm. Concentrations of Zn are high in this lake, in the range of 90–236 ppm (av. 193.2 ppm). Cu and Cr contents range from 11 to 38 and 18–35 ppm with averages of 30.6 and 30.1 ppm, respectively. The Kijima sediments contain less Ni (av. 11.8 ppm; range 8–16 ppm), and more Sr (av. 190 ppm; range 117–318 ppm) than the other lakes. The lowest contents of TiO₂, Fe₂O₃, and TS (av. 0.45, 3.87, and 0.10 wt%) were observed at Lake Hamahara, whereas the highest contents of Fe₂O₃, CaO, P₂O₅, and TS (av. 9.00, 1.58, 0.36, and 0.15 wt%, respectively) were found in Lake Kijima.

The concentrations of As, Pb, Zn, Cu, Ni, and Cr in the four lakes are illustrated in Fig. 3. Minimum, median, maximum and mean levels of Pb, Cu, Ni, and Cr are greatest in Lake Onbe, which had the lowest ORP values in the sediments. Mean Zn contents do not differ significantly between Lake Onbe and Lake Kijima, but levels are double those in Banryoko and Hamahara (Table 2). Minimum, median and mean levels of As are also higher in Lake Onbe than in the other three lakes.

Rare earth elements

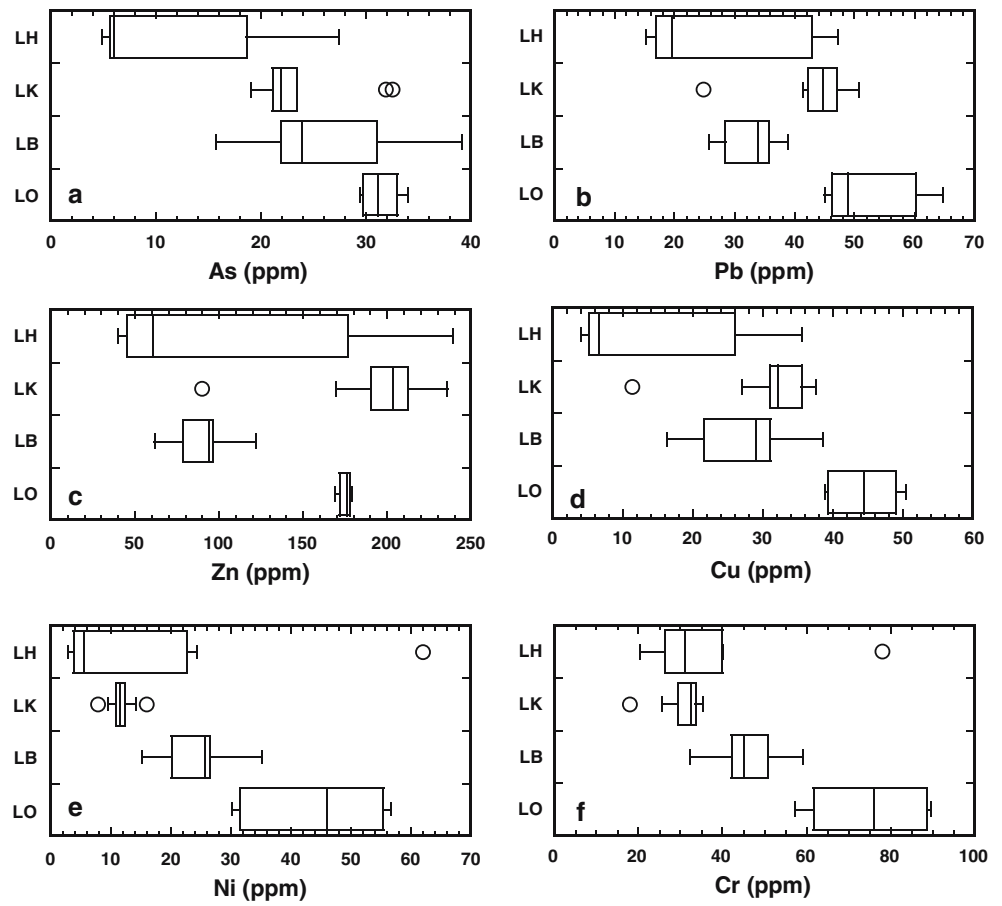
Analyses of REE (La, Ce, Sm, Eu, Gd, Tb, Yb, and Lu) and other minor elements (Sc, Hf, Ta, Th, Cs, Sb, and Rb) were made in selected samples to evaluate the possibility of differing source materials. The REE data were normalized to chondrite (Taylor and McLennan 1985) and compared with average upper continental crust. The samples from Lakes Hamahara, Kijima and Onbe show enrichment in light rare earth elements (LREE; averages La_N/Sm_N = 3.9, 3.2, 3.5) over heavy rare earth elements (HREE; av. Gd_N/Yb_N = 1.4, 2.1, 1.5) with negative Eu anomalies (av. Eu/Eu* = 0.40, 0.60, 0.68, respectively). Results are shown in Table 3.

Discussion

Evaluation of provenance

REE patterns have been used extensively in recent years for evaluation of provenance (Taylor and McLennan 1985; Condie 1993; McLennan et al. 1993). The patterns of the analyzed samples from Lakes Hamahara, Kijima and Onbe are characterized by light

Fig. 3 a–f Summary of concentrations of heavy metals in sediments in four lakes, Shimane prefecture, Japan. LH, LK, LB, and LO represent Lake Hamahara, Lake Kijima, Lake Banryoko, and Lake Onbe, respectively. Horizontal lines give the range, excluding outliers (circles); boxes enclose 50% of the data, and illustrate the 25% quartile, median (vertical bar) and 75% quartile. Outliers are defined as the upper or lower quartile ± 1.5 times the interquartile difference



REE enrichment (averages $La_N/Sm_N = 3.9, 3.2, 3.5$), clear depletion in Eu (av. $Eu/Eu^* = 0.40, 0.60, 0.68$) compared to other middle REE to heavy REE and HREE (av. $Gd_N/Yb_N = 1.4, 2.1, 1.5$, respectively). These values are broadly comparable with those of average upper continental crust (UCC in Fig. 4, $La_N/Sm_N = 3.2, Eu/Eu^* = 0.59, Gd_N/Yb_N = 1.7$; Condie 1993).

REE distributions fall into three groups: those with greatest LREE fractionation (av. $La_N/Sm_N = 3.9$), generally flat HREE (av. $Gd_N/Yb_N = 1.4$), and marked negative Eu anomalies (av. $Eu/Eu^* = 0.40$) at Lake Hamahara, those with slightly enriched LREE (av. $La_N/Sm_N = 3.2$), fractionated HREE (av. $Gd_N/Yb_N = 2.1$), negative Eu anomalies (av. $Eu/Eu^* = 0.60$) at Lake Kijima, and those with enriched LREE (av. $La_N/Sm_N = 3.5$), smaller negative Eu anomalies (av. $Eu/Eu^* = 0.68$) and relatively flat HREE (av. $Gd_N/Yb_N = 1.5$) at Onbe. Th/Sc ratios in Lakes Hamahara and Kijima (av. 1.6, 1.2) are slightly greater than the value of upper continental crust (0.97; Condie 1993, about 1.0; Taylor and McLennan 1985) indicate a felsic source. However, the ratio in Lake Onbe (av. 0.90) is comparable to the average upper continental crust.

The slight contrasts in the REE patterns in the three lakes are due to their differing source rocks in their catchments. The higher La/Sm ratios and strongly negative Eu/Eu^* at Hamahara reflects the highly felsic granitoids in its catchment. Lower La/Sm and Eu/Eu^* at Kijima are derived from granodiorite, and the UCC-like REE patterns of Lake Onbe are products of derivation from pelitic schist.

Heavy metal concentrations and comparison with sediment quality guidelines

In this study, As, Pb, Zn, Cu, Ni, and Cr in the lake sediments have greater concentrations than those of upper continental crust (Table 4). As noted above, elevated concentrations in sediments may cause adverse biological effects even though water quality criteria is not exceeded. Therefore, assessment of metal concentrations in the lake sediments is required. In order to evaluate if the metal concentrations are present in the lake environments at contaminant levels, their As, Pb, Zn, Cu, Ni, and Cr contents were compared with three sediment benchmarks developed by the US National Oceanographic and Atmospheric

Table 3 Distribution of REE and other trace elements in the sediments of Lakes Hamahara, Kijima and Onbe

Area (Source)	Lake Hamahara (Granite)				Lake Kijima (Granodiorite-Felsic Volcanic)					Lake Onbe (Pelitic schist)				
	LH-1	LH-2	LH-5	LH-7	LK-1	LK-3	LK-8	LK-10	LK-15	LO-1	LO-2	LO-3	LO-4	LO-7
REE (ppm)														
La	15.7	29.7	25.9	23.6	44.5	53.7	55.9	48.5	37.9	44.0	42.4	43.7	38.8	42.8
Ce	30.9	60.6	51.4	48.1	85.7	115.3	122.6	99.7	70.8	86.0	88.3	93.0	89.7	83.8
Sm	3.0	4.2	4.5	3.6	9.0	10.5	10.8	9.6	7.4	8.0	7.6	8.0	6.8	7.3
Eu	0.4	0.5	0.6	0.5	1.6	1.7	1.7	1.5	1.3	1.6	1.5	1.6	1.5	1.5
Gd	1.5	1.8	2.0	1.8	2.5	2.8	2.7	2.7	2.2	2.4	2.5	2.5	2.4	2.5
Tb	0.5	0.7	0.9	0.8	0.9	1.1	0.9	1.0	0.7	0.8	1.1	1.0	1.0	1.1
Yb	2.4	2.7	3.2	2.1	2.6	2.9	2.6	2.7	2.6	3.6	3.3	3.7	3.0	3.3
Lu	0.3	0.3	0.4	0.3	0.3	0.5	0.5	0.4	0.4	0.5	0.4	0.5	0.4	0.5
Chondrite normalized														
La	42.9	81.0	70.4	64.2	121.4	146.2	152.4	132.0	103.3	119.8	115.5	119.0	105.8	116.7
Ce	32.3	63.3	53.7	50.2	89.6	120.4	128.1	104.2	74.0	89.9	92.3	97.2	93.8	87.6
Sm	13.2	18.3	19.6	15.4	39.1	45.4	46.8	41.4	31.9	34.5	32.7	34.8	29.5	31.7
Eu	4.9	6.3	7.3	5.5	18.1	19.1	20.1	17.4	14.8	18.8	17.6	18.9	17.0	16.7
Gd	10.3	14.1	17.1	14.3	21.0	25.3	23.0	23.3	16.9	19.4	22.1	21.2	20.7	22.2
Tb	9.1	12.4	16.0	13.8	15.4	18.9	16.2	17.5	12.3	14.6	18.2	16.6	17.3	18.5
Yb	9.5	11.0	13.0	8.3	10.3	11.6	10.3	10.8	10.4	14.6	13.5	14.9	12.2	13.2
Lu	8.8	8.5	10.6	8.6	9.1	12.0	12.1	9.8	9.7	12.6	11.2	12.0	11.2	12.7
Eu/Eu*	0.42	0.39	0.40	0.37	0.63	0.56	0.61	0.56	0.64	0.72	0.66	0.70	0.69	0.63
Th/Sc	2.1	1.1	1.9	1.3	0.9	1.5	1.6	1.3	0.9	0.8	0.8	0.9	0.9	0.9
La _N /Sm _N	3.3	4.4	3.6	4.2	3.1	3.2	3.3	3.2	3.2	3.5	3.5	3.4	3.6	3.7
Gd _N /Yb _N	1.1	1.3	1.3	1.7	2.0	2.2	2.2	2.2	2.0	1.3	1.6	1.4	1.7	1.7
La _N /Yb _N	4.5	7.4	5.4	7.7	11.8	12.6	14.8	12.3	9.9	8.2	8.6	8.0	8.7	8.8
Trace elements (ppm)														
Sc	3.3	5.3	5.0	5.3	16.0	13.2	13.0	14.3	12.8	15.0	16.3	15.0	13.7	13.4
Hf	4.4	6.9	5.3	4.7	5.3	3.9	3.6	4.1	6.2	5.3	5.6	5.7	5.2	6.1
Ta	0.8	1.0	1.0	0.8	1.1	1.3	1.5	1.3	1.2	1.1	1.1	1.1	0.9	1.0
Th	7.0	6.0	9.3	7.0	15.0	20.0	21.0	18.4	11.1	11.9	12.3	13.4	12.4	12.4
Cs	3.2	3.2	5.0	3.9	7.6	9.5	10.1	7.9	6.2	9.1	9.1	11.0	12.5	13.3
Sb	2.5	3.8	3.1	2.8	3.1	2.5	2.3	2.6	3.5	3.1	3.3	3.3	3.1	3.6
Rb	126.0	115.0	130.0	150.0	138.0	135.0	147.0	134.0	138.0	123.0	123.0	149.0	145.0	126.0

Eu/Eu* $Eu_N/(Sm_N \times Gd_N)^{1/2}$, where $Gd = (Sm \times Tb^2)^{1/3}$ and N = chondrite normalized concentrations (after Taylor and McLennan 1985)

Administration (NOAA; Jones et al. 1997, cited from Ruiz-Fernández et al. 2003) and the New York State Department of Environmental Conservation (NYS-DEC 1999). These are (1) the Coastal Ocean Sediment Database (COSED) for marine and estuarine ecosystems, (2) Lowest Effect Level (LEL); and (3) Severe Effect Level (SEL) for the protection of aquatic organisms. The COSED values are indicative of metal contamination, and were used to quantify degradation of sediment quality in estuaries. If the LEL is exceeded, the metal may moderately impact biota health. If the SEL is exceeded, the metal may severely impact biota health.

Arsenic is sensitive to changes in redox conditions, and is released from lake sediments when reducing conditions prevail (Yang and Rose 2005). The main natural source of As for lake sediment is rock weathering, although mining activity may contribute to

natural As concentrations (Garcia-Sanchez and Alvarez-Ayuso 2003). Ishiga et al. (2000b) analyzed 25 surface soil samples from the surroundings of Lake Jaike, an area that has similar geology to that around Lake Kijima, and found average As concentrations of 11 ppm. The present study shows average As values in the lake sediments are two to three-fold greater, suggesting additional As has been contributed to the lake environments (Table 2). Yang et al. (2002) and Yang and Rose (2005) stated that the arsenic accumulation process in lake sediments in the United Kingdom was associated with changes in redox conditions. Kojima et al. (2003) also observed that under anoxic conditions As was released from sediments to the pore water near the sediment-water interface in Lake Biwa, Japan. The high As concentrations in the lake sediments here thus more likely resulted to burial of organic mud deposited under reducing conditions. Furthermore, a strong

Fig. 4 a–c Chondrite-normalized REE patterns for sediments from Lakes Hamahara, Kijima and Onbe in Shimane prefecture of Japan. UCC and Chondrite normalizing factors from Taylor and McLennan (1985)

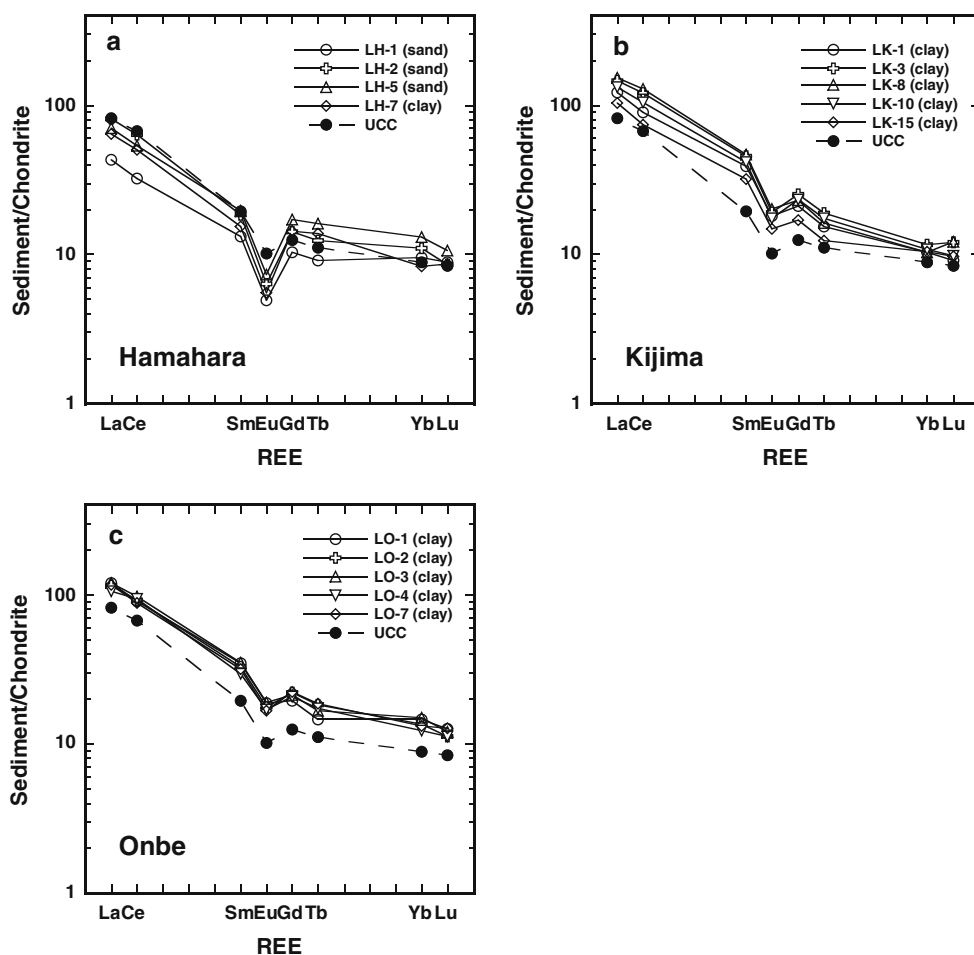


Table 4 Sediment quality criteria and metal concentrations (ppm) in lake sediments

Metals	UCC ^a	COSED ^b	LEL ^c	SEL ^d	LB	LO	LH	LK
As	1.5	13	6	33	27	31	11	24
Pb	20	45	31	110	33	52	26	43
Zn	71	135	120	270	90	175	96	193
Cu	25	42	16	110	27	44	13	31
Ni	20	42	16	50	25	44	13	12
Cr	35	125	26	110	46	75	35	30

^a Upper continental crust (UCC; Taylor and McLennan 1985)

^b Coastal ocean sediment database (COSED; Daskalakis and O'Connor 1995)

^c Lowest effect level (LEL; NYSDEC 1999)

^d Severe effect level (SEL; NYSDEC 1999)

LB Lake Banryoko, LO Lake Onbe, LH Lake Hamahara, LK Lake Kijima

positive relationship exists between As and Fe₂O₃ ($r^2 = 0.72$; $n = 27$; Fig. 5) in the Onbe, Hamahara and Kijima sediments, suggesting an association with authigenic Fe-oxides coatings in the sediments (Yang et al. 2002). The sediment samples in the lakes studied here are significantly enriched in As compared with UCC (1.5 ppm As) and Japanese granitic rocks

(3.8 ppm As; $n = 310$; Terashima and Ishihara 1986). The maximum values observed in Banryoko and Onbe sediments (39 and 34 ppm) exceed the SEL for As (33 ppm), and the COSED value (13 ppm) is exceeded in all lakes (Tables 2, 4). This is of particular importance as the concentrations of As could be detrimental to the majority of benthic species.

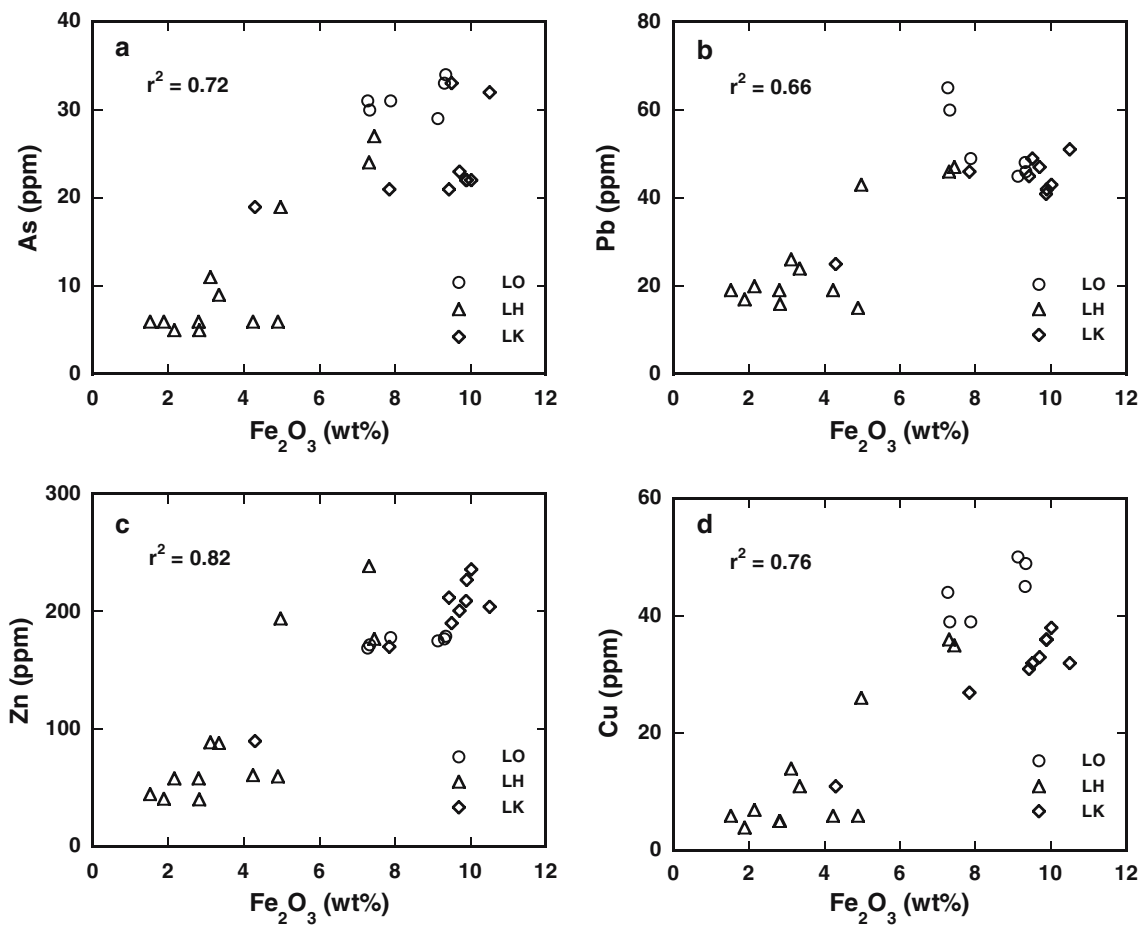


Fig. 5 a–d Correlations between Fe_2O_3 and As, Pb, Zn, and Cu in Lakes Onbe, Hamahara and Kijima ($n = 27$). LO Lake Onbe, LH Lake Hamahara, LK Lake Kijima

Lead is ubiquitous in aquatic sediments because it is a component of the detrital fraction. Freshwater surface sediments in Lakes Jaike and Jinzai in Shimane prefecture contain 22.3 and 16 ppm Pb, which may be associated with the Fe-phase, most probably with oxides, oxyhydroxides and sulfides of Fe, depending on the existing oxidation-reduction condition (Chandrajith et al. 1995; Ishiga et al. 2000b). Sediments at Banryoko, Onbe, Hamahara, and Kijima have Pb concentrations (av. 33, 52, 26, and 43 ppm) greater than those in other Shimane lakes (Jinzai and Jaike; Chandrajith et al. 1995; Ishiga et al. 2000b). Average Pb contents of 17.3 ppm in the $<180 \mu\text{m}$ fraction were reported by Ortiz and Roser (2003, 2006) for Kando River sediments (Table 2), collected from sites above Lake Kijima. Their study shows that abundance of Pb is not prone to major disturbances from anthropogenic sources, because there is no clear evidence of influence from human activity. The Pb abundances observed thus primarily reflects that of the source rock types, and of the soils developed on them. Contents of Pb in

Onbe and Kijima are more than double the crustal background (20 ppm) and local stream sediments (17.3 ppm). The higher Pb concentrations in these lake sediments likely reflect the fine-grained nature of the sediment prevalent in the lakes (Graney and Eriksen 2004), and rainstorms over the study areas, which produce, increased sediment load (Ruiz-Fernández et al. 2003). Moreover, post-depositional diagenetic remobilization can influence Pb migration toward the sediment-water interface and scavenging onto organic matter or Fe(oxy)hydroxides (Ruiz-Fernández et al. 2003), as suggested by the significant relationship of Pb with Fe_2O_3 ($r^2 = 0.66$; $n = 27$; Fig. 5) in Lakes Onbe, Hamahara and Kijima. The Pb concentrations observed in the Onbe and Kijima sediments are close to or greater than the COSED (45 ppm), also reflecting Pb enrichment. The LEL for Pb (31 ppm), a level that has moderate impact on benthic organisms, is also exceeded in Lakes Banryoko, Onbe and Kijima.

Sediments are the primary sink for Zn (Sprenke et al. 2000). Singh et al. (2005) suggested that Zn is

preferentially associated with fine-grained particles or is adsorbed on to authigenic clay minerals. Concentrations of Zn in Lakes Banryoko, Onbe, Hamahara, and Kijima (90, 175, 96, 193 ppm, respectively) are greater than average UCC composition (71 ppm; Table 4). Zinc concentrations in Lakes Onbe and Kijima exceed both the COSED (135 ppm) and the LEL (120 ppm) values, suggesting moderate contamination of Zn in the bottom sediments. However, with the exception of a few values, Zn abundances are much lower in Banryoko and Hamahara. The sediments in both Onbe and Kijima have greater contents of Zn compared to Lake Waco, Texas (74 ppm; Abraham 1998) and Lake Valencia, Venezuela (101 ppm; Mogollón et al. 1996). Ishiga et al. (2003) also reported that metal concentrations including Zn and Pb were high in dam lakes (e.g. Ichifusa Dam Lake) and coastal areas in southwest Japan. These authors also suggested that the changes in reducing conditions of the lake sediments were due to accumulation of organic matter (e.g. nutrients). Significant positive correlations between Fe₂O₃ and Zn ($r^2 = 0.82$; $n = 27$) and Cu ($r^2 = 0.76$; $n = 27$; Fig. 5) were observed in Lakes Onbe, Hamahara and Kijima, indicating Zn and Cu have similar behavior to Fe in the sedimentary processes, and thus these metals were most probably adsorbed on Fe oxides or sulfides (Fe-phase) coated grains in the lake sediments. This is consistent with previous reports by Chandrajith et al. (1995) and Ishiga et al. (2003) for lake sediments in southwest Japan.

Copper has a strong affinity with organic matter, Fe oxides and clay minerals, and may be fixed in sediments as authigenic sulfide minerals (Tessier et al. 1994; Tribovillard et al. 1994). Average Cu abundances are greater than UCC (25 ppm) at Onbe (44 ppm) and Kijima (31 ppm), similar at Banryoko (27 ppm), and somewhat lower at Hamahara (13 ppm; Table 4). Chandrajith et al. (1995) also reported greater Cu concentration (41 ppm) near the sediment water interface in Lake Jinzai of southwest Japan. These authors linked this surface enrichment to human activity, especially heavy use of agro-chemicals. Other

investigators (e.g. Ishiga et al. 2000b) have found Cu concentrations (av. 40 ppm) broadly similar to those of the study lakes. Concentrations of Cu exceed the NYSDEC lowest effect level (16 ppm) in Banryoko, Onbe and Kijima sediments, and COSED (42 ppm) in Lake Onbe.

Compared to average UCC (20 ppm Ni), Onbe sediments have greater concentrations of Ni (av. 44 ppm), similar values at Banryoko (av. 25 ppm), and lower concentrations in Hamahara (av. 13 ppm) and Kijima (av. 12 ppm; Table 4). Elevated concentrations of Ni reflect enrichment in organic matter or biogenic activities in sediments (Tribovillard et al. 1994). The greater concentrations of pollutants (e.g. Ni) in Onbe sediments are most probably related to natural sources and also domestic and agricultural wastes, as proposed by Chandrajith et al. (1995) for Lake Jinzai in southwest Japan. Lake Onbe has Ni concentrations similar to the value in COSED (42 ppm), whereas the other lakes are depleted in Ni. Average concentration in Lake Banryoko exceeds the LEL (16 ppm) for the protection of aquatic life. The lower concentrations (<UCC) at Hamahara and Kijima reflect the lower concentrations present in the felsic plutonic rocks (average 4 ppm, Ortiz and Roser 2006), which form the majority of their catchments.

Chromium is a toxic heavy metal and is a definite health hazard due to its carcinogenic effects (Zereen et al. 2000). Lakes Banryoko and Onbe have high average Cr concentrations (46 and 75 ppm), whereas those at Hamahara (35 ppm) and Kijima (30 ppm) are similar to UCC (35 ppm). Although the Cr concentrations found in these lakes are below the COSED level (125 ppm), they are slightly greater than the LEL (26 ppm). Therefore, Cr concentrations in the study lakes fall in the low to intermediate level.

Heavy metal concentrations in the study lakes and other lakes in differing geological regions such as Lake Ontario, Canada (Marvin et al. 2004), Lake Eijsden, Netherlands (Albering et al. 1999), Lake Gulshan, Bangladesh (Ahmed et al. 2005), and Lake Chapala, Mexico (Rosales-Hoz et al. 2000) are shown in Table 5

Table 5 Concentrations of heavy metals (ppm) in bottom sediments from Lakes Ontario (Marvin et al. 2004), Eijsden (Albering et al. 1999), Gulshan (Ahmed et al. 2005), Chapala (Rosales-Hoz et al. 2000), and Banryoko, Onbe, Hamahara and Kijima (this study)

Metals	Ontario	Eijsden	Gulshan	Chapala	Banryoko	Onbe	Hamahara	Kijima
Pb	5–200	39–191	34–44	73–100	26–39	45–65	15–47	25–51
Zn	11–1300	149–970	143–410	97–150	62–122	169–179	40–239	90–236
Cu	4–110	29–115	39–50	25–34	16–39	39–50	4–36	11–38
Ni	Na	NA	75–102	33–49	15–35	30–57	3–62	8–16
Cr	Na	NA	112–122	52–83	32–59	57–89	20–78	18–35

NA not available

for comparison. The maximum Zn, Pb, and Cu contents found in Ontario and Eijsden sediments are far greater than those from the study lakes. Marvin et al. (2004) and Albering et al. (1999) reported that Lakes Ontario and Eijsden were impacted by point sources (e.g. anthropogenic sources). Therefore, the lakes in southwest Japan are unlikely to have been influenced by point sources.

The results overall show that the concentration ranges of the suite of the elements As, Pb, Zn, Cu, Ni, and Cr in the sediments are well in excess of the established LEL. However, they are below the SEL for aquatic sediments, following the guidelines of NYS-DEC (1999). The average Pb and Cu concentrations are comparable to COSED, whereas As and Zn exceed this value, suggesting metal enrichment has occurred in both Onbe and Kijima. Metal concentrations are greater in Onbe than the other lakes (Fig. 3), possibly due to the strong reducing conditions prevailing in the Onbe sediments (ORP -150 to -230 mV). In contrast, metal contents of the Hamahara sediments are lower due to their sandier nature and their granitoid source rocks. As there are no major industries in the catchments of the lakes, and no known point sources for

metal enrichment in the sediments, it is therefore likely that metals observed are housed in the sediment matrix (e.g. weathering of bedrock), with additional modifications depending on the redox conditions of the sediments, anthropogenic sources and surface soil erosion.

Relationships among the geochemical data

Strong positive correlations were observed between the concentrations of Fe_2O_3 and As, Pb, Zn, Cu, Ni, Cr, V, TiO_2 , and P_2O_5 , and between V and As, Pb, Zn, Cu, Ni, and Cr, and also between TS and Zn, Ni, Cr, TiO_2 , and CaO in Lake Banryoko (Table 6). Negative or poor relationships for Sr and CaO suggest a differing control for these elements. At Onbe, Fe_2O_3 concentrations are strongly correlated with Zn, Cu, Ni, Cr, V, and TiO_2 ($r = +0.74, +0.80, +0.97, +0.96, +0.95, +0.84$, respectively), and TiO_2 with Cu, Ni, Cr, and V ($r = +0.96, +0.84, +0.82, +0.95$, respectively; Table 6). Non-significant correlations for Pb, Sr, CaO, P_2O_5 , and TS reflect a different source for these elements in Onbe sediments. Strong positive relationships of Fe_2O_3 with As, Pb, Zn, Cu, Ni, and Cr, of P_2O_5 with As, Pb, Zn, Cu, Ni, Fe_2O_3 , and CaO, and of TS with As, Pb, Zn,

Table 6 Correlations between the elements in sediments of Lakes Banryoko and Onbe

Lake Banryoko ($n = 19$)													
	As	Pb	Zn	Cu	Ni	Cr	V	Sr	TiO_2	Fe_2O_3	CaO	P_2O_5	TS
As	1.00	0.56	0.28	0.49	0.31	0.19	0.65	-0.31	0.33	0.79	-0.49	0.61	0.05
Pb		1.00	0.67	0.86	0.56	0.52	0.78	-0.32	0.53	0.86	-0.22	0.78	0.24
Zn			1.00	0.86	0.85	0.82	0.86	-0.16	0.76	0.73	0.35	0.63	0.76
Cu				1.00	0.75	0.73	0.87	-0.31	0.62	0.87	-0.01	0.84	0.44
Ni					1.00	0.89	0.86	-0.21	0.92	0.71	0.16	0.42	0.65
Cr						1.00	0.77	0.09	0.86	0.65	0.32	0.37	0.66
V							1.00	-0.32	0.83	0.93	-0.06	0.68	0.56
Sr								1.00	-0.15	-0.24	0.55	-0.29	0.15
TiO_2									1.00	0.68	0.17	0.25	0.66
Fe_2O_3										1.00	-0.21	0.77	0.33
CaO											1.00	-0.11	0.73
P_2O_5												1.00	0.25
TS													1.00
Lake Onbe ($n = 6$)													
As	1.00	-0.37	0.62	0.26	0.37	0.33	0.32	-0.42	0.14	0.54	-0.18	0.18	0.10
Pb		1.00	-0.90	-0.59	-0.92	-0.91	-0.80	0.65	-0.69	-0.88	0.79	0.43	0.58
Zn			1.00	0.30	0.72	0.71	0.54	-0.51	0.37	0.74	-0.73	-0.44	-0.54
Cu				1.00	0.77	0.72	0.92	-0.76	0.96	0.80	-0.28	0.31	-0.09
Ni					1.00	0.99	0.95	-0.74	0.84	0.97	-0.70	-0.30	-0.36
Cr						1.00	0.94	-0.74	0.82	0.96	-0.74	-0.38	-0.40
V							1.00	-0.83	0.95	0.95	-0.58	0.07	-0.28
Sr								1.00	-0.84	-0.83	0.71	0.08	0.53
TiO_2									1.00	0.84	-0.51	0.06	-0.33
Fe_2O_3										1.00	-0.68	-0.18	-0.34
CaO											1.00	0.73	0.87
P_2O_5												1.00	0.64
TS													1.00

Bold text highlights strong correlations

Table 7 Correlations between the elements in sediments of Lakes Hamahara and Kijima

Lake Hamahara (<i>n</i> = 12)													
	As	Pb	Zn	Cu	Ni	Cr	V	Sr	TiO ₂	Fe ₂ O ₃	CaO	P ₂ O ₅	TS
As	1.00	0.98	0.94	0.99	0.90	0.65	0.09	0.04	-0.08	0.87	0.52	0.93	0.80
Pb		1.00	0.97	0.99	0.85	0.55	0.01	0.02	-0.15	0.82	0.49	0.95	0.81
Zn			1.00	0.97	0.72	0.44	0.09	-0.01	-0.08	0.84	0.63	0.99	0.92
Cu				1.00	0.86	0.59	0.09	-0.01	-0.09	0.87	0.56	0.95	0.85
Ni					1.00	0.84	0.13	0.04	-0.01	0.76	0.22	0.68	0.48
Cr						1.00	0.51	0.18	0.43	0.75	0.25	0.38	0.23
V							1.00	0.21	0.95	0.55	0.32	0.04	0.03
Sr								1.00	0.41	0.21	0.39	-0.01	-0.06
TiO ₂									1.00	0.40	0.26	-0.14	-0.15
Fe ₂ O ₃										1.00	0.71	0.81	0.74
CaO											1.00	0.65	0.80
P ₂ O ₅												1.00	0.93
TS													1.00
Lake Kijima (<i>n</i> = 9)													
As	1.00	0.65	0.24	0.29	0.85	0.46	0.54	-0.75	0.44	0.48	-0.88	-0.17	-0.54
Pb		1.00	0.72	0.75	0.82	0.71	0.84	-0.84	0.83	0.85	-0.74	0.13	-0.58
Zn			1.00	0.98	0.46	0.94	0.93	-0.71	0.96	0.95	-0.31	0.66	-0.18
Cu				1.00	0.46	0.95	0.95	-0.71	0.95	0.96	-0.33	0.69	-0.14
Ni					1.00	0.55	0.65	-0.81	0.65	0.61	-0.85	-0.11	-0.69
Cr						1.00	0.95	-0.74	0.93	0.95	-0.39	0.70	-0.09
V							1.00	-0.88	0.98	0.99	-0.58	0.52	-0.34
Sr								1.00	-0.85	-0.84	0.88	-0.08	0.69
TiO ₂									1.00	0.98	-0.53	0.51	-0.39
Fe ₂ O ₃										1.00	-0.53	0.55	-0.29
CaO											1.00	0.35	0.84
P ₂ O ₅												1.00	0.58
TS													1.00

Bold text highlights strong correlations

Cu, Fe₂O₃, CaO, and P₂O₅ were observed in the Hamahara sediments (Table 7). In contrast, V, Sr, TiO₂, and CaO have negative or weak relationships in this lake. Significant associations of V, TiO₂, and Fe₂O₃ with Pb, Zn, Cu, Ni, and Cr, and of Cr with Pb, Zn, and Cu (*r* = +0.71, +0.94, +0.95, respectively) were observed in Lake Kijima (Table 7). Conversely, concentrations of Sr, CaO, P₂O₅, and TS again show no relationships, indicating different behavior of these elements in the sediments.

The correlation matrices show that metallic elements are strongly correlated with total Fe (Tables 6, 7), suggesting that Fe₂O₃ may exert a major role in controlling the metal concentrations in the lake sediments. The strong positive correlations of Zn, Ni, Cr, TiO₂, and CaO with TS in Lake Banryoko and As, Pb, Zn, Cu, Fe₂O₃, CaO, and P₂O₅ with TS in Hamahara indicate their concentrations may be related to pyritization, as reported by Jones and Manning (1994) for sediments in the United Kingdom. Excluding Lake Hamahara, the good positive correlations of a suite of metals (As, Pb, Zn, Cu, Ni, and Cr in Banryoko; Cu, Ni, and Cr in Onbe; Pb, Zn, Cu, Ni, and Cr in Kijima) with V suggest the possibility of formation of com-

plexes with organic matter. This is consistent with the study conducted by Tribovillard et al. (1994) of sediments in the UK. The negative or poor correlations of Sr and CaO in all lakes imply a different control, almost certainly association with detrital plagioclase (Roser 2000), and therefore are depleted in muds relative to UCC. Inter-relationships between As, Pb, Zn, Cu, Ni, and Cr show that all are significantly correlated with each other, indicating a common source or a similar enrichment mechanism in the lake sediments.

Conclusions

The results show that the waters of Lakes Banryoko, Onbe, Hamahara and Kijima are approximately neutral to alkaline in nature, and temperature, pH and DO display slight stratified conditions. The lake sediments are in reducing condition, as indicated by negative ORP values. REE distributions fall into three groups: those with LREE fractionation, marked negative Eu anomalies and flat HREE at Hamahara, those with slight LREE enrichment and fractioned HREE at Kijima, and those with LREE enrichment, negative Eu

anomalies and relatively flat HREE at Onbe. These distributions are consistent with the varying composition of the respective source rocks. As, Pb, Zn, Cu, Ni, and Cr abundances in the lake sediments are greater than average upper continental crust. These elevated concentrations are seemingly related to the sediment matrix, redox conditions of the bottom sediments, anthropogenic sources, and surface soil erosion from the hinterland. According to the NYSDEC guidelines, the sediments in Lakes Onbe and Kijima are moderately contaminated with respect to As and Zn, and slightly contaminated with Cu, whereas Pb enrichment is significant. Ni and Cr contents in the lake sediments also exceed the lowest effect level in aquatic sediments. Similarly, Pb and Cu concentrations are comparable to COSED, whereas As and Zn exceed this value in Lakes Onbe and Kijima, indicating the concentrations of As, Pb, Zn, and Cu are potentially toxic. Therefore, further studies should be devoted to a more comprehensive assessment of the toxic effects of pollutants on biota in the lakes of southwest Japan.

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