Environ Monit Assess (2011) 173:167–180
DOI 10.1007/s10661-010-1379-6

Recent sedimentary environment of coastal lagoon in southwestern Japan: evidence from major and trace elements

Faruque Ahmed · M. Hawa Bibi ·
Takehiko Fukushima · Koji Seto · Hiroaki Ishiga

Received: 31 August 2009 / Accepted: 11 February 2010 / Published online: 9 March 2010

Abstract A geochemical study of the bottom sediments of Lake Shinji and the River Ohashi in southwestern Japan was carried out to determine their elemental compositions and to evaluate the pollution status of lake sediments by employing enrichment factor (EF), pollution load index (PLI), and geoaccumulation index (I_{geo}). Present-day water quality was also assessed. Results showed that the water quality of Lake Shinji contrasts slightly between the upper and lower parts. The chemical composition of the sediments, as measured by X-ray fluorescence, included major and trace elements and total sulfur (TS). Average abundances of As, Pb, Zn, Cu, Ni, and Cr in the Shinji sediments were 10, 29, 143, 27, 19, and 54 ppm, respectively, compared to 6, 18, 57, 16, 10, and 37 ppm in the river sediments. Based on the EF, PLI, and I_{geo}, the lake sediments are moderately to strongly polluted with respect to As, moderately polluted with Pb, Zn, and Cr, and unpolluted with Cu and Ni. The high EF and I_{geo} for As, Pb, and Zn in the lake sediments indicate that metal concentration has occurred in Shinji. Increases in the abundances of these metals are likely related to the fine-grained nature of the sediments, reducing conditions of the bottom sediments, enrichment in organic matter, and possibly a minor contribution from non-point anthropogenic sources. Trace metal contents are strongly correlated with Fe_2O_3 and TS, suggesting that Fe oxides and sulfides play a role in controlling abundances in the investigated areas.

Keywords Coastal lagoon sediment · Trace metals · Enrichment factor · Geoaccumulation index · Southwest Japan

Introduction

Coastal lagoon sediments are recognized as carriers and possible sources of pollutants in aquatic systems. Out of these pollutants, heavy metals are of major concern due to their persistent and bioaccumulative nature. These chemical elements

F. Ahmed (✉) · T. Fukushima
Graduate School of Life and Environmental Sciences,
University of Tsukuba, 1-1-1 Tennoudai,
Tsukuba 305-8572, Japan
e-mail: frahmed2007@yahoo.com

M. H. Bibi
Department of Environmental Science
and Technology, Saitama University,
255 Shimo-okubo, Saitama 338-8570, Japan

K. Seto
Research Center for Coastal Lagoon Environments,
Shimane University, Matsue 690-8504, Japan

H. Ishiga
Department of Geoscience, Shimane University,
Matsue 690-8504, Japan

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). Once released into the aquatic systems, trace elements are transferred to the sediments by adsorption onto suspended matter and subsequent sedimentation. Some trace elements, notably Cu and Zn, are essential micronutrients for living organisms, although many of these elements (e.g., As, Pb, and Cr) are considered to be toxic with respect to human health and aquatic life (Esen et al. 2010). Over the last few decades, many geochemical studies have been directed at coastal and lake sediments to determine the extent of contamination from trace metals (e.g., Soares et al. 1999; Ruiz-Fernández et al. 2003; Bibi et al. 2007; Esen et al. 2010).

The modern industrial revolution in Japan started in the early 1950s and continued through the 1970s (Yoshimura et al. 2005). However, the drainage basins of lakes and lagoons in southwest Japan have been affected by numerous human activities over the last century, and these could have resulted in anthropogenic trace element emissions into the atmosphere and deposition in the lake systems. Ishiga et al. (2000) reported that the large-scale exploitation of residual iron sands in the catchments of Lake Shinji and Nakaumi Lagoon in southwest Japan led to extensive deforestation in the hinterland 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.

In the past few decades, much attention has been paid to paleolimnologic and organic geochemical studies of Lake Shinji, a brackish coastal lagoon, and its sediments (e.g., Sampei et al. 1997; Yamamuro and Kanai 2005). Details of the geological setting and development of Shinji are described by Tokuoka et al. (1990). However, very little is known about the concentrations and distributions of trace elements and heavy metals in the Shinji sediments. Recently, both public and government sectors have become increasingly interested in controlling the water and sediment qualities of Lake Shinji. Elevated heavy metal concentrations in sediments may cause adverse biological effects, even though water quality criteria are not exceeded (NRC 1989). Therefore, an assessment of metal concentrations in the Shinji sediments is needed.

The main objectives of this study were to gain insight into (1) water quality and the nature of the water column in Shinji Lagoon and (2) geochemical compositions of the bottom sediments, including trace element concentrations and their spatial distributions and sources. An assessment of metal concentrations in the Shinji sediments was made based on enrichment factor, pollution load index, and geoaccumulation index.

Materials and methods

Geologic and hydrologic outlines of Lake Shinji and River Ohashi

Lake Shinji has an area of 79.2 km^2 (average water depth, 4.5 m) and is located in the central Japan Sea coast within the Shimane prefecture of southwest Japan (Fig. 1). It is representative of a strongly enclosed coastal estuarine system in Japan and has been one of the largest brackish lakes in the country since the last sea-level rise in the Holocene (Ichikawa et al. 2007). The western sea opening of Shinji was closed by the Hii River delta at approximately 6,000 years BP, while the eastern side of Nakaumi has been semi-closed by the development of the Yumigahama sand bar from 2,400 years BP (Tokuoka et al. 1990). At present, Lake Shinji and eastern Lake Nakaumi are connected by the 8-km-long River Ohashi, which occasionally supplies more saline water to Shinji from the adjacent polyhaline Lake Nakaumi (Fig. 1). Consequently, a dense population of the filter-feeding bivalve *Corbicula japonica* spp. is found in the shallow sandy area, which accounts for about 14% of the yearly production in Japan. The lakes and their environments serve as recreational areas for the local residents as well as support aquatic flora and fauna.

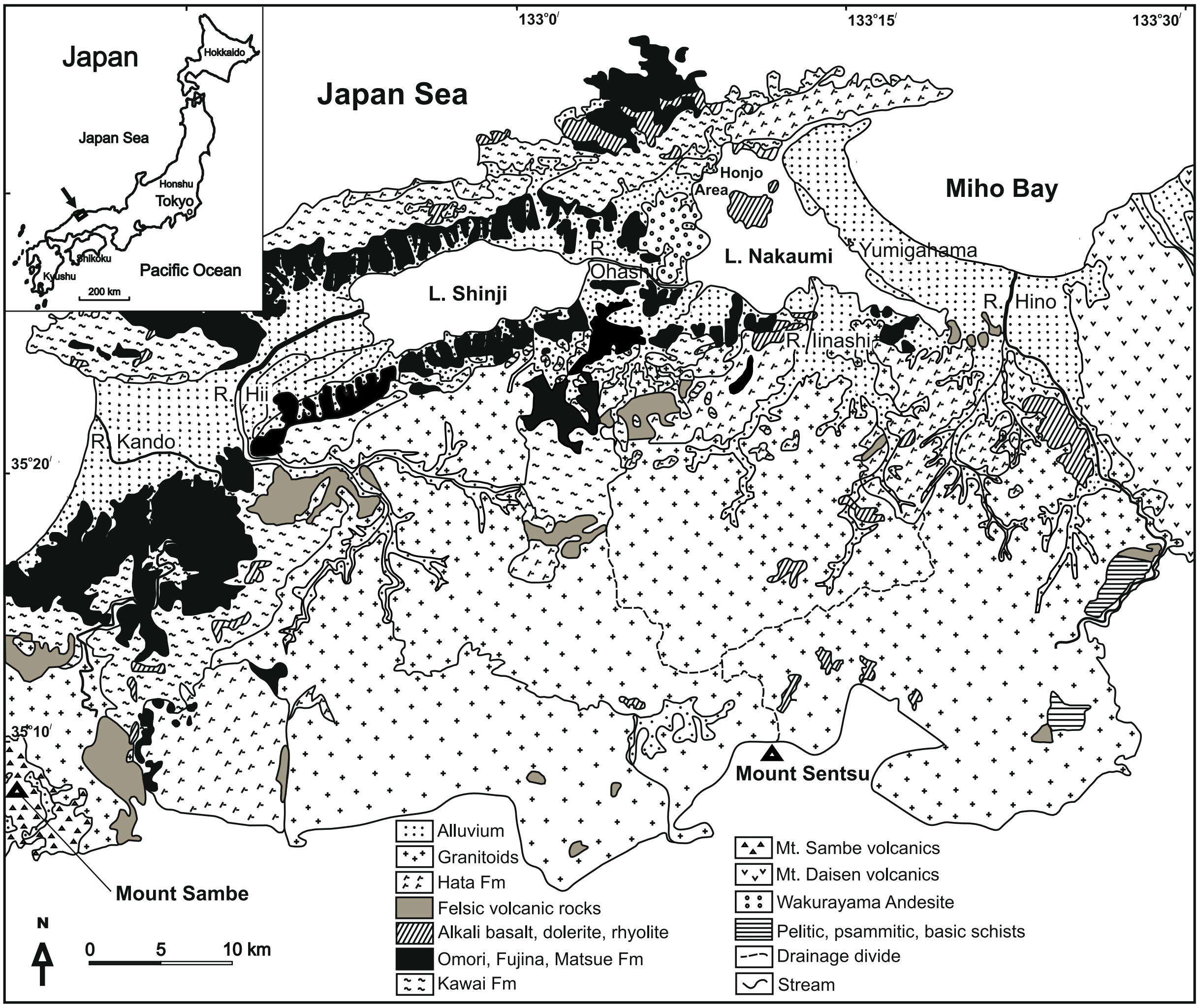

Fig. 1 Simplified basement geology and the locations of Lake Shinji and River Ohashi in Shimane prefecture. *Inset*, location in Japan. Geology based on the 1:200,000 geological maps of Shimane prefecture (EBGMSP 1997) and Takahashi (Teraoka et al. 1996)

Geologically, the southern part of Lake Shinji is underlain by Cretaceous to Paleogene granitic and volcanic rocks (Fig. 1). These are covered by a complex sequence of Miocene sedimentary and volcanic rocks. Thick Miocene strata occur beneath the Holocene lagoon sediments (Yamauchi et al. 1980). Average annual freshwater discharge to the lake is 1.3×10^9 m^3, and 74% of it is through River Hii. The watershed of Hii (catchment area of ~920 km^2) is mostly agriculture dominated with rice paddy (240 km^2), and Shinji thus receives wastewater from irrigation. Flatlands flanking the River Ohashi are also used for paddy cultivation. Moreover, an agricultural field is located in northeastern Shinji. The study area is characterized by a humid climate, with an average annual temperature of about 15°C and average annual precipitation of a little more than 2,000 mm. The eastern and western fringes of the lake are moderately urbanized, whereas the northern and southern margins are mostly forested, with a mixture of native broadleaf species, plantation forests, and bamboo. Matsue City, the capital of the Shimane prefecture, is situated at the east end of Lake Shinji and has a population of over 160,000 inhabitants.

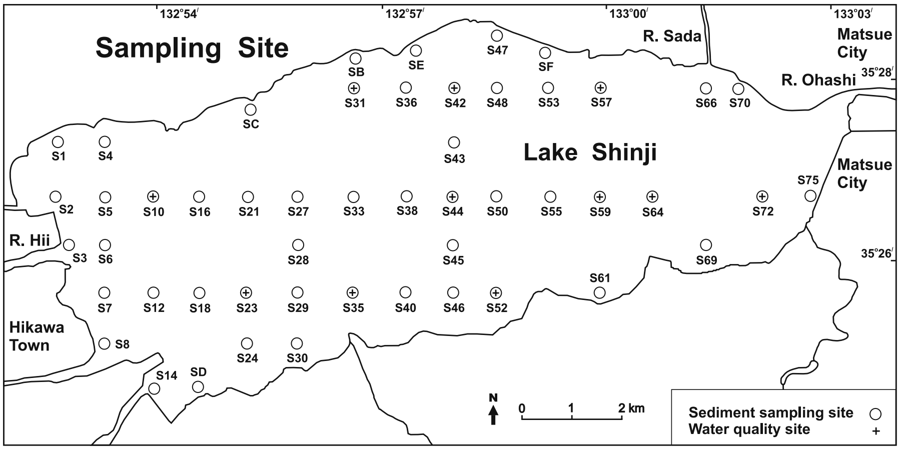

Fig. 2 Locations of water quality and sediment sample sites in Shinji Lagoon in Shimane prefecture, SW, Japan

Sediment sample collection and description

Fifty-five sediment samples were collected from Lake Shinji ($n = 51$) and River Ohashi ($n = 4$) in the second week of August 2006 (Fig. 2). Samples were collected when the weather was fine. The uppermost 2 cm of the bottom sediments were collected using an Ekman-Berge Bottom Sampler (Rigo Co. Ltd., Japan). Composite samples were taken from the surface portion of the catcher with a plastic spatula. Sediment samples weighing about 60–100 g were packed in Ziploc® bags and stored in a cooler box at 4°C for transport to the laboratory.

The sediment samples were mainly very soft, slightly silty, fine clays with a black, olive black, or greenish black color. Fine sands and silts were abundant in some samples that also contained occasional marine shells or shell fragments, but most contained a high proportion of clays. Silt and clay are >90% of the Shinji sediment contents at water depths of more than 3 m (Fig. 3; Yamamuro and Koike 1998). Kaolinite and illite represent more than 80% of total clay minerals. The clay particles often appeared to be coated with Fe(oxy)hydroxides, which can act as carriers of metallic pollutants by adsorption. Total sulfur in Shinji sediments (0.4–1.5 wt.%) is primarily contained in iron sulfide (pyrite and FeS; Ishiga et al. 2000). The reported average concentrations of total organic carbon and total nitrogen in Shinji sediments were 2.3 and 0.3 wt.%, respectively (Yamamuro and Kanai 2005). The preservation and accumulation of organic matter is enhanced

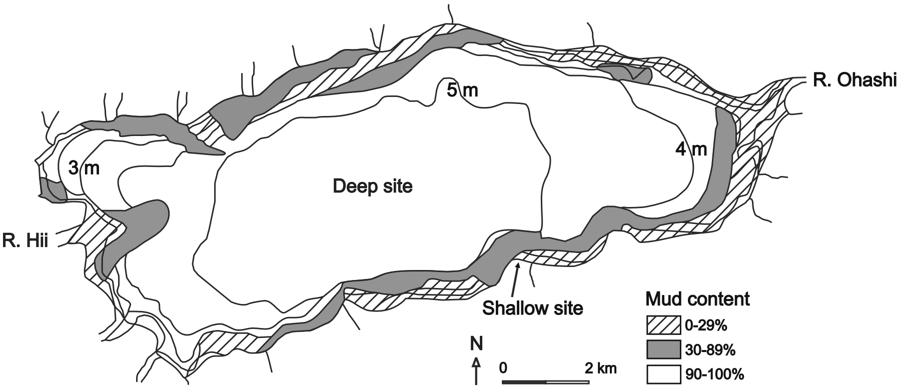

Fig. 3 The distribution of mud content (silt and clay against total dry wt.%) of surface sediment (after Yamamuro and Koike 1998)

by the anoxic conditions occurred in sediments. The black color and the unpleasant smell of the sediments is also an evidence of these conditions.

Analytical procedures

Measurement of water quality

Water parameters including depth, temperature, electrical conductivity (EC), salinity, chlorophyll-a, turbidity, and dissolved oxygen (DO) concentrations were measured in the field during sediment sampling, using a portable Horiba U-22 multi-monitoring system (Horiba Co. Ltd., Japan). Data collected from different depths at 11 locations from Lake Shinji are summarized in Table 1.

Sediment sample preparation

Approximately 60 g of each sediment 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 to produce homogenous powders with particle sizes of $<63\ \mu$m. The powdered samples were then compressed into briquettes using a force of 200 kN for 60 s.

X-ray fluorescence analysis

Selected major oxide [TiO_2, $Fe_2O_3^*$ (total iron expressed as $Fe_2O_3^*$), MnO, CaO, and P_2O_5], total sulfur (TS), and trace element (As, Pb, Zn, Cu, Ni, Cr, V, and Sr) concentrations were determined by X-ray fluorescence (XRF) at Shimane University, using a RIX-2000 spectrometer (Rigaku Denki Co. Ltd., Japan) equipped with a Rh-anode X-ray tube. All analyses were made on pressed powder briquettes, following the method of Ogasawara (1987). Average errors for all elements are less than ±10% relative. Analytical results for US Geological Survey standard SCo-1 (Cody Shale) were acceptable compared to the proposed values of Potts et al. (1992) (Table 2).

Table 1 Water quality of Lake Shinji in southwest Japan

Site		Depth (m)	Temperature (°C)	EC (mS/cm)	Salinity (psu)	Chlorophyll-a (ppb)	Turbidity (FTU)	DO (mg/l)
S-10 (*n* = 86)	U Range	0.08–2.88	20.3–20.4	3.5–3.8	2.0–2.2	1.3–1.5	1.4–2.5	8.3
	L Range	2.93–4.46	20.4–20.5	3.8–3.9	2.2–2.3	1.2–1.4	1.3–10.0	7.7
S-23 (*n* = 98)	U Range	0.04–3.33	20.5–20.8	3.3–3.5	1.9–2.0	1.4–2.3	2.2–4.1	8.3
	L Range	3.40–5.25	20.6–20.8	3.5–3.9	2.1–2.3	1.6–2.3	2.5–10.4	7.7
S-31 (*n* = 85)	U Range	0.05–3.28	20.5–21.6	3.6–3.9	2.0–2.3	1.5–2.3	1.5–2.2	8.1
	L Range	3.32–4.51	20.5–21.2	4.0–5.5	2.3–3.2	1.2–2.1	1.4–8.7	2.9
S-35 (*n* = 107)	U Range	0.04–3.63	20.4–21.4	3.1–3.5	1.7–2.0	1.2–3.0	1.4–2.9	8.1
	L Range	3.68–5.40	20.7–21.0	3.6–7.4	2.1–5.4	2.7–3.7	2.1–11.0	3.0
S-42 (*n* = 94)	U Range	0.04–3.27	20.9–21.7	3.8–3.9	2.1–2.3	2.7–4.0	2.1–3.3	9.7
	L Range	3.33–5.02	20.8–21.0	3.9–5.7	2.2–3.4	1.7–2.8	2.1–11.9	3.5
S-44 (*n* = 99)	U Range	0.04–3.81	20.9–21.3	3.7–4.0	2.1–2.3	2.4–3.6	1.8–2.9	9.5
	L Range	3.87–5.47	20.8–21.0	4.0–6.2	2.3–3.7	2.5–5.2	2.0–10.5	5.7
S-52 (*n* = 95)	U Range	0.03–3.47	21.1–21.8	3.9–4.1	2.2–2.4	2.1–4.3	1.7–3.5	9.6
	L Range	3.53–5.16	20.9–21.0	4.1–4.2	2.4	2.5–3.7	2.0–6.6	7.8
S-57 (*n* = 88)	U Range	0.04–3.21	20.7–21.0	4.1–4.5	2.4–2.6	2.3–3.3	1.8–4.5	8.2
	L Range	3.25–4.56	20.7–20.8	4.5–5.3	2.6–3.1	2.7–4.9	5.4–22.1	6.5
S-59 (*n* = 87)	U Range	0.03–3.47	20.8–20.9	3.7–4.0	2.1–2.3	2.3–3.5	1.7–5.1	9.2
	L Range	3.53–4.88	20.9–21.0	4.1–5.8	2.4–3.5	3.5–7.4	1.6–8.5	7.8
S-64 (*n* = 92)	U Range	0.04–3.02	20.7–21.0	3.7–4.3	2.1–2.5	2.4–4.6	1.6–2.8	9.1
	L Range	3.08–4.75	20.8–21.0	4.4–5.8	2.5–3.5	4.6–8.0	1.7–10.0	6.8
S-72 (*n* = 81)	U Range	0.04–3.48	20.8–21.4	4.4–4.5	2.6	3.2–4.8	1.1–2.1	9.6
	L Range	3.53–4.12	20.8	4.5–4.7	2.6–2.8	1.8–4.6	1.6–7.4	5.3

EC electrical conductivity, *DO* dissolved oxygen (surface and bottom layers), *U* Upper, *L* Lower, *FTU* formazin turbidity unit, *n* number of measurements (4–7 cm intervals from surface to bottom)

Table 2 Comparison of USGS SCo-1 (Cody Shale) values of trace elements (ppm) and major oxides and TS (wt.%) obtained in this study with certified values

Element	As	Pb	Zn	Cu	Ni	Cr	V	Sr	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5	TS
Measured values	13.4	28.2	106.1	27.6	28.1	75.4	145.1	177.0	0.55	5.70	0.05	2.72	0.19	0.068
Certified values	12.4	31.0	103.0	28.7	27.0	68.0	131.0	174.0	0.63	5.14	0.05	2.62	0.21	0.063

Statistical analysis

In order to establish inter-element relationships, correlation coefficients for the 14 elements were analyzed. One-way analysis of variance was used to test for differences between four groups of data from Lakes Shinji and Nakaumi and Rivers Ohashi and Hii. Significant differences between group means were established by the least significant difference test ($p < 0.05$) using the statistical package StatView 5.0 (SAS Institute Inc.).

Spatial analysis

Geostatistical methods in geographical information systems (GIS) are widely applicable tools used to develop a statistically valid surface. Surface fitting with this method involves three key steps: exploratory spatial data analysis, structural analysis, and surface prediction and assessment of results. Following the method of inverse distance weighting, the trace metal concentrations were used as the input data for a contouring map to study the distribution of metals in the surface sediments. A GIS software (ArcView 9.2) was used to conduct the spatial analysis for the current study.

Results

Water quality and the water column

Physicochemical properties (EC, salinity, chlorophyll-a, turbidity, and DO) of the water body of Lake Shinji contrast slightly between the upper and lower parts (Table 1). The lake water data show that surface and deep water temperatures are rather constant (range, 20.3–21.8°C). In the present study, the surface waters of Shinji were more oxic (DO = 8.1–9.7 mg/l) than the bottom water layers (DO = 2.9–7.8 mg/l). This is in agreement with previous reports (Sampei et al. 1997) showing that the bottom water layers of Shinji become anoxic or oxygen poor in the summer. Kamiya et al. (1996) also found that DO concentrations in Lake Shinji were <0.5 mg/l in the water immediately above the bottom sediments. The weak water exchanged between Shinji lagoon and the open sea and the increase in pollutant loading of organic substances and nutrients result in the formation of oxygen-depleted water in the bottom layer during summer. With such anoxic water masses in summer in the central basin (at depths >5 m), the macrobenthos community does not exist in Lake Shinji (Yamamuro and Koike 1998). Salinity values in the deeper parts (range, 2.1–5.4 psu, practical salinity units) were relatively higher than those in overlying water layers (range, 1.7–2.6 psu; Table 1). The salinity variation was largely affected by the amount of freshwater discharge from the Hii River. A similar observation was made by Sampei et al. (1997), who noted the salinity of the bottom layers of the lagoon (about 5 psu) were slightly higher than those in overlying water layers (about 4 psu). The lower parts of the waters in the study area were more turbid than the upper parts, with a maximum turbidity of 22.1 formazin turbidity units. Concentrations of chlorophyll-a in the deeper parts of Shinji (range, 1.2–8.0 ppb) were higher than those in the overlying water layers (range, 1.2–4.8 ppb). The concentration range of chlorophyll (1.2–8.0 ppb) indicates that the water body of the lake is under mesotrophic conditions.

Major and trace elements

Elemental compositions of the bottom sediments analyzed by XRF are summarized in Table 3. River Hii (Figs. 1 and 2) stream sediment data from sites above Lake Shinji (Ortiz and Roser 2006), Lake Nakaumi sediment data from Ahmed et al. (2009), and average upper continental crust

Table 3 Geochemical compositions of Lake Shinji and River Ohashi sediments in southwest Japan

Area		Trace elements (ppm)								Major oxides and TS (wt.%)					
		As	Pb	Zn	Cu	Ni	Cr	V	Sr	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5	TS
LS ($n = 51$)	Range	3–14	11–39	16–201	3–43	3–40	18–242	4–523	81–402	0.15–2.60	1.14–10.83	0.06–0.54	1.07–7.81	0.07–0.34	0.04–1.10
	Mean	9.9^{a}	28.7^{a}	142.6^{a}	27.1^{a,b}	18.7^{a,b}	54.4^{a}	152.5^{a}	175.8^{a}	0.71^{a}	7.78^{a}	0.26^{a}	1.84^{a}	0.20^{a}	0.48^{a}
	SD	3.4	9.5	57.4	13.1	8.1	34.5	74.7	63.4	0.36	2.74	0.09	1.06	0.06	0.34
LN ($n = 40$)	Range	4–19	12–35	42–208	8–51	7–50	24–94	17–151	116–774	0.17–0.60	1.60–7.96	0.07–1.09	1.03–15.85	0.10–0.25	0.20–2.12
	Mean	11.7^{b}	25.4^{a,b}	134.6^{a}	31.5^{a}	21.0^{a}	46.2^{a,b}	94.6^{b}	333.1^{b}	0.44^{b}	5.36^{b}	0.19^{b}	3.22^{b}	0.16^{b}	1.02^{b}
	SD	4.5	7.7	55.9	14.8	9.7	14.2	41.8	207.5	0.11	1.82	0.18	2.88	0.03	0.56
RO ($n = 4$)	Range	5–8	16–23	42–71	8–28	8–13	30–54	13–68	138–234	0.17–0.45	1.59–3.29	0.13–0.32	1.62–3.68	0.12–0.21	0.32–0.72
	Mean	6.0^{c}	18.0^{b}	57.4^{b}	15.8^{b}	10.4^{b}	37.4^{a,b}	37.1^{b}	191.8^{a,b}	0.28^{b}	2.38^{c}	0.21^{a,b}	2.58^{a,b}	0.16^{a,b}	0.48^{a}
	SD	1.2	3.4	15.3	8.6	2.0	11.4	26.4	39.7	0.14	0.91	0.08	1.09	0.05	0.18
RH ($n = 3$)	Range	na	19–30	na	na	13–20	27–41	90–157	205–236	0.64–0.86	6.02–8.33	0.20–0.27	2.19–2.50	0.09–0.19	na
	Mean		24.7^{a,b}			17.3^{a,b}	32.7^{b}	124.3^{a,b}	224.7^{a,b}	0.74^{a}	6.96^{a,b}	0.24^{a,b}	2.34^{a,b}	0.15^{a,b}	
	SD		5.5			3.8	7.4	33.5	17.1	0.11	1.21	0.04	0.16	0.05	
UCC	Mean	2	20	71	25	20	35	60	350	0.50	5.00	0.08	4.20	0.16	na

Means with different superscript letters in a column are significantly different ($p < 0.05$). Lake Nakaumi (LN) sediment data from Ahmed et al. (2009). River Hii (RH) stream sediment data from sites above Lake Shinji from Ortiz and Roser (unpublished data, 2006). Upper continental crust (UCC; Taylor and McLennan 1985)
LS Lake Shinji, *RO* River Ohashi, *na* not available, *UCC* upper continental crust

from Taylor and McLennan (1985) are also included for comparison.

The wide range of variation in the element concentrations in the sediments of the Lake Shinji area could be partly related to the presence of different sediment types. Abundances of major and trace elements in the Shinji sediments were higher than in those from the River Ohashi and Hii (Table 3). However, Nakaumi sediments have greater contents of As, Cu, Ni, Sr, CaO, and TS compared to Shinji sediments. Shinji sediments contain the lowest and highest concentrations of Pb, Cr, and V among the four water bodies. On average, the Shinji sediments contain 9.9 ppm As, 28.7 ppm Pb, 142.6 ppm Zn, 27.1 ppm Cu, and 18.7 ppm Ni. Excluding marked enrichments in the northernmost part (100–242 ppm), Cr abundances in this lake were relatively uniform (about 47 ppm), similar to those found in the neighboring Lake Nakaumi (46 ppm Cr; Table 3). Abundances of V, CaO, and TS show significant variation in Shinji and Nakaumi sediments. Ca and Sr have similar geochemical behavior in sediments, and therefore, both CaO and Sr are enriched in the surface samples (Ahmed et al. 2005).

The River Ohashi sediments contain less As, Pb, Cu, and Cr than in either the Shinji or Nakaumi sediments. Maximum and average concentrations of Zn, Ni, and V differ significantly between the river and lake sediments, with levels at least two to three times greater in the Shinji and Nakaumi sediments (Table 3). The highest average values of P_2O_5 and TS were observed in Shinji and Nakaumi, respectively. Average concentrations of P_2O_5 were almost identical in Nakaumi and the Ohashi and Hii Rivers. However, Shinji and River Hii sediments have slightly greater contents of TiO_2, Fe_2O_3, and MnO than Nakaumi; the contrast is much larger with River Ohashi sediments.

Spatial variability of metal concentrations

Geochemical maps for As, Pb, Zn, Cu, Ni, and Cr were constructed using a GIS software (ArcView 9.2) to examine their spatial distributions in the bottom sediments of Lake Shinji (Fig. 4). In these maps, metal concentrations (As, Pb, Zn, and Cu) increase toward southwest and

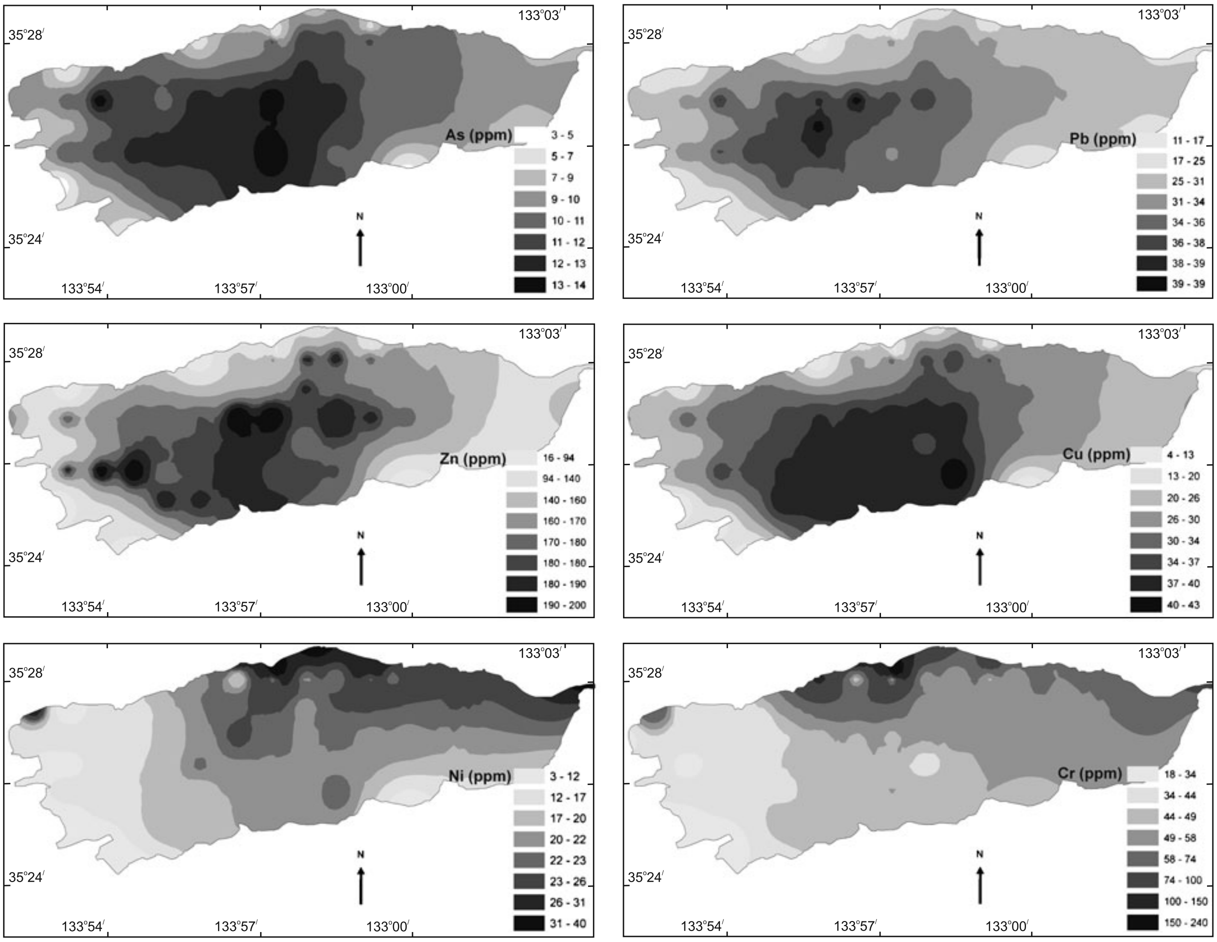

Fig. 4 Geochemical maps of As, Pb, Zn, Cu, Ni, and Cr concentrations in bottom sediments of Lake Shinji

central parts of Shinji and also near the Hii River mouth. This provides a refinement and confirmation of the results from the correlation analysis (Table 4), in which strong correlations were found among these metals. In Lake Shinji, the formation of oxygen-depleted water appeared in summer in the southwestern part of the lake, and the western side of the lake was fed by organic detritus from the River Hii (Sampei et al. 1997; Ishiga et al. 2000). Morphologically, the central part of Shinji is a deeper part of the lagoon (at water depths of >4 m), where more than 99% of the sediment consists of silt and clay (Yamamuro and Koike 1998; Fig. 1, deep site). The horizontal distribution of organic carbon concentrations in the surface sediment showed greater values in the western half of the lake than those in the eastern half (Yamamuro 2000).

Similar spatial distribution patterns of Ni and Cr were observed in the northern part of the lake (Fig. 4). This could be due to an increased load of nutrients from irrigation ponds (about 100) and agricultural fields in the northern Shinji. Liaghati et al. (2003) noted that elevated Cr concentrations in the coastal sediments in Australia originated from agricultural material (e.g., nitrate fertilizers). Irrigation ponds are, by nature, strongly affected by human factors such as unpredictable water fluctuation, farming runoff, and so on. The elements Ni and Cr always migrate in colloidal form in aquatic environments and deposit in the bottom sediments while encountering

Table 4 Correlations between the elements in sediments of Lake Shinji and River Ohashi

	As	Pb	Zn	Cu	Ni	Cr	V	Sr	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5	TS
Lake Shinji ($n = 51$)														
As	1.00	*0.93*	*0.96*	*0.96*	0.26	−0.37	0.28	−0.55	−0.06	*0.91*	0.42	−0.45	0.53	*0.78*
Pb		1.00	*0.93*	*0.96*	0.11	−0.49	0.16	−0.58	−0.21	*0.85*	0.34	−0.35	0.50	*0.76*
Zn			1.00	*0.96*	0.30	−0.33	0.35	−0.49	0.01	*0.96*	0.46	−0.42	*0.67*	*0.69*
Cu				1.00	0.23	−0.40	0.26	−0.58	−0.11	*0.90*	0.43	−0.43	0.52	*0.79*
Ni					1.00	*0.65*	*0.66*	0.12	*0.65*	0.42	0.39	−0.08	0.23	0.26
Cr						1.00	*0.69*	0.48	*0.87*	−0.16	0.11	0.27	−0.10	−0.26
V							1.00	0.19	*0.91*	0.53	0.36	0.05	0.38	0.18
Sr								1.00	0.45	−0.38	−0.06	*0.78*	−0.03	−0.54
TiO_2									1.00	0.20	0.19	0.20	0.19	−0.10
Fe_2O_3										1.00	0.53	−0.39	*0.70*	0.64
MnO											1.00	−0.15	0.49	0.17
CaO												1.00	−0.08	−0.36
P_2O_5													1.00	−0.01
TS														1.00
River Ohashi ($n = 4$)														
As	1.00	0.29	*0.82*	0.11	0.23	0.19	0.62	0.43	0.58	*0.74*	*0.75*	0.50	0.16	0.35
Pb		1.00	*0.76*	*0.94*	*0.92*	*0.99*	*0.93*	−0.74	*0.95*	*0.86*	−0.39	−0.42	−0.49	*0.99*
Zn			1.00	*0.65*	*0.73*	*0.69*	*0.95*	−0.14	*0.93*	*0.98*	0.30	0.18	−0.07	*0.82*
Cu				1.00	*0.98*	*0.94*	*0.83*	−0.81	*0.84*	*0.72*	−0.46	−0.32	−0.28	*0.96*
Ni					1.00	*0.90*	*0.86*	−0.71	*0.86*	*0.77*	−0.31	−0.15	−0.13	*0.96*
Cr						1.00	*0.88*	−0.80	*0.91*	*0.80*	−0.49	−0.50	−0.55	*0.97*
V							1.00	−0.43	*0.99*	*0.99*	−0.01	−0.10	−0.29	*0.95*
Sr								1.00	−0.48	−0.29	*0.89*	*0.74*	0.56	−0.69
TiO_2									1.00	*0.98*	−0.08	−0.18	−0.36	*0.96*
Fe_2O_3										1.00	0.13	−0.02	−0.25	*0.88*
MnO											1.00	*0.87*	0.63	−0.30
CaO												1.00	*0.92*	−0.28
P_2O_5													1.00	−0.35
TS														1.00

Italic text highlights strong correlations

clay or organic matter or sudden physicochemical changes of water (Wang et al. 2008). Moreover, soil erosion, anthropogenic material from urban sources, and riverine input may have influenced the elevated concentrations of these metals in the surface sediments. Therefore, the highest concentrations of trace metals are present in the areas where carbon-rich clay-sized sediments dominate.

Discussion

Evaluation of sediment pollution

Various methods have been suggested for quantifying metal enrichment in aquatic sediments. The central notion is to produce a numerical result comparing the metal content of each sample with a background level, such as the average shale values or the upper continental crust (Wedepohl 1995). In the present study, pollutant indicators were calculated based on the average crustal abundances from Wedepohl (1995). For the calculation of pollutant indicators the factors discussed below have been suggested.

Enrichment factor

The enrichment factor (EF) is an indication of the extent to which trace elements are enriched or reduced relative to a specific source. The EF was calculated using the following equation:

$$\mathrm{EF} = [C_x/C_{\mathrm{ref}}]_{\mathrm{sample}} \,/\, [C_x/C_{\mathrm{ref}}]_{\mathrm{background}}$$

where C_x is the concentration of the element of interest, and C_{ref} is the concentration of reference element for normalization. Ti was selected as the reference element because it has a short residence time and low concentration in natural waters and hence should be transferred quantitatively from source to sediments (Taylor and McLennan 1985). Arsenic, Pb, Zn, and Cr have EF values >1 (Fig. 5a), suggesting anthropogenic sources; lower EF values are encountered in the shallower part of Lake Shinji. The maximum values of the EF were close to 6 for As (moderately severe) and close to 3 for Pb and Zn (moderate enrichment).

Based on past studies (Ishiga et al. 2000; Ahmed et al. 2009), arsenic was not considered to pose the greatest risk in the area; nevertheless, its EF values are the highest among all other elements (Fig. 5a). In most sediment samples, the EF values for Zn were equal to 3, showing a moderate anthropogenic enrichment. The highest EF value for Pb of 3.3 (average, 1.4) in the sediment samples likely reflects minor enrichment and the upriver drainage sources from the River Hii. The EF values for Cu in the sediments were <1.5 (less enrichment), and therefore, the anthropogenic input of Cu were not significant. Nickel and Cr did not show significant spatial distribution with low EF (except EF = >3 for Cr; $n = 3$) and can be attributed to the local substrate. The concentration and distribution of Cr indicate that although the contamination of this metal in Lake Shinji is not as obvious as As and Zn, it has been influenced more or less by minor anthropogenic input and coastal detrital input as the main sources.

Pollution load index

Pollution load index (PLI) is the geometric mean of the contamination factor of each of its constituent samples present in the studied area (Tomlinson et al. 1980). The PLI was computed by the following formula:

$$\mathrm{PLI} = \left[\mathrm{CF}_{\mathrm{As}} \times \mathrm{CF}_{\mathrm{Pb}} \times \mathrm{CF}_{\mathrm{Zn}} \times \mathrm{CF}_{\mathrm{Cu}} \times \mathrm{CF}_{\mathrm{Ni}} \times \mathrm{CF}_{\mathrm{Cr}}\right]^{1/6}$$

According to Tomlinson et al. (1980), PLI values of 0, 1, or >1 suggest the absence of baseline pollutants, the presence of them, or the progressive deterioration of sediment quality, respectively. The study results show that the PLI, calculated for the selected metals, indicates a considerable level of pollution for As, moderate pollution for Pb and Zn, and low levels for Cu and Cr in the Shinji sediments. The PLI values calculated for the Shinji sediments (1.8 and 2.4 for Pb and Zn, respectively) suggest that this basin is moderately impacted by Pb and Zn. Sediments show low averaged values of about 1 for Cu and Cr, whereas the highest PLI for As (4.5) reveals considerable contamination of As in the lake sediments. The values of PLI (1.4) for Ni were closer to the baseline pollutant.

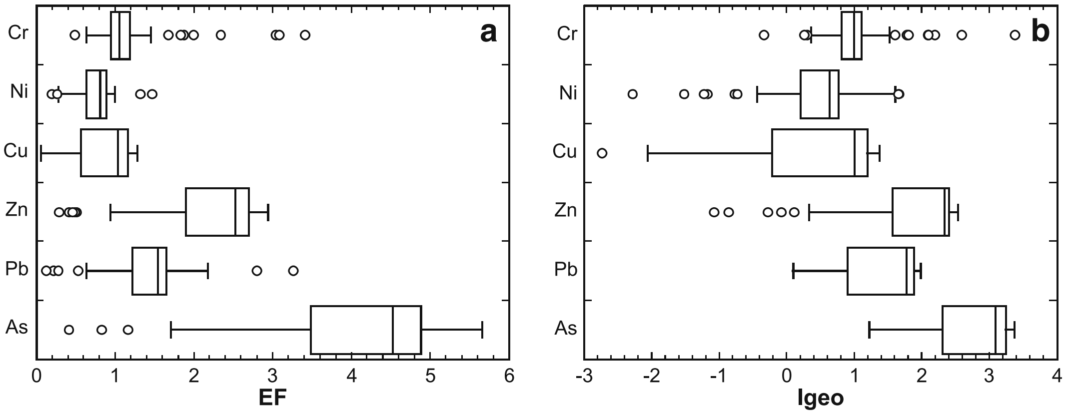

Fig. 5 Plot shows EF (**a**) and I_{geo} (**b**) values for As, Pb, Zn, Cu, Ni, and Cr in bottom sediments of Lake Shinji

Geoaccumulation index

In order to characterize the level of pollution in the sediments, geoaccumulation index (I_{geo}) values were calculated using the procedure (Müller 1969):

$$I_{\mathrm{geo}} = \log_2 \left[C_{\mathrm{n}} / 1.5 B_{\mathrm{n}} \right]$$

where C_{n} is the measured concentration of the element n and B_{n} is the geochemical background value of element n in average crust (Wedepohl 1995). The 1.5 factor is introduced to include possible variations of the background values due to lithogenic effects. The following classification is given for I_{geo} (Müller 1969): <0 = practically unpolluted, 0–1 = unpolluted to moderately polluted, 1–2 = moderately polluted, 2–3 = moderately to strongly polluted, 3–4 = strongly polluted, 4–5 = strongly to extremely polluted, and >5 = extremely polluted. According to this classification, the surficial sediments from Shinji can be categorized as moderately polluted with Pb and Zn and moderately to strongly polluted with As (Fig. 5b).

The I_{geo} values for As ranged from 1.2 to 3.4, corresponding to the moderately to highly polluted class. However, Cu and Ni exhibit averaged I_{geo} values (0.4 for each) corresponding to an uncontaminated situation. Lead and Zn can be considered as moderate pollutants ($1 <$ average $I_{geo} < 2$ for both traces) in the study area. The I_{geo} values (average, 1.1) determined for Cr in the lake sediments also indicate moderate enrichment. Overall, I_{geo} shows the general tendency already proven by the EF and PLI and that the sediments in Lake Shinji are considerably polluted with respect to As; moderately polluted with Pb, Zn, and Cr; and unpolluted to moderately polluted with Cu and Ni.

Sources of trace elements in the sediments

The results of this study show that As, Pb, Zn, Cu, and Cr concentrations in the Shinji sediments are greater than those of the upper continental crust (Table 3). The elevated EF values (Fig. 5a) suggest human impact in the lake sediments. The previous study conducted by Ishiga et al. (2000) also shows that trace element abundances in this lake have been disturbed by human activities and soil erosion. The sediment samples in the studied lake are also significantly enriched in As compared with Japanese granitoids (4 ppm As; n = 310; Terashima and Ishihara 1986), representatives of which occupy a large proportion of the Hii River catchment. Kojima et al. (2003) reported that near the sediment–water interface and under reducing conditions (produced by abundant organic matter), As was released from sediments to the pore water in Lake Biwa, Japan. Oxygen concentrations in Shinji sediments at water depths >3 m decrease to 0 mg/l within only 0.5–3 mm from the sediment–water interface, even when the overlying water is saturated with O_2 (Yamamuro and Kanai 2005). The high As concentrations in the lake sediments here are thus more likely the result of the burial of organic mud deposited under anoxic conditions. Moreover, significant positive correlations exist between As and Fe_2O_3 ($r^2 = 0.85$; $p < 0.0001$; $n = 51$) and TS ($r^2 = 0.71$; $p < 0.0001$; $n = 51$) in the surface samples, also suggesting an association with authigenic Fe oxide and sulfide coatings in the sediments.

Sediments at Shinji have Pb and Zn concentrations greater than those in Lake Nakaumi and the River Ohashi (Table 3). The enrichment factor values were also about 3 for these metals. The occurrence of Pb in <180 μm fractions of stream sediments from the Kando (average 17 ppm; Ortiz and Roser 2006) and Hii Rivers, also in Shimane, has been attributed to natural origin from soil leaching. The greater concentrations of Pb also likely reflect the fine-grained nature of the sediment prevalent in the study areas, as well as seasonal rain falls in the hinterland that produce increased suspended sediment load (Ruiz-Fernández et al. 2003). Furthermore, post-depositional diagenetic remobilization can influence heavy metal migration toward the sediment–water interface and scavenging onto organic matter or Fe oxy-hydroxides (Ruiz-Fernández et al. 2003). Tessier et al. (1994), Tribovillard et al. (1994), and Singh et al. (2005) observed that Cu, Ni, and Zn have strong affinity with organic matter, Fe oxides, and clay minerals, and may be fixed in sediments as authigenic sulfide minerals. The EF values for Cu, Ni, and Cr in the sediments were low, and therefore, the concentrations of these metals seem to be controlled by parent rock composition. The high values of Cr in some sampling sites were primarily the results of anthropogenic activities. As there are no major industries in the catchments of the lake and no known point sources for metal enrichment in the sediments, the metal abundances observed are likely housed in the sediment matrix (e.g., weathering of bedrock), with additional modifications depending on the redox conditions of the sediments, enrichment in organic matter, anthropogenic sources (e.g., road runoff), and surface soil erosion.

Correlation analysis was performed on elemental concentrations to assess possible similar sources of the elements. The possible sources of elements with positive correlations were considered to be similar. Relationships among the geochemical data show that metallic elements are strongly correlated with total Fe (Table 4), suggesting that Fe_2O_3 may exert a major role in controlling the metal concentrations in the Shinji and Ohashi river sediments, as discussed by Singh et al. (2005) for river sediments in India. The moderate ($r \geq 0.50$) to high correlation ($r \geq 0.70$) between the elements (As, Pb, Zn, Cu, and Fe_2O_3) and P_2O_5 suggest that nutrients transported to this lake contributed, to some extent, to the enrichment of metals in the bottom sediments (Zhang et al. 2007). The strong positive correlations of As, Pb, Zn, Cu, and Fe_2O_3 with TS in Lake Shinji and Pb, Zn, Cu, Ni, Cr, V, TiO_2, and Fe_2O_3 with TS in River Ohashi indicate that their concentrations may be related to pyritization in general terms (Ishiga et al. 2000). The strong positive correlation matrices of a suite of metals (Ni and Cr in Shinji; As, Pb, Zn, Cu, Ni, and Cr in Ohashi) with V suggest the possible formation of complexes with organic matter. This is consistent with the study conducted by Tribovillard et al. (1994) of sediments in the UK. Titanium, a detrital indicator, was also significantly correlated with Ni, Cr, and V in the Shinji and As, Pb, Zn, Cu, Ni, Cr, and V in the Ohashi river sediments, suggesting that they have a detrital origin. Sr, MnO, and CaO have negative or weak relationships in both areas, indicating different behaviors of these elements in the sediments. Significant associations between Sr and CaO were observed in the study areas, and these are most likely related to their similar geochemical behavior and association with shell material. Inter-relationships between As, Pb, Zn, Cu, Ni, and Cr (except Ni and Cr in Shinji) show that all are significantly correlated with each other, indicating a common or a similar geochemical behavior or origin.

Conclusions

The results show that the water masses of Shinji Lagoon were slightly stratified with respect to the measured physicochemical properties (EC, salinity, chlorophyll-a, turbidity, and DO). However, more detailed monitoring is required to characterize the water qualities in the study area. Concentrations of As, Pb, Zn, Cu, Ni, and Cr in the Shinji sediments were greater than those in the Ohashi River sediments. The spatial distribution of metals in the lake sediments indicates that minor anthropogenic contribution has occurred in the case of As, Pb, and Zn, especially in the southwest and central parts of Shinji and gradually decreasing toward the shallower parts of the lagoon. The calculated results of EF, PLI, and I_{geo} of heavy metals reveal that Shinji sediments are moderately contaminated with respect to Pb and Zn and slightly contaminated with Cr, whereas As enrichment is significant. These elevated concentrations are seemingly related to the very fine-grained nature of the sediments, reducing bottom conditions produced by abundant organic matter, anthropogenic sources, and surface soil erosion from the hinterland. The correlations of the trace metals with iron suggest their adsorption onto Fe (oxy)hydroxides during diagenesis, whereas correlations with sulfur indicate precipitation of sulfide phases in both Shinji and Ohashi sediments. Enrichment of metal concentrations suggests that regular monitoring may be desirable, even where no point sources of metal pollution exist.

Acknowledgements We thank Professor Yoshihiro Sawada for access to the XRF facilities; Dr. Hiroyuki Takata, Dr. Kengo Kurata, Keiko Yamaguchi, Hiroki Ogusa, Hajime Yanagitani, and Kosei Noda for their help with sampling; Dr. Edwin Ortiz for his help with Fig. 1; and

Daham Taranga Jayawardana for his assistance with Fig. 4. This work was carried out under the Priority Research Project on Estuarine and Coastal Lagoon Environment, Shimane University, Japan.

References

Ahmed, F., Bibi, M. H., Monsur, M. H., & Ishiga, H. (2005). Present environment and historic changes from the record of lake sediments, Dhaka City, Bangladesh. *Environmental Geology, 48*(1), 25–36. doi:10.1007/s00254-005-1248-8.

Ahmed, F., Bibi, M. H., Seto, K., Ishiga, H., Fukushima, T., & Roser, B. P. (2009). Abundances, distribution and sources of trace metals in Nakaumi-Honjo coastal lagoon sediments, Japan. *Environmental Monitoring and Assessment* (in press). doi:10.1007/s10661-009-1065-8.

Bibi, M. H., Ahmed, F., & Ishiga, H. (2007). Assessment of metal concentrations in lake sediments of southwest Japan based on sediment quality guidelines. *Environmental Geology, 52*(4), 625–639. doi:10.1007/s00254-006-0492-x.

EBGMSP (Editorial Board of Geological Map of Shimane Prefecture) (1997). *Geological map of Shimane prefecture at 1:200,000*. Tokyo: Naigai-Chizu.

Esen, E., Kucuksezgin, F., & Uluturhan, E. (2010). Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. *Environmental Monitoring and Assessment, 160*(1–4), 257–266. doi:10.1007/s10661-008-0692-9.

Ichikawa, T., Aizaki, M., & Takeshita, M. (2007). Numerical study on amelioration of water quality in Lakes Shinji and Nakaumi: A coastal brackish lagoon system. *Limnology, 8*, 281–294. doi:10.1007/s10201-007-0222-4.

Ishiga, H., Nakamura, T., Sampei, Y., Tokuoka, T., & Takayasu, K. (2000). Geochemical record of the Holocene Jomon transgression and human activity in coastal lagoon sediments of the San'in district, SW Japan. *Global and Planetary Change, 25*, 223–237. doi:10.1016/S0921-8181(00)00005-9.

Kamiya, H., Ishitobi, Y., Inoue, T., Nakamura, Y., & Yamamuro, M. (1996). Origin of nutrients accumulated in the bottom water of Lake Shinji in summer. *Japanese Journal of Limnology, 57*, 313–326.

Kojima, S., Saito, T., Takada, J., Furukawa, M., Oda, H., Nakamura, T., et al. (2003). Neutron activation analysis of trace elements at sediment–water interface in the Biwa Lake, Japan. *Journal of Radioanalytical and Nuclear Chemistry, 255*(1), 119–123. doi:10.1023/A:1022292100994.

Liaghati, T., Preda, M., & Cox, M. (2003). Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. *Environment International, 29*, 935–948. doi:10.1016/S0160-4120(03)00060-6.

Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geological Journal, 2*, 108–118.

NRC (National Research Council) (1989). *Contaminated marine sediments: Assessment and remediation* (p. 496). Washington, DC: NRC, National Academy of Sciences, National Academy Press.

Ogasawara, M. (1987). Trace element analysis of rock samples by X-ray fluorescence spectrometry, using Rh anode tube. *Bulletin of the Geological Survey of Japan, 38*(2), 57–68.

Ortiz, E., & Roser, B. P. (2006). Major and trace element provenance signatures in stream sediments from the Kando River, San'in district, southwest Japan. *Island Arc, 15*, 223–238. doi:10.1111/j.1440-1738.2006.00523.x.

Potts, P. J., Tindle, A. G., & Webb, P. C. (1992). *Geochemical reference material compositions* (p. 313). Caithness: Whittles.

Ruiz-Fernández, A. C., Hillaire-Marcel, C., Páez-Osuna, F., Ghaleb, B., & Soto-Jiménez, M. (2003). Historical trends of metal pollution recorded in the sediments of the Culiacan River Estuary, Northwestern Mexico. *Applied Geochemistry, 18*, 577–588. doi:10.1016/S0883-2927(02)00117-8.

Sampei, Y., Matsumoto, E., Tokuoka, T., & Inoue, D. (1997). Changes in accumulation rate of organic carbon during the last 8,000 years in sediments of Nakaumi Lagoon, Japan. *Marine Chemistry, 58*, 39–50. doi:10.1016/1016/S0304-4203(97)00024-8.

Singh, M., Sharma, M., & Tobschall, H. J. (2005). Weathering of the Ganga alluvial plain, northern India: Implications from fluvial geochemistry of the Gomati River. *Applied Geochemistry, 20*, 1–21. doi:10.1016/j.apgeochem.2004.07.005.

Soares, H. M. V. M., Boaventura, R. A. R., Machado, A. A. S. C., & Esteves da Silva, J. C. G. (1999). Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): Multivariate analysis of data. *Environmental Pollution, 105*, 311–323. doi:10.1016/S0269-7491(99)00048-2.

Taylor, S. R., & McLennan, S. M. (1985). *The continental crust: Its composition and evolution* (p. 312). Oxford: Blackwell.

Teraoka, Y., Matsuura, H., Makimoto, H., Yoshida, F., Kamitani, M., Hiroshima, T., et al. (1996). *Geological map of Japan 1:200,000*. Takahashi: Geological Survey of Japan.

Terashima, S., & Ishihara, S. (1986). Copper, lead, zinc, arsenic and sulfur of the Japanese granitoids (3): Green Tuff Belt of northeast Japan and outer zone of southwest Japan. *Bulletin of the Geological Survey of Japan, 37*(12), 605–624.

Tessier, A., Carignan, R., & Belzile, N. (1994). Processes occurring at the sediment–water interface: Emphasis on trace elements. In J. Buffle & R. R. DeVitre (Eds.), *Chemical and biological regulation of aquatic system* (pp. 137–173). Boca Raton: Lewis.

Tokuoka, T., Onishi, I., Takayasu, K., & Mitsunashi, T. (1990). Natural history and environmental changes of

Lakes Nakaumi and Shinji. *Memoirs of the Geological Society of Japan, 36*, 15–34.

Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoland Marine Research, 33*, 566–575.

Tribovillard, N. P., Desprairies, A., Verges, E. L., Bertrand, P., Moureau, N., Ramdani, A., et al. (1994). Geochemical study of organic-matter rich cycles from the Kimmeridge Clay Formation of Yorkshire (UK): Productivity versus anoxia. *Palaeogeography, Palaeoclimatology, Palaeoecology, 108*, 165–181. doi:10.1016/0031-0182(94)90028-0.

Wang, S., Cao, Z., Lan, D., Zheng, Z., & Li, G. (2008). Concentration distribution and assessment of several heavy metals in sediments of west-four Pearl River Estuary. *Environmental Geology, 55*, 963–975. doi:10.1007/s00254-007-1046-6.

Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica Cosmochimica Acta, 59*, 1217–1232.

Yamamuro, M. (2000). Chemical tracers of sediment organic matter origins in two coastal lagoons. *Journal of Marine Systems, 26*, 127–134. doi:10.1016/S0924-7963(00)00049-X.

Yamamuro, M., & Kanai, Y. (2005). A 200-year record of natural and anthropogenic changes in water quality from coastal lagoon sediments of Lake Shinji, Japan. *Chemical Geology, 218*, 51–61. doi:10.1016/j.chemgeo.2005.01.021.

Yamamuro, M., & Koike, I. (1998). Concentrations of nitrogen in sandy sediments of a eutrophic estuarine lagoon. *Hydrobiologia, 386*, 37–44. doi:10.1023/A:1003414028040.

Yamauchi, S., Mitsunashi, T., & Yamamoto, Y. (1980). Miocene of the Shimane Peninsula. In *Guide book for the geoexcursion* (p. 39). 87th Annual Meeting of the Geological Society of Japan.

Yang, H., & Rose, N. (2005). Trace element pollution records in some U.K. lake sediments, their history, influence factors and regional differences. *Environment International, 31*, 63–75. doi:10.1016/j.envint.2004.06.010.

Yoshimura, C., Omura, T., Furumai, H., & Tockner, K. (2005). Present state of rivers and streams in Japan. *River Research & Applications, 21*, 93–112. doi:10.1002 rra.835.

Zhang, M., Xu, J., & Xie, P. (2007). Metals in surface sediments of large shallow eutrophic lake Chaohu, China. *Bulletin of Environmental Contamination and Toxicology, 79*, 242–245. doi:10.1007/s00128-007-9191-x.