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Geochemical records in Holocene lake sediments of northern China: Implication for natural and anthropogenic inputs

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ABSTRACT

Daihai Lake is located in a hydrologically closed basin within the transitional zone of the East Asian monsoon, which has experienced significant lake-level fluctuations. The sedimentary sequence of a 12.08 m core was analyzed for mobile (Ca, Mg, and Sr) and immobile elements (Al and Fe) and trace metals (e.g., Co, Ni, Cu, Zn, and Pb) in order to study the changes of natural chemical compositions and the potential influences of the historical mining and use of metals during the Holocene period. Climate changes have a significant influence on the concentrations of mobile elements in the Holocene lake sediment; high concentrations occurred during the times with high lake level, resulting from enhanced catchment weathering due to strong monsoon effects. Different from these mobile elements, the variation of immobile elements and trace metals in Daihai Lake sediment shows clear anthropogenic impact of the mining and use of metals in the last several millenniums. A gradual increase in the concentrations and fluxes of metals from ~5000 cal. a B.P. is correlated well with the emergence of Chinese civilization. The concentrations and fluxes of these metals and immobile elements in the sediments increased rapidly between 2100 and 1250 cal. a B.P., indicating the extensive use of metals during the Warring States Period (475–221 B.C.), and the early Han Dynasty (206 B.C.–220 A.D.). Further increase of trace metals, such as Cu, Ni, Co, and Pb, after the Medieval Warm Period (1200–800 a B.P.) likely reflects the increased metal emissions associated with extensive mining and utilization activities. Similar patterns of sedimentary metals between Daihai Lake in northern China and Liangzhi Lake in central China further indicate significant environmental impacts of the mining and utilization of metals in the progress of Chinese civilization in the past several thousand years.

1. Introduction

Anthropogenic activity has significant environmental impact on the whole ecosystem, including greenhouse gases (e.g., CO_2, CH_4), organic pollutants, and potentially harmful metals. Metals are released into the atmosphere in large quantities during their mining and use by humans, and are preferentially transported, accumulated and buried within fine-grained sediments (Boutran et al., 1994; Weiss et al., 1999; Van de Velde et al., 2005). Therefore, besides reconstructing the variability of the natural climate, sedimentary records have also been used to evaluate the rate of historical influx of metals and other pollutants in the past (Howard et al., 2000; Van de Velde et al., 2005; Han et al., 2007). In particular, the records of past depositions of metals from ice, lake sediments and peat deposits were related to the progress of human civilizations (Hong et al., 1994; Shotyk et al., 1998; Hammarlund et al., 2008). For example, a two thousand year record of lead concentration from Greenland ice was regarded as evidence of Greek and Roman civilizations (Hong et al., 1994).

China has a long history of mining and utilization of metals (e.g., Ma, 1986; Chen and Yang, 1997; Wei, 2007). However, little is known about the history of the inputs of metals into the environment and human impact along with the progress of Chinese civilization. The history of atmospheric lead pollution in Europe has

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been constructed by studying lead concentrations and lead isotopic ratios in lake sediments and peat deposits (e.g., Renberg et al., 1994, 2000; Shotyk et al., 1998). Recently, a 7000-year record on the utilization of metals in ancient China was reconstructed by metal concentrations and lead isotopes of a sediment core of about 268 cm long from Liangzhi Lake in central China (Lee et al., 2008). A 2000-year record of copper pollution in South China Sea derived from seabird excrement was used to indicate for copper production and civilization of China (Yan et al., 2010). To better estimate the regional-scale environmental impacts of Chinese civilization, more high-resolution records are crucial. This study presents a Holocene record of elemental deposition from Daihai Lake in north China, and assesses the temporal and spatial influence of anthropogenic activities on the concentrations of metals, and the processes affecting their changes. Comparisons with the results obtained in Liangzhi Lake in central China are also conducted in order to evaluate the regional impacts of historical metal mining and utilization.

2. Study area, sampling and analyses

Daihai Lake is located at 40°28′–40°39′N, 112°32′–112°48′E, with a drainage area of 2289 km^2 (Fig. 1A). As a hydrologically closed lake, Daihai Lake is long, steep-sided, and flat-bottomed. It is a brackish water lake, covering an area of 133.46 km^2 and with an average water depth of 14 m. The water and sediment supplies to the lake are mainly from the Gongba and Wuhao Rivers in the west, and the Muhua River in the east. The mean annual water discharge is 0.11 km^3 (Wang et al., 1990). On the basis of the lake terrace outcrops, mainly at western and eastern parts of the basin, the lake level during the mid-Holocene was 40 m higher relative to that of the modern days (Fig. 2), associated closely with the strong East Asian monsoon (Wang et al., 1990; Sun et al., 2009) (Fig. 1A). Archean metamorphosed igneous rocks (gneiss) and basalt are the two prevalent lithologies cropping out in the catchment area (Fig. 1). The former prevails in the northwestern and southwestern alpine chains, and the latter outcrops in the

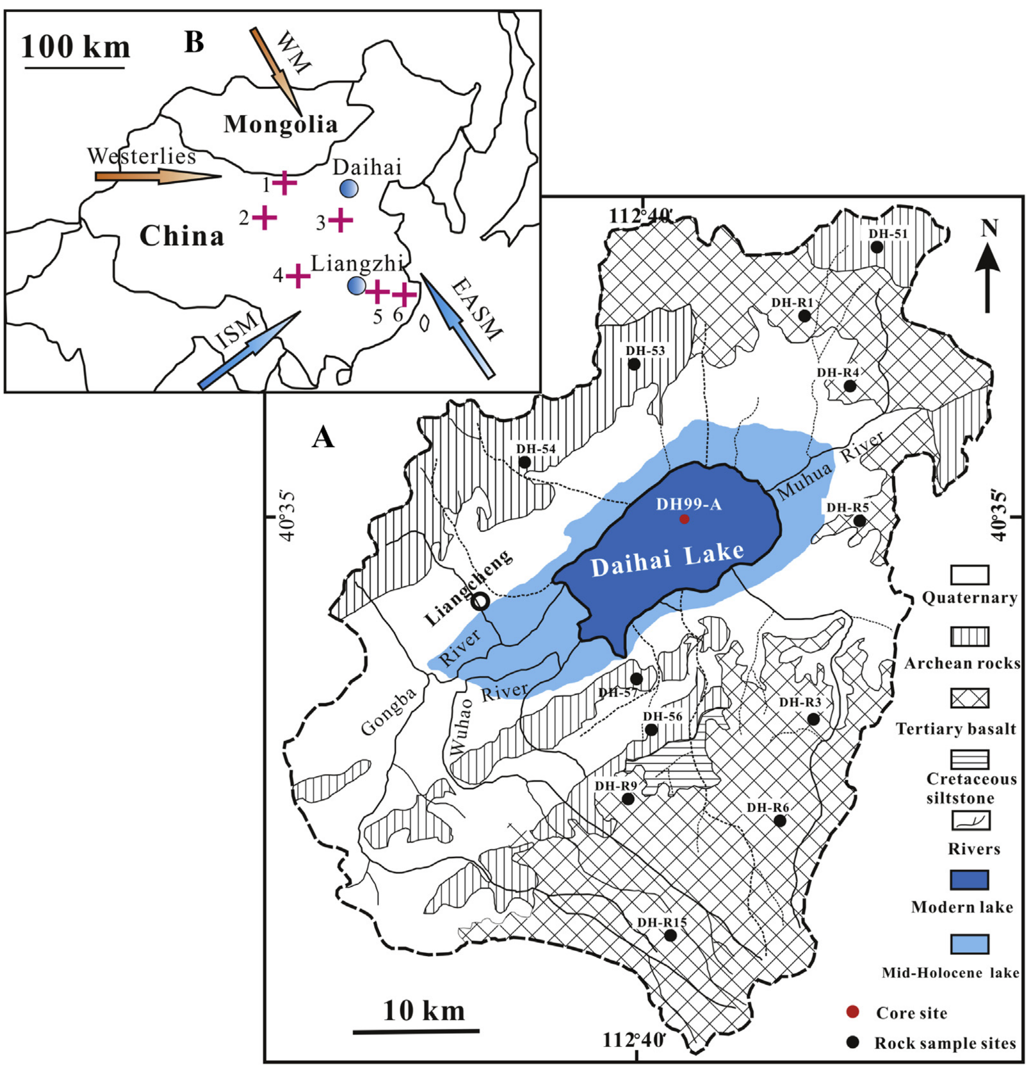

Fig. 1. (A) Geological map of Daihai Lake showing lithological units, the modern and mid-Holocene lake areas, and major rivers feeding the lake (modified after Jin et al., 2006b). The data of the lake areas are from Wang et al. (1990). The sampling sites for core sediment and bedrock are shown. The Daihai Lake catchment boundary is shown as dashed lines. (B) Locations of Daihai and Liangzhi Lakes and modern climate system affecting the Mainland China, i.e. Westerlies, ISM (Indian summer monsoon), EASM (East Asian summer monsoon), and WM (winter monsoon). Also shown are six important archaeological sites of metallic ore deposits (cross with number) in northern and central China that had been exploited during the Bronze Age (Ma, 1986; Chen and Yang, 1997; Wei, 2007). 1. Linxidajing, Inner Mongolia; 2. Zhaobi Mountain, Ningxia; 3. Zhongtiao Mountain, Shanxi; 4. West Qinling Mountain, Shaanxi and Gansu; 5. Tonglu Mountain, Hubei; 6. Tongling and Nanling, Anhui.

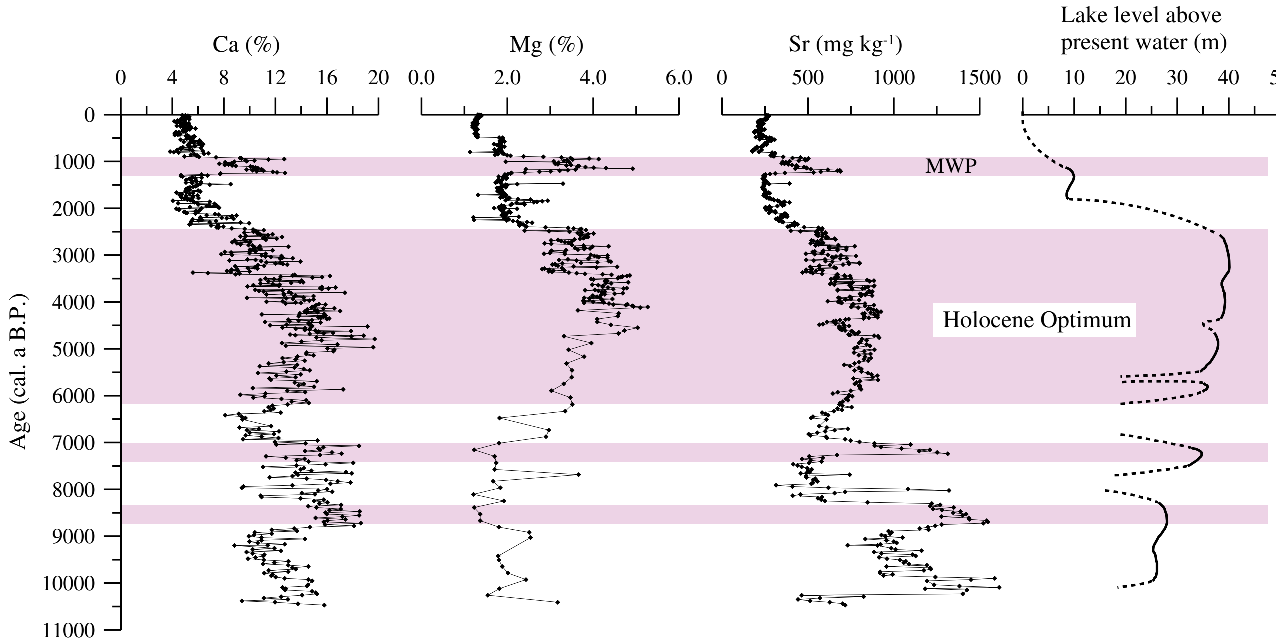

Fig. 2. Vertical profiles of mobile elements (Ca, Mg, and Sr) in sediments of Daihai Lake. Also shown reconstructed lake level from Sun et al. (2009), whose chronology was established by considered reservoir effect (Peng et al., 2005) using our improved age model. Shading indicates relatively high lake level, correlated with high concentrations of mobile elements, with an exception of Mg concentrations in early Holocene.

northern and southern hilly and alpine areas (Jin et al., 2006b). Half of the catchment is overlain by the Quaternary to recent alluvial and lacustrine sediments, mainly surrounding the lake and major rivers.

Due to its huge water body in the transitional zone of monsoon and the arid areas of northern China, Daihai Lake has great ecological and economical values, today and in the past. Ancient people settled around the lake about 4.8–4.3 ka, and developed a so-called "Laohushan Culture" (Fang and Sun, 1998; IMICRA, 2000) as one of the important components of the ancient Chinese civilizations. However, the lake gradually shrank since the late Holocene (Wang et al., 1990; Sun et al., 2009). The present water in Daihai Lake is low in both nutrients and toxic pollutants due to its relative remoteness. Compared to lakes in the populated areas such as the lower reaches of the Yangtze River, Daihai Lake has been relatively less influenced from the discharges of local wastewater in the last few decades. Therefore, it is an ideal site to study hydrological changes and the impact of past human activities at a regional scale on an enclosed aquatic ecosystem.

The climate of Daihai Lake in summer is influenced by the East Asian summer monsoon, resulting in most rainfall from June to September. In winter, the climate is controlled by the Siberian–Mongolian High and the Westerlies. Annual average air temperature (1959–1999) is ~3.5 °C, and the mean annual precipitation is 400 mm. However, the evapotranspiration in this region reaches 1938 mm a^{-1}.

A 12.08 m long sediment core (DH99-A) was collected below a water depth of 15.50 m in the center (the deepest part) of Daihai Lake in August 1999 using a piston coring device. The diameter of the core was 6.9 cm. The sediment core, with a recovery rate over 95%, contains irregularly laminated, gray–black silty clay whose carbonate contents varying from 8% to 49% (Jin et al., 2006a). A calendar age of the core dating back to 10,500 years was obtained by six accelerator mass spectrometry (AMS) ^{14}C (Jin et al., 2006a) and two Thermal Ionization Mass Spectrometry U–Th dating results (Sun et al., 2001).

Core DH99-A was sliced into 597 samples at 2-cm intervals. All sediment samples were oven dried at 60 °C for 24 h, and subsequently ground to fine particles less than 38 μm. All samples were analyzed for Sr concentrations by a VP–320 X-ray fluorescence (XRF) spectrometry and Ca concentrations by gram titration with 1 N HCl. The error was less than 1 ppm for Sr and 0.2% for Ca. Total 394 sediment (one for every 5 samples below 7.0 m) and 12 rock (five gneiss and seven basalt collected within the catchment, Fig. 1A) samples were digested using the strong acid digestion method followed the detailed procedures described by Ip et al. (2007). The concentrations of major and trace elements were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES; Perkin–Elmer Optima 3300DV) at the Hong Kong Polytechnic University. Reagent blanks, replicates, and standard reference material (NIST SRM 1646a Estuarine Sediment) were used as the QA/QC protocols during the analysis. The precision and bias assessed by the reagent blanks and replicate samples were <5% of the mean analytical concentrations for all of the elements. The recovery rates in the standard reference material (NIST SRM 1646a) for all of the measured elements were around 80–105%.

3. Results

3.1. Variations in mobile elements in the sediment profile

The down-core distributions of mobile elements, including Ca, Mg, and Sr, in the core DH99-A are shown in Fig. 2. The concentrations of Sr have a large range, from 174 to 2227 mg kg^{-1}, whereas Ca and Mg range from 3.8% to 19.7% and 1.1% to 5.3%, respectively. The variations of these elements in the sediment profile are high, but they correlate very well with a similar pattern, especially for Sr and Ca. The high Ca concentrations are observed at early Holocene, Holocene Optimum, Medieval Warm Period (MWP, 1.2 to 0.9 cal. ka B.P.) and to decrease gradually toward modern times. The pattern of Mg and Sr since the Holocene Optimum is similar to that of Ca. However, during the early Holocene, the concentrations of Sr vary significantly, but the concentrations of Mg show generally low values with less variation (Fig. 2).

3.2. Variations in immobile and metal elements in the sediment profile

Fig. 3 shows the down-core distribution of trace metals and immobile elements, including Al, Ni, Fe, Zn, Co, Pb, and Cu, in the DH99-A sediment core. In general, the variations of these trace metals demonstrate an increasing trend toward the surface with a similar pattern (Fig. 3), suggesting a highly significant relationship among them. Before 5.0 cal. ka B.P., the concentrations of these metals in the sediments are relatively low and constant with the average values of 22.5, 58.9, 9.4, 12.6, and 31.0 mg kg^{-1} for Ni, Zn, Co, Pb, and Cu, respectively (Table 1), with lowest values at about 5.0 cal. ka B.P. From about 5.0 to 1.2 cal. ka B.P., these elements show a gradual increase in concentrations in bulk sediments. During the MWP, a rapid decrease in concentrations of elements, such as Al, Ni, Fe, Zn, and Co, is observed in the sediments. Subsequently, the concentrations of these metals increased, and an apparent enrichment is observed for Zn and Cu (up to 118 and 84 mg kg^{-1}, respectively). Toward the top, the concentrations of Fe, Ni, and Zn remain almost constant, whereas both Cu and Pb show decreasing trends.

bringing to the lake by river runoff and that the concentrations of Ca, Sr, and to some extent Mg in the Daihai Lake sediments are closely related to the input of these mobile elements. A detailed geochemical investigation indicated that there were high concentrations of Ca, Mg and Sr in the sediment at greater water depth, resulting from increased authigenic carbonate precipitation and sediment focusing (Jin et al., 2006b). A record of Holocene weathering history of Daihai Lake showed that the high input of dissolved Ca and Sr to the lake reflected an increase in climate-induced weathering under warm and humid conditions, because much of the Ca and Sr is held in easily weathered feldspar in both basalt and gneiss within the catchment (Jin et al., 2006a). Therefore, the accumulation of these mobile elements in the sediments is associated with the strength of catchment weathering, lake level and water depth and, in turn, the amount of rainfall over the basin. As the correlation between the concentrations of mobile elements and the reconstructed lake level, high-stands correspond to high concentrations of both Ca and Sr in the sediments (Fig. 2). This correlation further supports the control of the amount of rainfall on the accumulation of authigenic carbonates in the sediments. For the concentrations of Mg, its variation is same as that of Ca and Sr since 5.0 cal. ka B.P., whereas high-stands correspond to low Mg concentrations before the Holocene Optimum. This might be attributed to limited aragonite precipitation from lake water during the early Holocene. As a consequence of the high-stand conditions during the Holocene Optimum, through enhanced catchment weathering, the concentrations of all mobile elements are high in the sediment (Fig. 2). Therefore, the composition of mobile elements in the sediments reflects the accumulation of authigenic carbonates.

Table 1
Concentrations (mg kg^{-1}) and fluxes (mg m^{-2} a^{-1}) of immobile elements and metals in sediments of Daihai Lake

	Time	Al	Fe	Co	Cu	Ni	Pb	Zn
Concentration	0–50 a B.P.	57,893 ± 6720	36,248 ± 1055	16.9 ± 1.1	54.4 ± 3.3	43.3 ± 1.8	18.4 ± 1.3	106.4 ± 2.9
	0–500 a B.P.	59,675 ± 6674	36,300 ± 1327	16.8 ± 0.8	59.9 ± 8.9	42.7 ± 1.8	17.0 ± 1.9	105.7 ± 7.2
	1200–500 a B.P.	53,472 ± 7879	34,378 ± 4245	14.0 ± 1.9	42.2 ± 4.9	34.1 ± 4.5	18.0 ± 1.8	78.7 ± 9.1
	2060–1200 a B.P.	56,275 ± 4745	35,729 ± 1887	14.8 ± 0.9	44.3 ± 3.8	36.0 ± 2.4	18.2 ± 1.6	85.6 ± 7.8
	2500–2060 a B.P.	45,477 ± 4596	31,782 ± 1952	13.0 ± 0.9	40.4 ± 5.2	31.5 ± 2.1	17.3 ± 2.5	71.7 ± 6.9
	5000–2500 a B.P.	31,960 ± 6124	23,718 ± 4263	9.6 ± 2.0	30.9 ± 6.2	23.2 ± 4.3	13.2 ± 2.9	55.9 ± 10.2
	Before 5000 a B.P.	30,842 ± 4987	21,997 ± 2903	9.4 ± 1.3	31.0 ± 5.9	22.5 ± 3.4	12.6 ± 2.2	58.9 ± 9.6
Flux	0–50 a B.P.	36,226 ± 15,475	19,881 ± 5631	10.2 ± 3.0	35.9 ± 9.3	26.5 ± 6.7	9.7 ± 2.8	64.0 ± 18.5
	0–500 a B.P.	39,161 ± 10,245	20,709 ± 4245	10.5 ± 2.1	42.9 ± 11.2	27.2 ± 5.1	9.2 ± 3.2	68.7 ± 13.6
	1200–500 a B.P.	33,102 ± 7794	18,989 ± 4199	7.6 ± 1.9	24.8 ± 4.8	18.6 ± 4.5	10.2 ± 1.8	40.9 ± 9.0
	2060–1200 a B.P.	36,007 ± 4683	20,384 ± 1838	8.4 ± 0.9	26.8 ± 3.7	20.5 ± 2.3	10.5 ± 1.6	47.9 ± 7.8
	2500–2060 a B.P.	17,995 ± 3114	13,589 ± 1892	5.5 ± 0.9	18.7 ± 3.6	13.4 ± 2.1	8.3 ± 3.3	26.0 ± 3.2
	5000–2500 a B.P.	11,036 ± 5834	7883 ± 4048	3.1 ± 1.9	12.8 ± 6.1	7.3 ± 4.2	5.1 ± 2.7	17.1 ± 9.7
	Before 5000 a B.P.	4287 ± 2015	2687 ± 1187	1.2 ± 0.5	5.5 ± 2.3	2.8 ± 1.4	1.9 ± 0.9	8.5 ± 3.8

4. Discussion

4.1. The Holocene sediment sequence and mobile elements

Holocene sedimentation processes in Daihai Lake started with a lake-level rise, dated to 11 cal. ka B.P., due to the strengthened monsoon in this region (Fig. 2; Sun et al., 2009). This rise was followed by two sharp declines at *ca*. 8.4–7.5 and 7.0–6.1 cal. ka B.P., with a temporary lake expansion between two these low-stands. The changes of water depth reached ∼20 m on the basis of sediment terraces. A high lake stand occurred between 6.1 and 2.5 cal. ka BP, when lake level was ∼35–40 m higher than the present, and the lake water depth reached a maximum of ∼65 m. The large area of this high-stand was associated with the strong monsoon during the Holocene Optimum. Since *ca*. 2.5 cal. ka B.P., the lake level has shrunk gradually, with a relative high-stand during the MWP (Fig. 2).

As a hydrologically closed lake, Daihai Lake presently is alkaline and supersaturated with respect to carbonate minerals. The predominant authigenic carbonate mineral in modern and Holocene sediments is calcite, and some aragonite was formed in middle to late Holocene (Jin et al., 2006a). Thus, it appears that carbonate precipitation balances the amount of dissolved mobile elements

4.2. Enrichment and flux variations of immobile elements and metals in the sediment

The variation patterns of immobile elements and trace metals (Fig. 3) are distinct from those of mobile elements (Fig. 2), indicating different processes controlled respective variations in the Daihai Lake sediments. The positive correlations of Co ($r^2 = 0.920$), Fe ($r^2 = 0.931$), Ni ($r^2 = 0.902$), Cu ($r^2 = 0.701$) and Zn ($r^2 = 0.815$) with Al indicate that these immobile elements and trace metals have similar sources. To interpret the down-core variations in these silicate-associated metals and immobile elements, two evaluations were approached. Firstly, the concentrations of these elements were recalculated on carbonate-free basis (the data of carbonate concentration from Jin et al., 2004) in order to avoid the dilution effect of variable content of carbonates. As shown in Fig. 4, variations in the concentrations of these immobile elements and trace metals after carbonate-free calculation have same patterns as those

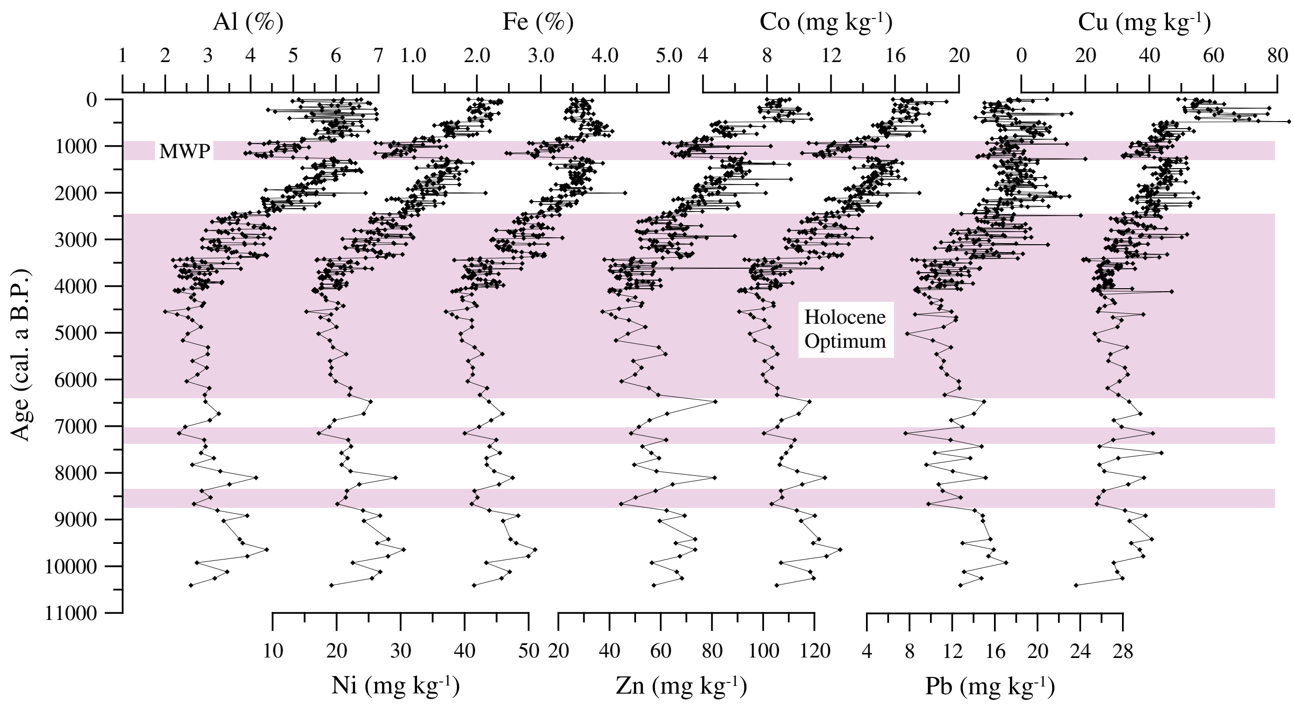

Fig. 3. Distribution of Al, Ni, Fe, Zn, Co, Pb, and Cu in Daihai Lake Holocene sediment.

of the bulk sediments, but are still different from those of mobile elements (Fig. 2). Thus, high concentrations of these immobile elements and trace metals after *ca.* 5.0 cal. ka B.P. might be not associated with decreased carbonate precipitation. Then, the variations of the carbonate-free concentrations of these immobile elements and trace metals were compared with grain size changes of silicate fraction. Similar to the mobile elements, the trend of the grain sizes is much different from that of these silicate-associated metals and immobile elements. For example, high and variable median size of the Daihai lake sediments between 7.9 and

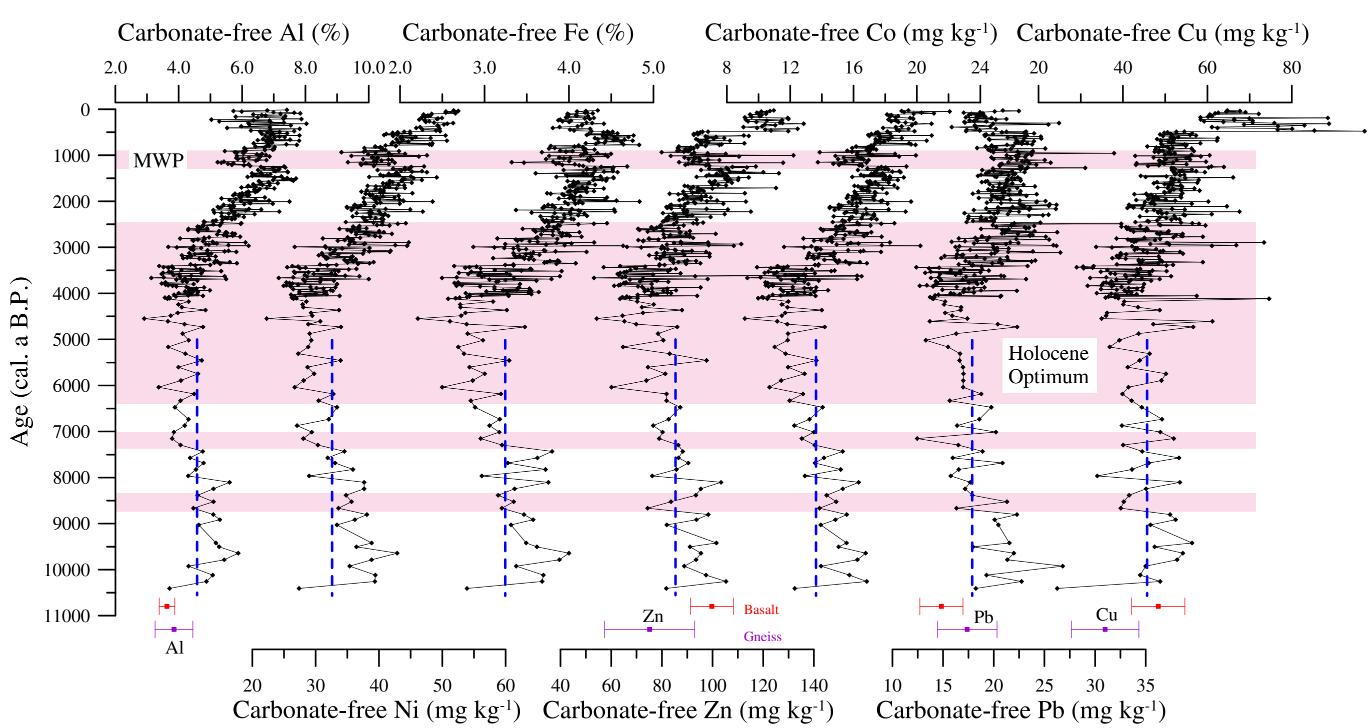

Fig. 4. Distribution of carbonate-free concentrations of Al, Ni, Fe, Zn, Co, Pb, and Cu in Daihai Lake Holocene sediment along with age. Dashed lines mark the average compositions of these elements in the sediments older than 5.0 cal. ka B.P.. The average compositions of Al, Zn, Pb, and Cu of major parent rocks (Neogene basalt; Archean gneiss) collected from the catchment are shown for referencing.

3.1 cal. ka B.P. is followed by decreased median size and silt fraction (Peng et al., 2005). However, the relatively low and constant concentrations of these silicate-associated metals and immobile elements in the sediments occurred before 5.0 cal. ka B.P., even when lake level and grain size fluctuated frequently (Peng et al., 2005; Sun et al., 2009), indicating that the control of hydrology on these trace metals was limited. On the other hand, the gradual increase in concentrations of these trace metals observed since about 5.0 cal. ka B.P. when the lake stayed at a high level, further indicates that the variation of these silicate-associated metals and immobile elements was also irrelevant with sediment focusing or catchment detrital input. Considering that the provenance of the Daihai Lake sediments has not changed over the Holocene, indicated by silty clay throughout the core (Jin et al., 2006a), the increase in these silicate-associated metals and immobile elements since 5.0 cal. ka B.P. is more related to anthropogenic inputs along with the development of the Chinese civilizations.

Along with the long history of the Chinese ancient civilizations, extensive mining and utilization of trace metals in China appeared *ca*. 2000 B.C., the Bronze Age (2000 B.C. to 200 A.D., Ma, 1986). Therefore, the low and generally constant carbonate-free concentrations of silicate-associated metals and immobile elements before *ca*. 5.0 cal. ka B.P. may represent the natural background from the parent bedrock within the catchment. This is supported by low concentrations of Al and trace metals (Cu, Zn, and Pb) in catchment bedrock (both gneiss and basalt, Table 2 and Fig. 4) that are close to the means of the sediments before *ca*. 5.0 cal. ka B.P. The decreased concentrations of trace metals and immobile elements in the bulk sediments to some extent from the early Holocene to *ca*. 5.0 cal. ka B.P. can be attributed to (1) a dilution of increased accumulation of authigenic carbonates and/or (2) a decreased long-distant transport of detritus during high-stands, the relatively low concentrations at both 8.5 and 7.1 cal. ka B.P. (Fig. 3).

Han et al., 2009). A 500-a record of atmospheric metal deposition from the Daihai Lake sediments was suggested to be related to historical industrial activities (Han et al., 2007). Therefore, variations in these silicate-associated metals and immobile elements in the sediment (Fig. 3) are believed to be closely tied to (1) dry/wet atmospheric fallout and/or (2) hydrological conditions. These trace metals might be introduced into the system via dry/wet atmospheric fallout (Han et al., 2009; Jin et al., 2010), originating from mining and uses of the trace metals in western to central China where Chinese ancient civilizations had been developed (Ma, 1986; Wei, 2007). Meanwhile, significant quantities of trace metals would initially settle on the soil surface mainly via atmospheric fallout. Runoff would remove and gather these trace metals from the soil surface to lake sediments.

As shown in Fig. 3, there is a noticeable decrease in the concentrations of these silicate-associated metals and immobile elements in the bulk sediments during the MWP. The decrease in concentrations of these elements can be related to a dilution of increased accumulation of authigenic carbonates and/or a decreased transport of detritus during the MWP, resulting from high concentrations of mobile elements (Fig. 2). During the MWP, the contents of carbonates of Daihai Lake sediment range from 18% to 32% (averaging 24%), resulting from a significant increase of chemical weathering under a warm and humid environment (Jin et al., 2002). Limited decrease in concentrations of these elements after carbonate-free calculation (Fig. 4) further supports this interpretation.

The patterns of various trace metals and immobile elements after the MWP are different to some extent. For example, Co and Ni increase gradually toward modern times, whereas Fe and Cu decrease after a rapid increase since the MWP. Meanwhile, Al, Pb and Zn stay at steady levels after an increase since the MWP. These differences possibly mark changes in mining practices and in the use of these trace metals, as indicators of past trace metal emission from later military and industrial periods.

Table 2
Concentrations of Al, Fe, Cu, Pb, and Zn of major bedrock within the Daihai Lake catchment

Rocks	Sample no	Al %	Fe %	Cu mg kg^{-1}	Pb mg kg^{-1}	Zn mg kg^{-1}
Gneiss	DH-51	4.16	3.05	44.10	13.63	84.10
	DH-53	4.08	2.45	22.50	16.09	99.70
	DH-54	4.53	2.25	36.30	18.68	75.60
	DH-56	3.43	1.59	37.70	16.96	60.50
	DH-57	3.05	1.53	38.30	21.51	56.00
	Average	3.85 ± 0.60	2.17 ± 0.63	35.78 ± 8.00	11.37 ± 2.94	75.18 ± 17.78
Basalt	DH-R1	3.35	4.25	41.90	10.73	91.90
	DH-R3	4.10	3.50	42.70	15.87	99.40
	DH-R4	3.67	4.26	57.10	15.81	115.60
	DH-R5	3.71	3.83	42.00	16.23	102.60
	DH-R6	3.45	3.94	48.90	13.66	103.10
	DH-R9	3.48	4.16	54.60	14.45	91.20
	DH-R15	3.64	4.13	51.30	17.06	94.40
	Average	3.63 ± 0.24	4.01 ± 0.28	48.36 ± 6.30	14.83 ± 2.13	99.74 ± 8.51

In ancient China (3000 B.C. to 200 A.D.), copper was alloyed with lead to make various bronze tools, weapons, and ritual vessels (Ma, 1986; Chen and Yang, 1997; Wei, 2007). There are many mining sites of metallic ore deposits that had been exploited during the Bronze Age (Fig. 1B), including Linxidajing, Zhaobi and Zhongtiao Mountains surrounding the study area (Ma, 1986; Chen and Yang, 1997; Wei, 2007). The gradual increase in the concentrations of these silicate-associated metals and immobile elements in the sediments since 5.0 cal. ka B.P. may indicate an increase in the mining and utilization of metals in China since the Bronze Age. Although there might be limited mining of trace metals around the Daihai Lake catchment, metals could enter the drainage system through atmospheric deposition along the Westeriles and the Asian monsoons, and be preserved in the sediment bed (Lee et al., 2008;

As a second approach, estimation of human influences can further be conducted through the enrichment relative to natural baseline concentrations. Elemental background values in the same core are best as references for the assessment of anthropogenic enrichment factors (EFs). As taken the average composition of older than 5.0 cal. ka B.P. sediments in Daihai Lake as background (Fig. 4), the EFs of these trace metals and immobile elements are higher than one (>1) after 3.5 cal. ka B.P., further indicating the input and accumulation of metal-bearing minerals. The increase in EFs toward the top can be attributed to increased mining and utilization of trace metals since the establishment of the first dynasty in China (the Xia Dynasty, 2100–1600 B.C.).

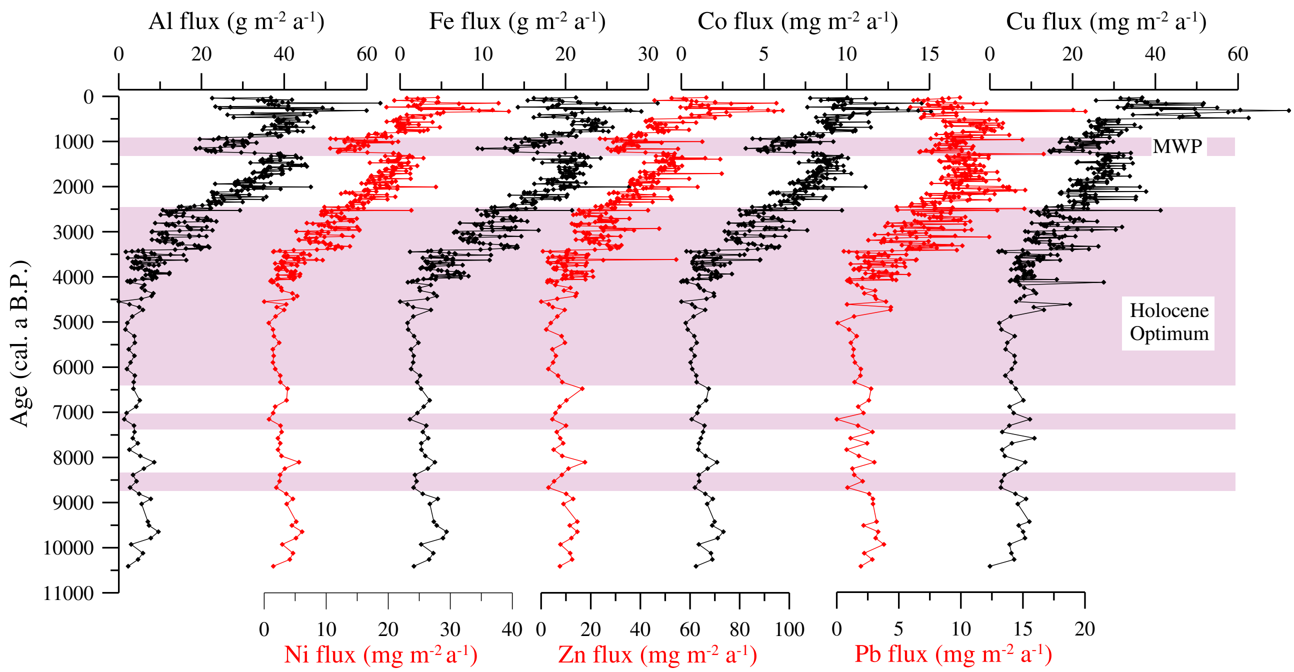

Fig. 5. Fluxes of Al, Ni, Fe, Zn, Co, Pb, and Cu over the background concentrations (the sediments before 5.0 cal. ka B.P. in the core DH99-A).

After subtracting the average compositions of older than 5.0 cal. ka B.P. Daihai Lake sediments as the background, the fluxes of excess trace metals were calculated by the concentrations multiplied by sedimentation rates as shown in Fig. 5. Average fluxes (mg m^{-2} a^{-1}) of trace metals to Daihai Lake before 5.0 cal. ka B.P. are low, 1.2 ± 0.5 for Co, 5.5 ± 2.3 for Cu, 2.8 ± 1.4 for Ni, 1.9 ± 0.9 for Pb, and 8.5 ± 3.8 for Zn, respectively (Table 1). Similar to the variations in their concentrations, the fluxes of these trace metals increase gradually since 5.0 cal. ka B.P., with a decrease during the MWP followed by a maximum (Fig. 5). The average fluxes of these trace metals are 4.5–9.6 times higher than those of the background. On average, 9.7 ± 2.8 and 35.9 ± 9.3 mg m^{-2} of excess Pb and Cu, respectively have been deposited annually in Daihai Lake since the last 50 years. The Pb flux is comparable to values reported in Europe from peat bogs for the period before the Industrial Revolution (4.5–15.5 mg m^{-2} a^{-1}), and to the Lake Qinghai sediments (12.2 ± 3.5 mg m^{-2} a^{-1}), both of which were thought to receive pollutants solely from atmospheric deposition (Weiss et al., 1999; Martínez et al., 2002; Jin et al., 2010). The Cu flux is similar to that of marsh surface sediments from Medway Estuary in UK (31.8 mg m^{-2} a^{-1}, Spencer et al., 2003) and from Long Island Sound in USA (~30 mg m^{-2} a^{-1}, Cochran et al., 1998).

4.3. Correlation of trace metals in the sediments between lakes

If trace metals entered the drainage system mainly through atmospheric deposition, there would be correlative records of trace metal variations associated with the Chinese civilization in wide geographic regions. Through comparison with the records of Cu, Pb, and Zn between Daihai Lake and Liangzhi Lake in central China (Lee et al., 2008), similar patterns of trace metal variation are observed (Fig. 6). In both lakes, the concentrations of Cu, Pb, and Zn increase

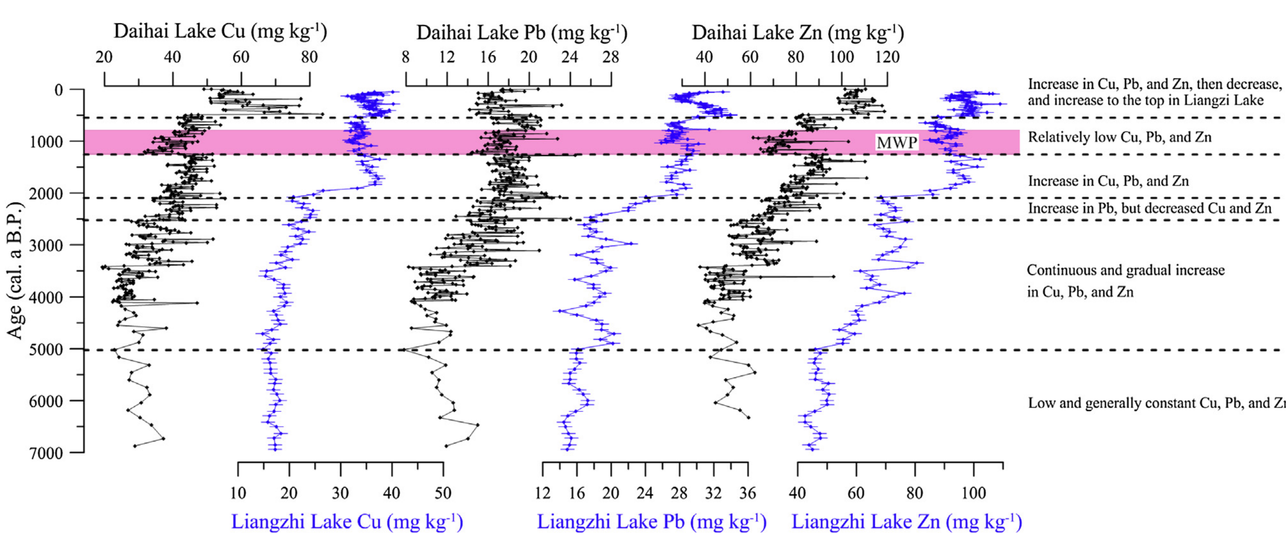

Fig. 6. Comparison of variations of trace metals (Cu, Pb, and Zn) in the sediments between Daihai Lake and Liangzhi Lake in the past 7000 years. Data for Liangzhi Lake are from Lee et al. (2008).

gradually from *ca*. 5.0 to 2.5 cal. ka B.P., indicating increased mining and use of bronze articles since the Xia Dynasty. The center of the Xia Dynasty was located at the areas between Daihai and Liangzhi Lakes, the modern Shanxi and Henan Provinces. The fluctuation during the period might reflect hydrological and/or depositional effects, possibly associated with the activities and strength of the East Asian summer monsoon. During the period of 2.5 to 2.06 cal. ka B.P., there is a rapid increase in the Pb concentrations (followed by a decrease in Daihai Lake), with decreased Cu and Zn in the sediments of both lakes. From 2.06 to *ca*. 1.2 cal. ka B.P., the concentrations of Cu, Pb, and Zn increase in the sediments, indicating an extensive use of these trace metals at that time.

Similar to decreased concentrations of Cu, Pb, and Zn in the Daihai Lake sediments during the MWP, the sediment records from Liangzhi Lake also show a decrease in the concentrations of Cu and Zn after a peak in 221 A.D. (Lee et al., 2008, Fig. 6). The decreased concentrations of these trace metals in Liangzhi Lake during the MWP are correlated to the end of the Bronze Age in China, when iron tools and vessels began to be used (Lee et al., 2008). Besides the end of the Bronze Age, the role of the dilution of sedimentary accumulation during the MWP may also be important in the decrease in concentrations of these trace metals, as indicated by the Daihai Lake sediments. The significant increase in the concentrations of Cu, Zn, and Pb took place in both lakes just after the MWP, related to social instability (increased peasant wars) across the country due to famine and adverse climatic conditions (Zhang et al., 2005; Lee et al., 2008). Unlike a decrease of Cu or a steady level of Pb and Zn in the Daihai Lake sediments toward the surface, there is a significant increase in the concentrations of Cu, Zn, and Pb in Liangzhi Lake (Fig. 6). The difference of the trace metals in the surface sediments may be attributed to World War II and postwar industrial development in central China. More high-resolution records from other lake and/or marine sediments are needed to test the hypothesis.

5. Conclusion

Lakes and their sediments have rapid response to the changes of source input and sedimentation processes associated with natural environment and anthropogenic activities. Using the accumulation of various elements as indicators, the Holocene record of the core sediments from Daihai Lake provides distinct remarks not only from the hydrological point of view, but also from the impact assessment of anthropogenic activities. Due to sensitivity to the East Asian summer monsoon, hydrological conditions have experienced dramatic fluctuation during the entire Holocene, resulting in significant variation of mobile elements associated with the strength of catchment weathering and water budget. In the context of the low background concentrations of various trace metals and immobile elements before *ca*. 5.0 cal. ka B.P., an increased accumulation of silicate-associated metals and immobile elements in the Daihai Lake sediments is attributed to the increased inputs of these trace metals from atmospheric deposition, mainly due to anthropogenic activities. Importantly, similar patterns in the concentrations of Cu, Zn, and Pb of the lake sediments from two lakes $\sim$1500 km apart (Daihai and Liangzhi Lakes) further indicate extensive impacts of mining and use of trace metals in ancient times along with the Chinese civilization.

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