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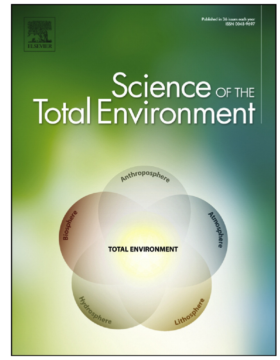

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Spatio-temporal variations of sedimentary metals in a large suburban lake in southwest China and the implications for anthropogenic processes

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ABSTRACT

Environment quality of suburban and urban lakes receives special attention due to their great impacted by human perturbations and important roles in ecosystem services. Herein, the spatio-temporal variations of 10 metal and metalloid elements in 13 sediment cores from a large suburban lake (Dianchi) were studied to explore the changes in sedimentary environment and pollution and their associations with human activities since the last century. Concentrations of each element were largely varied at spatial scales, but showed similar vertical trends among the profiles, suggesting comparable changes in sedimentary processes in each lake region. Cluster analysis showed two groups of elements: group I includes Al, Ti, Cu, Cr and Ni, and group II includes As, Cd, Hg, Pb and Zn. Temporally, concentrations of all elements were generally constant until the 1950s. Thereafter, group I elements along with the clay percentage started to decrease, indicating accelerated input of coarser soils due to strengthening human perturbation and changing land use. However, group II elements showed increasing values of concentrations, particularly the enrichment factors (EF=1.0-10.8), which peaked between mid-1990s and 2000, indicating continued pollutants input with watershed economic development. With the implementation of environment management measures, pollution was initially restrained or reduced in recent decades as indicated by the stable EFs and sedimentary fluxes of Cd, Hg, Pb and Zn and decreasing values of As. Spatially, the stocks of anthropogenic As, Cd, Hg, Pb and Zn were higher in the northern while lower in the southern lake area. This spatial difference was mainly due to the large input of industrial and domestic wastewaters in the northern compared to the area in the southern that receives runoff from agricultural and forested land. Overall, the spatio-temporal patterns in accumulation of metal and metalloid elements in the lake reliably reflected the impacts of watershed human activities.

Keywords: Lake Dianchi, metals and metalloids, sedimentary environment, pollution, spatio-temporal changes, human activities.

1. Introduction

Contamination of metals and metalloids (hereafter termed as “metals” for simplicity of exposition) is a severe global problem due to their toxicity, bioaccumulation/biomagnification in the food web, and negative effects to aquatic ecosystems and human health (Järup, 2003). Metals accumulated in the lake sediments can be either natural (e.g., weathering of rocks and soils) or anthropogenic (e.g., mining and smelting, chemical industry, agriculture, sewage and atmospheric deposition) (Landre et al., 2011; Li et al., 2019; Viers et al., 2009; Yang et al., 2014). Metals derived from lithogenic sources are closely associated with the watershed soil erosion capacity and runoff characteristics (Lin et al., 2018; Yu et al., 2019; Zafra et al., 2017), and that from anthropogenic sources are closely associated with the stages of economic development and spatial distribution of pollution sources (Bing et al., 2016; Landre et al., 2011; Li et al., 2019). Thus, metals accumulated in the sediments of a lake may vary over space and time. Studying the spatio-temporal variations of metal accumulations in lake sediments will be helpful to understand the causes of lake environmental evolution. Establishing the relationships of economic development, metal pollution and ecological degradation of a lake will provide a basis for the restoration and remediation (Gao et al., 2018; Wang et al., 2019).

For urban and suburban lakes, ecological deterioration and environmental pollution, such as eutrophication and trace metals pollution, have become more prominent compared to remote lakes due to intensive human perturbations (Cheng et al., 2015; Nowell et al., 2013; Yang et al., 2015), and thereby diminishing ecological functions of a lake especially the roles in industry, agriculture and drinking water supply (Wang et al., 2018b; Yang et al., 2014). A large proportion of natural and anthropogenic metals transported to the lake is accumulated in the sediments by sorption with the inorganic and/or organic particles (Buyang et al., 2019; Outridge et al., 2007). Most studies on sediment metals pollution in lakes in an urban area and across the rural-urban interface (e.g., Chalmers et al., 2007; Nowell et al., 2013; Yang et al., 2014; Yang et al., 2015; Zhang et al., 2017) have found a general decreasing trend in pollution levels and stocks of anthropogenic metals away from the urban core. Typically, metals pollution levels show significant relationships with the adjacent industry development and land use types (Belabed et al., 2017; Chalmers et al., 2007; Ma et al., 2016; Wang et al., 2019; Zhang et al., 2007; Zhang et al., 2016). With the rapid expansion of an urban area, a rural lake becomes a suburban and even an urban lake with time. However, these associated impacts of continuing urban expansion, modern agricultural and industrial developments on the spatial and temporal patterns of trace metals accumulation in such lakes remained largely unknown.

Dianchi is a large suburban lake near Kunming city, the capital of Yunnan Province in China (Fig. 1). Since the last century, rapid urban expansion and development of industrial and agricultural economy in the watershed and the associated wastewater discharge had resulted in a serious eco-environmental problem in and around the lake (Guo et al., 2017; Ma and Wang, 2015). The lake became mesotrophic in the early-1980s and increasingly eutrophic since the late-1980s (Wang et al., 2018c). Studies indicated that the eutrophication and spatio-temporal accumulation of phosphorus (P) in the sediments of Lake Dianchi were closely correlated to the anthropogenic disturbances in the watershed (e.g., Cao et al., 2016; Huang et al., 2014; Huang et al., 2018; Zhu et al., 2018). A few studies have reported sediment metals pollution in Dianchi Lake (e.g., Cheng et al., 2015; Wang et al., 2012; Wei and Wen, 2012; Yang et al., 2016; Yang et al., 2017; Zhang et al., 2014). Nevertheless, the surface sediments, mostly characterized by top 20 cm in previous studies, obtained by using a grab sampler, have low time resolution, and therefore cannot accurately reflect the current pollution levels and historical trends. Moreover, the sedimentary environment of Dianchi may have changed over the past decades because of the changes in the watershed coverages (Huang et al., 2014; Yu et al., 2019). Such variations potentially influence the sediment texture, which were not considered in previous metal pollution assessment studies (e.g., Cheng et al., 2015; Li et al., 2013; Zhang et al., 2014). Therefore, making reasons of varied metal concentrations in sediments in response to pollution or changes in detritus input were less effectively defined. Since the 21st century, the implementation of environmental control measures such as the operation of sewage treatment facilities, closure of 'highly polluting' industries and construction of wetlands surrounding the lake have restrained eutrophication (Huang et al., 2014; Meng, 2016; Wang et al., 2018c), but the effects on lake sediment quality with respect to trace metals pollution remain largely unknown.

In this study, the concentrations of potentially toxic trace metals (e.g., As, Cd, Cr, Cu, Hg, Ni, Pb and Zn), major lithogenic metals (Al and Ti) and grain size compositions were measured in 13 sediment cores of Lake Dianchi. The objectives are: (1) to assess the effect of strengthened human activities in the watershed on the sedimentary environmental changes of Dianchi over the last century, (2) to explore the temporal and spatial variations in concentrations of sediment trace metals, and (3) to quantify the trace metals pollution in recent sediments and to decipher their relationships with human activities.

2. Materials and methods

2.1. Study area

Dianchi (N24°40′-25°02′, E102°02′-102°47′) is the largest freshwater lake in the Yunnan-Guizhou Plateau in southwest China and the sixth largest freshwater lake in China. The lake is divided into two parts by an artificial dam (Fig. 1c): the northern part (Caohai) has a surface area of 7.5 km^2 and an average depth of 2.5 m, and the southern part (Waihai) has a surface area of 292 km^2 and an average depth of 4.4 m (Wang et al., 2018c). The watershed area of Dianchi is 2,920 km^2 (Wang et al., 2018c). The climate is characterized by subtropical southwest monsoon, with an annual mean temperature of 14.4°C and an average precipitation of 1,000 mm (Wang et al., 2018c). Dianchi is mainly fed by precipitation and runoff from rivers such as the Xinhe, Panlong and Baoxiang in the northern and Dongdahe, Chaihe, Dahe and Liangshi in the southern and eastern (Fig. 1b). The lake water has a residence time of approximately 2.7 years.

Historically, Dianchi watershed was dominated by the agricultural economy. Recent development of this area was started after the founding of new China in 1949. The population of Kunming city, the biggest city in the watershed, was increased from less than 0.8 million in the early 1950s to nearly 4.9 million in 2017, and the city's GDP was increased from 1.2×10^2 to 4.9×10^5 million Chinese yuan during the same period (Statistics Bureau of Kunming, 2018). The land use within Dianchi watershed is primarily forest, farmland and construction land (commercial, residential and industrial) (Fig. 1b), but has changed largely with the expansion of population and economic development (Fig. S1). During 1974-2009, forest land had decreased from around 40% of the watershed area to around 36%, farmland had declined from 45% to 32%, while the urban area had increased from 2.5% to 32% (Huang et al., 2014). Spatially, the northeastern part of the watershed was strongly modified to urban construction land from farmland represented by the expansion of Kunming city from 98 km^2 to ~330 km^2 (Huang et al., 2014). The wetlands surrounding the lake were reclaimed mainly for agricultural purposes during 1950s-1970s, leading to about 30 km^2 decline in Dianchi surface area, occurred mainly in the northern part of the lake (Wang et al., 2018c).

2.2. Sampling and laboratory analysis

Caohai was dredged in 1998. In contrast, the sedimentation in the main basin of Dianchi (Waihai) were rarely disturbed and remained continuous (Huang et al., 2018). Therefore, 13 short sediment cores (25-45 cm in length) were only collected from the Waihai part of Dianchi using an UWITEC gravity corer in 2015 (Fig. 1c). The cores, which had undisturbed sediment-water interfaces, were sectioned in the field into 1-cm thick slices, placed into polyethylene bags and refrigerated at 4°C until analysis.

In the laboratory, the sediment samples were freeze-dried and weighed to calculate the water content and dry density. The freeze-dried samples were ground in an agate mortar and digested by HCl-HNO_3-HF-$HClO_4$ for the analysis of metals (Lin et al., 2016). The concentrations of As, Cd, Cr, Cu, Ni and Pb were determined using ICP-MS (Agilent 7700x), and the concentrations of Al, Ti and Zn were determined using ICP-AES (Leeman Labs, Profile DV). Hg concentration was determined using Hg analyzer Hydra-C (Leeman Labs). Data quality was ensured by measuring blanks and standard reference materials (GBW07358; Chinese geological reference materials) after every tenth sample. The accuracy, expressed as a recovery of the reference material, was 92-106%. No contamination was detected in the laboratory or in the procedural blanks.

About 0.5 g freeze-dried samples were pre-treated with 5% H_2O_2 to remove organic matters, followed by 10% HCl to remove carbonates, and then the grain size analysis was done using a Malvern Mastersizer-2000. This instrument has an accuracy of ±1% on the Dv50 using the Malvern Quality Audit Standard. Mass specific low frequency magnetic susceptibility (χ_{lf}) of the sediment samples was measured at 0.47 kHz using a Bartington MS2 Meter. The organic carbon (OC) content was measured using a Euro 3000 elemental analyzer after samples were pre-treated with 1 mol L^{-1} of HCl to remove carbonates. Analyses of standard reference material, GSS-9 (lacustrine sediment, from National

Institute of Metrology of China), was within the certified ranges.

A master chronology was determined for core DC2 based on the gamma spectroscopy (^{210}Pb and ^{137}Cs) and CRS modeling (detailed in the Supporting Information). Sediment chronologies were not constructed for the other 12 cores, but a chronological marker was identified to correlate the records using an inflection point of magnetic susceptibility (χ_{lf}) which stated to decrease in the lower section of each core (Fig. S2), c.1950 as per the chronology of the dated core DC2.

2.3. Contamination assessment

Fine sediments (e.g., clay) generally contain elevated levels of lithogenic trace metals than that in coarse sediments, which are usually depleted in trace metals (Birch, 2017; Ontiveros-Cuadras et al., 2014). To compensate for the potential influence of varying sediment texture on trace metal concentrations and to evaluate anthropogenic vs. lithogenic contribution, the enrichment factor (EF) was calculated (Clark et al., 2014; Ontiveros-Cuadras et al., 2014).

$$EF = (M/X)_{sample} / (M/X)_{background} \quad (1)$$

Where M is the evaluated element, X is the reference element, and $(M/X)_{sample}$ and $(M/X)_{background}$ are the ratios of the evaluated and the reference elements in the target and background sediments, respectively. An EF close to 1 indicates that a metal is lithogenic in origin, while a ratio >1 implies an anthropogenic input (Viers et al., 2009).

In this study, Ti, a conservative lithogenic element (Wei and Wen, 2012), is used as a reference element in EF calculation. Previous studies have indicated that the use of sedimentary cores have the greatest advantage than the materials of global shale and crust, catchment soils and rocks for metal background determination of lake sediment (Birch, 2017; Chalmers et al., 2007; Ontiveros-Cuadras et al., 2014). The deeper sections of the sediment cores from Lake Dianchi should have deposited prior to the recent industrial period (since the 1950s) (section 3.2 for detailed description). Therefore, the metal concentrations in the deepest sediments of the cores could be used as a reference to evaluate the metal pollution during the industrial period though the values were not of geologic backgrounds. The pre-industrial background in different lake regions may vary due to the differences in geological settings in the sub-basin (Birch, 2017; Lin et al., 2018). Therefore, the deepest samples in each of the cores were used as a respective background.

Anthropogenic contribution of metals could be calculated using the following equation:

$$[M]_{anthropogenic} = [M]_{sample} – [X]_{sample} \times (M/X)_{background} \qquad (2)$$

Where $[M]_{anthropogenic}$ and $[M]_{sample}$ are the anthropogenic and total concentrations of metals in the evaluated samples, respectively.

The mass accumulation flux of anthropogenic metals in core DC2 was calculated by multiplying the mass accumulation rate and concentrations of anthropogenic metals.

$$[M]_{flux} = [M]_{anthropogenic} \times MAR \qquad (3)$$

Where $[M]_{flux}$ is the mass accumulation flux of anthropogenic metals, and the MAR is mass accumulation rate (g cm^{-2} y^{-1}) of dry bulk sediment.

The stocks of anthropogenic metals per unit area were calculated by multiplying concentrations of anthropogenic metals in the cores with the bulk density in each sediment layer (Bing et al., 2016; Clark et al., 2014). The anthropogenic metals in the undetermined layers were estimated by averaging the adjacent layers using interpolating method.

2.4. Statistical analysis

Pearson correlation analysis and hierarchical cluster analysis were performed to determine the relationships among the metals and grain sizes to explore the origin and geochemical behaviors of metals (Birch, 2017; Coxon et al., 2016). Paired-sample t test was applied to identify the similarities and differences in metal concentrations between the surface and pre-industrial sediments. The statistical analysis is performed using the IBM SPSS21 statistics software for Windows. The spatial distributions in EFs, concentrations and accumulation inventories of metals were plotted using the Ordinary Kriging (point Kriging) interpolation methods in Surfer 10 software package (Golden Software Inc., USA).

3. Results

3.1. Vertical variations in grain sizes and metal concentrations in the sediment cores

The sediments from Lake Dianchi were predominantly fine grained (Fig. S3). Clay (<4 μm) and silts (4-63 μm) were 32-62% (average: 43%) and 36-66% (average: 54%), respectively. The average sand (>63 μm) percentage was 1.3% with ranges of 0-5.1%. Vertically, clay percentages showed general decreasing trends upwards in all cores and the median grain sizes varied opposite to clay content (Fig. S3). The magnetic susceptibility (χ_{lf}) exhibited similar vertical trends among the cores with a clear inflection point in the deeper depths (Fig. S2). The OC contents were 9.3-131 g kg^{-1}, which showed low values in the deeper depths and increasing values upwards (Fig. S4).

The descriptive statistics of metal concentrations in sediments of Lake Dianchi are listed in Table 1. The concentrations of Cd, Hg and Zn varied largely, with coefficients of variation of 0.52, 0.43 and 0.40, respectively. The other meals showed relatively small variations with coefficients of variation <0.25. The metals exhibited varied vertical trends (Figs. 2 and S5). According to hierarchical cluster analysis, the metals can be classified into two groups (Fig. 3). Group I contains Al, Ti, Cr, Ni and Cu, and these metals are positively correlated (P = 0.01) among themselves and clay percentages (Table S1). Group Ⅱ contains As, Cd, Hg, Zn and Pb, and these metals show positive correlations ($P \leq 0.05$) among each other, but show negative correlations (P = 0.01) with the clay percentages and the metals in group I (Table S1). The metals in each group showed similar vertical distributions among the cores from each lake region. Specifically, group I metals exhibited relatively high values in the deeper depths than that in the upper depths (Figs. 2 and S5), consistent with the distributions of clay percentage and magnetic susceptibility (Figs. S2 and S3), but opposite to the OC (Fig. S4). Whereas, group II metals exhibited relatively low values in the deeper depths than that in the upper depths, which showed relatively high values (Figs. 2 and S5).

The data from core DC2, having detailed chronology, are used to exemplify the temporal variations of metals in Dianchi sediments. The metals showed two-stage variations (Fig. 2). Before the 1950s, the values of group I metals and clay were high and remained fairly constant, while after the 1950s the values started to decrease. Group II metals also showed fairly constant values prior to the 1950s with the exception of Pb which showed decreasing trend. Since the 1960s, the As concentrations started to increase gradually and reaching the highest values during the mid-1990s and then started to decrease gradually during recent decades. The concentrations of Cd and Hg increased gradually from 1960s to ~2000 and then remained steady during recent decades. The concentrations of Pb and Zn had started to increase since around 1980 and reached the highest values around 2000, then the values started to decrease. The mean concentrations of Cd, As and Hg in core DC2 since the 1960s were enriched by 2.6-, 1.4- and 1.2- times above the background values, whereas, Al, Ti, Cr, Cu, Ni, Pb and Zn were below the background values.

3.2. Spatial variations in metals in surface and pre-industrial sediments

According to age of the sediments in core DC2 (Fig. S6) and magnetic susceptibility (χ_{lf}) inflection point (c.1950) (Fig. S2), the deepest sediments recovered from each of the cores were deposited during the pre-industrial period. In addition, the metal concentrations below the inflection point were low and fairly stable in the cores (Figs. 2 and S5). Thus, the deepest sediments of each core were used as a pre-industrial reference for comparisons with surface (0-1 cm) sediments. Aluminum and Ti showed similar vertical variations (Figs. 2 and S5) and are strongly correlated to each other (Table S1). Therefore, Ti was used as a representative to illustrate the spatial variations of lithogenic metals.

The spatial variations of metals in pre-industrial and surface sediments are shown in Figure 4. The concentrations of Ti, Cr, Cu and Ni are significantly ($P < 0.01$) lower in the surface sediments than in the pre-industrial sediments, whereas the concentrations of As, Cd and Hg are significantly ($P < 0.02$) higher in the surface sediments than in the pre-industrial sediments (Table S2). No significant differences ($P = 0.05$) in Pb and Zn concentrations exist between surface and pre-industrial sediments (Table S2). The grain size compositions (e.g., clay percentage) exhibit significant ($P < 0.01$) differences between the surface and pre-industrial sediments, with relatively coarse sediments in the surface.

Spatially, Cu and Ti concentrations showed high values in the northern part, whereas Pb showed high values in the southern part of the lake in both surface and pre-industrial sediments (Fig. 4). However, no obvious spatial trends can be observed for Cr and Ni (Fig. 4). Cadmium, Hg and Zn showed high values in the northern part, while As showed high values in the southeastern part of the lake in the surface sediments; but in the pre-industrial sediments no marked spatial variations of these metals were observed (Fig. 4). Besides the difference in spatial patterns, the concentrations of As, Cd, Hg and Zn in the surface sediments showed large ranges than that in the pre-industrial sediments (Fig.

4, Table S2). The changes in spatial trends and increase in concentrations of As, Cd, Hg and Zn in the surface sediments relative to the pre-industrial sediments may relate to the anthropogenic input.

3.3. Enrichment factor and anthropogenic metals accumulation

The EF ranges of Cr, Ni, Cu, Pb, Zn, As, Hg and Cd were 0.9-1.3, 0.9-1.2, 0.9-1.6, 0.9-2.3, 0.9-6.1, 0.9-3.9, 0.9-6.3 and 0.9-10.8, and the averages were 1.0, 1.0, 1.1, 1.4, 1.7, 1.7, 1.8 and 3.5, respectively (Fig. 5). Lead, Zn, As, Hg and Cd are the typical pollutants with Cd being the most polluted metals.

3.3.1. Temporal variations in EF

The EF profiles of each metal showed similar patterns between the cores (Figs. 2 and S5). The core DC2 is used in explaining temporal trends because of detailed chronology. In core DC2, the EFs of Cr, Ni and Cu were close to 1 (Fig. 2). The EFs of Zn, As, Hg, Pb and Cd were close to 1 before the 1960, increased gradually till the mid-1990s to 2000, and then the values of Zn, Hg, Pb and Cd remained generally stable, while the EF of As decreased during recent decades.

The values of mass accumulation fluxes of anthropogenic As, Cd, Hg, Pb and Zn in core DC2 were nearly 0 before the 1960, and thereafter increased gradually (Fig. 6). The mass accumulation fluxes of anthropogenic Cd, Hg, Pb and Zn had reached the highest values at around 2000, which were 1.4 mg m^{-2} y^{-1}, 89.3 μg m^{-2} y^{-1}, 25.8 mg m^{-2} y^{-1} and 71.0 mg m^{-2} y^{-1}, respectively, and then remained high or decreased slightly during recent decades (Fig. 6). While, the mass accumulation fluxes of anthropogenic As reached the highest value (23.0 mg m^{-2} y^{-1}) during the mid-1990s and then decreased sharply (Fig. 6).

3.3.2. Spatial variations in EF and anthropogenic metals

Spatial variations in EFs and anthropogenic concentrations of metals in the surface sediments are shown in Figure 7. The EFs of Cr, Cu and Ni were nearly 1, and the values of Pb, As, Zn, Hg and Cd were 1.4-1.9, 1.1-2.4, 1.5-4.4, 1.5-5.4 and 2.8-7.9, with an average of 1.6, 1.8, 1.9, 2.3 and 4.6, respectively. As expected, Cd was the most polluted element in the surface sediments. Anthropogenic As, Cd, Pb, Hg and Zn varied from 3.6 to 18.7 mg kg^{-1}, 0.74 to 1.87 mg kg^{-1}, 15.2 to 30.7 mg kg^{-1}, 49 to 391 μg kg^{-1} and 49.6 to 287 mg kg^{-1} (Fig. 7), with an average of 11.8 mg kg^{-1}, 1.05 mg kg^{-1}, 23.3 mg kg^{-1}, 128 μg kg^{-1} and 96.1 mg kg^{-1}, accounting for 42%, 77%, 37%, 55% and 43% of the total concentrations, respectively. High concentrations of anthropogenic Cd, Hg and Zn were mainly restricted to the northern part of the lake, while high concentrations of As was restricted to the southeastern part (Fig. 7). Lead was evenly distributed across the lake except low values in the northeastern (Fig. 7).

In order to understand the long-term negative effects of anthropogenic metals input on the sediment quality of Lake Dianchi, the stocks of anthropogenic Cd, Zn, As, Pb and Hg during the industrial period were evaluated. The values were in the ranges of 28-155 mg m^{-2}, 2.4-37 g m^{-2}, 0.23-2.5 g m^{-2}, 0.49-2.4 g m^{-2} and 1.3-26 mg m^{-2}, respectively (Fig. 8). High stocks of anthropogenic metals were found in the northern part of the lake, which is near to the urban area of Kunming, while the low values occurred in the southeastern part where the rivers primarily drained agricultural and forest land (Fig. 1). Low anthropogenic metal stocks were also observed in the northeastern part of the lake (Fig. 8), an area rarely recharged by the rivers (Fig. 1). The differences in the stocks of anthropogenic Pb between areas in the northern and southern parts were similar to the average Pb concentrations in the 0-10 cm sediments reported by Zhang et al. (2014).

4. Discussion

4.1. Evolution of sedimentary environment

The vertical distributions of metal concentrations, grain size parameters and magnetic susceptibility in the cores suggest a uniform sedimentary sequence throughout the Lake Dainchi, which is differed from the typical floodplain shallow lakes influenced by the stronger hydrodynamic conditions and human disturbances (Lintern et al., 2018; Shen et al., 2011). The association between fine sediments and high concentrations of lithogenic elements (such as the metals in group Ⅰ) indicates a relatively stable input of detrital materials to the lake prior to the 1950s, which is consistent with the more-limited human perturbation in the catchment before and early stages of economic development. However, the gradual decreases in clay percentages and detrital elemental concentrations since the 1950s indicate an increasing deposition of coarser detritus.

Variations in sedimentary detritus composition may respond to the fluctuations of lake level, intensities of soil erosion and sources in the watershed (Seguin et al., 2019; Wang et al., 2015; Xu et al., 2015; Yu et al., 2019). Under stable detritus supply, the decrease in lake level may extend the soil transport, thus coarser detritus may deposit gradually during the transportation process, while the finer materials are transported to the lake; on the contrary, coarser detritus is transported to the lake (Wang et al., 2015). The water depth of Lake Dianchi averages 4.4 meters and did not show any large fluctuation during the past hundred years (Wang et al., 2018c). Therefore, the temporal variations in grain size in the cores should not be affected by the fluctuation of water level.

The soil runoff and erosion intensity is subjected to the watershed hydrology (Yu et al., 2019). When the precipitation is high, surface runoff develops, and its erosion and transportation capacity increases, leading to coarser detritus transport (Li et al., 2019; Yu et al., 2019). However, the trend of precipitation in Kunming from 1950 to 2014 was generally stable and even decreased during recent decades (Fig. S7), which was differed from the increasing trend of median grain size in the cores. It can be inferred that the variations in sedimentary detritus composition were less affected by the precipitation.

In addition to the hydrological condition, the sources and transport of detritus are generally subjected to human activities within the watershed (Clark et al., 2014). Intensive human activities and alteration in landscapes, such as conversion of farmland and forest to construction land in the Dianchi watershed, have reduced vegetation cover leading to the reduction in soil stability and favoring the gully erosion, and thereby enhancing the transport of coarse-grained detritus from weak weathered subsoil (Gaspar et al., 2019; Xie et al., 2017). Moreover, agricultural intensification can increase the runoff connectivity due to enhanced overland flow (Gaspar et al., 2019). The increase in the construction land can increase the impervious surfaces (Russell et al., 2018). Both these factors facilitated accelerated transport of coarser detritus into the lake (Gaspar et al., 2019; Russell et al., 2018). Therefore, strengthening of human activities might have been the main driver of changing sedimentary environment in Lake Dianchi. Additionally, the reclamation of lake may also increase the input of detritus. This might have been the reason for high sedimentation rate in the northern lake area (Fig. S8).

The metals in the deepest layer of the cores considered as pre-industrial levels showed different spatial trends, which may be due to their different levels in the parental soils and rocks within the sub-basin (Lin et al., 2018). The spatial trends in lithogenic elements (e.g., Ti) in the surface sediments are similar to that in the pre-industrial sediments though the values have decreased. The erosion of coarser-particles has occurred in the whole basin though the intensities have been different in each sub-basin (Huang et al., 2014). Because of this reason, the synchronous changes in sedimentary environment in different lake regions of Dianchi were observed. Despite of the changes in the sedimentary environment of Lake Dianchi since the 1950s, the lake ecological deterioration was typically since the 1980s with increasing nutrient levels (Wang et al., 2018c), suggesting the limited effects of changing detritus input on the lake ecological environment.

4.2. Spatio-temporal variations in trace metals pollution

The positive correlations ($P < 0.01$) between most metals and clay fractions suggest that the sediment texture has a great influence on the metal concentrations in Lake Dianchi, particularly lithogenic components (Birch, 2017; Lin et al., 2018; Ontiveros-Cuadras et al., 2014). To test the effectiveness of Ti normalization in compensating for the sediment texture variations in Lake Dianchi, metal EFs were also calculated using Al as a reference element. The metal EFs in surface sediments using Ti alone and Al and Ti combined as reference elements were comparable (Table S3), which suggests that Ti normalization can effectively compensate for the sediment texture variations. It was indicated that organic particles may favor the accumulation of metals in sediments via the scavenging effect (Buyang et al., 2019; Ontiveros-Cuadras et al., 2014; Outridge et al., 2007). The OC content in the sediment cores of Lake Dianchi have increased gradually in recent one hundred years (Fig. S4), similar to previous study (Huang et al., 2017). However, the concentrations of most metals showed negative correlations with OC ($P \leq 0.05$) (Table S1), thus suggesting that the variations in OC do not play a significant role in metals enrichment. Therefore, the metal EF values faithfully reflect the pollution (Li et al., 2019; Lin et al., 2018; Ontiveros-Cuadras et al., 2014).

Chromium, Ni and Cu pollution was largely absent in sediments of Lake Dianchi. Pollution of Pb, Zn, As, Hg and Cd were low to moderate based on the grading criteria (Sutherland, 2000), while Cd was the most polluted metal. These observations are generally in agreement with the previous study (Zhang et al., 2014). The EFs approved that the difference in spatial patterns of As, Hg and Cd concentrations, and the large range of As, Cd, Hg and Zn in surface sediments compared to that in pre-industrial sediments were caused by the pollution.

4.2.1 Temporal variations in anthropogenic metals

The EFs trends for each of the Zn, As, Hg, Pb and Cd along depths were similar among the cores, indicating a consistent temporal pattern in metal pollution across the lake over the past one hundred years. All these metals were primarily derived from lithogenic sources prior to 1960. After 1960s, the increasing enrichments and mass accumulation fluxes of anthropogenic As, Zn, Hg, Pb and Cd suggest aggravating pollution with the watershed economic development (Fig. 6). However, since 2000, the stricter environmental regulations and pollution control measures (e.g., closure of 'highly polluting' industries and construction of ecological wetland around the lake) had led to the reduced pollutants input to Dianchi (Guo et al., 2017; Ma and Wang, 2015; Meng, 2016), leading to the reduction of mass accumulation fluxes of anthropogenic Zn, Hg, Pb and Cd in the sediments (Fig. 6). Besides, anthropogenic As entered into lakes can be from the use of agricultural pesticides and fertilizers (Landre et al., 2011; Nezat et al., 2017), which might have occurred in Dainchi Lake watershed. Lin et al. (2016) have indicated that agricultural sources largely contributed to As pollution in a nearby lake in this region. However, due to the restriction in the use of arsenical pesticides and herbicides since the 1980s in China, the accumulation of As in agricultural soils and the legacy input from soils to the lake would be reduced (Coxon et al., 2016; Dias-Ferreira et al., 2016). This is the reason why As pollution was peaked earlier and show a sharp decline in the mass accumulation fluxes during recent decades than the other metals.

The historical process of trace metal pollution in Lake Dianchi was similar to another suburban lake (Erhai) (Li et al., 2017), but the process was different for lakes in remote and agricultural regions in southwest China, e.g., Lugu, Fuxian and Chenghai (Lin et al., 2018; Liu et al., 2013; Yu et al., 2017), where the metal pollution had started in the 1980s. This suggests a distinct negative effects of urbanization especially the local industrial development on the degradation of lake environmental quality.

4.2.2. Spatial variations in anthropogenic metals

The stocks of anthropogenic metals reflect a long-term negative effects of pollutants input on the sediment quality. The in-lake sediment focusing may have influenced the accumulation of metals in the sediment, however, sediment focusing is predominant in small lakes with a steeper topography (Lin et al., 2018; Engstrom and Rose, 2013). Dianchi is a shallow water lake with mean water depth of 4.4 m (Wang et al., 2018c). The in-lake sediment focusing should have a little influence on the redistributions of all metals. Thus, the spatial variations of anthropogenic metals were related to the differences in input relating to the intensity and types of human activities in different parts of the watershed (Gao et al., 2019; Yang et al., 2015; Zhang et al., 2017).

It was estimated that approximately 90% of the industrial wastewaters and domestic sewages from Kunming city entered into the Lake Dianchi via the rivers in the northern before the 1990s (Huang et al., 2014; Wang et al., 2014; Zhang et al., 2014). This had resulted in the high stocks of anthropogenic As, Cd, Zn, Pb and Hg in the northern lake area (Meng, 2016; Wang et al., 2012). The urban runoff contains substantial amount of metals due to increasing impervious surfaces and emission from construction sites and vehicular exhausts (Ma et al., 2018; Zafra et al., 2017). Urban runoff is largely untreated and forms a substantial source of metals into the lake, which may also contribute to the accumulation of metals in the northern part of the lake. The low stock of anthropogenic Cd, Zn, As, Pb and Hg in the southeastern part of the lake was due to insignificant input of metals from the agricultural and forested areas (Guo et al., 2017), while the low stock of anthropogenic metals in the northeastern part was due to the absence of direct runoff.

The metals in the surface sediments represent the more recent status of lake pollution (Landre et al., 2011; Wang et al., 2012; Yang et al., 2014). In the case of Dianchi, high concentrations of anthropogenic Cd, Hg and Zn in the northern part is consistent with the higher levels of anthropogenic metal stocks. While, the spatial trends of anthropogenic As and Pb in the surface sediments were differed from their stocks. The anthropogenic metals per unit mass of the sediments is dependent on the relative contributions of anthropogenic vs. lithogenic sources. High detritus input may dilute the concentrations of anthropogenic metals. Therefore, the difference in the spatial patterns of anthropogenic concentrations of As and Pb in the surface sediments with that of the stocks was due to the high sedimentation rate in the northern lake area and the dilution of the anthropogenic fractions of As and Pb by the detritus (Birch, 2017). Similarly, the relatively high anthropogenic As in the surface sediments of southeastern part of the lake may be due to the combined influence of legacy As input and low sedimentation rate (Landre et al., 2011). This suggests that the sedimentation rate must be considered to assess the spatial difference of anthropogenic impact in a lake.

Our study indicates that the land use types and the intensity of human activities had a great influence on the anthropogenic metals pollution in Lake Dianchi. Urbanization and industrial development in Kunming district had significantly contributed to the accumulation of metals in the northern part of Dianchi, which is similar to the observation in Lake Simcoe (Landre et al., 2011) and other lakes along the rural-urban gradient (Chalmers et al., 2007). The spatial patterns of anthropogenic Cd and Zn in the surface sediments and their stocks are consistent with the results of water monitoring data in October 2014 (Meng, 2016). Arsenic in the water also showed similar spatial trends to the anthropogenic As stocks in the sediments (Wang, 2018; Yang et al., 2016). These indicate the long-term negative impact of anthropogenic metals input on the lake environmental quality. Though the large volume of wastewaters were discharged into the lake, the metal concentrations in the water of Dianchi were all conformed to grade I drinking water quality standard (GB3838-2002) in China (Wang, 2018). This might be due to the precipitation of dissolved metals in various forms (Ontiveros-Cuadras et al., 2014; Viers et al., 2009).

4.2.3. Potential influence of atmospheric deposition and diagenesis in the metal accumulation

Besides wastewater input from industrial, agricultural and domestic sources, atmospheric deposition also contributed much to the accumulation of anthropogenic trace metals in lakes of industrialized and urbanized regions, such as the Pearl River Delta of China (Wong et al., 2003). The atmospheric input had also contributed to the trace metals pollution in remote areas in southwest China due to mining exploration bloom and poorly controlled smelting emissions (Bing et al., 2016; Lin et al., 2018; Liu et al., 2013). Though the temporal trends of trace metals pollution in Lake Dianchi were synchronized with the atmospheric emission (Tian et al., 2015), the accumulation inventories of anthropogenic metals were substantially higher in Lake Dianchi than in other remote lakes (e.g., Caohaizi and Lugu) in southwest China (Bing et al., 2016; Lin et al., 2018). Moreover, anthropogenic

As, Cd, Pb, Hg and Zn stocks in the sediments of Lake Dianchi showed a strong spatial variations, which is different from the general uniform features of atmospheric metals deposition (Landre et al., 2011). Therefore, the atmospheric deposition may not have contributed much to the accumulation of anthropogenic metals in Lake Dianchi, which is in agreement with the conclusion from another lake (Yangzong) in southwest China (Wang et al., 2018a).

After the deposition, the distribution of metals in sediments may change due to their diagenesis under changing environmental conditional, such as the redox state (Landre et al., 2011; Mehlhorn et al., 2018). The absence of positive correlations between Mn, an indicator of sediment diagenesis (Percival and Outridge, 2013), and other trace metals (Table S4) suggests that the diagenesis do not strongly influence the mobility of trace metals in the sediments of Lake Dianchi. Nevertheless, the hotspots of anthropogenic metal stocks were coincided with the areas of eutrophic regions of Dianchi (Huang et al., 2014; Yang et al., 2018). Therefore, in view of the potential phytoplankton uptake, accumulation and bio-magnification of metals (Tomczyk et al., 2018; Wang et al., 2010) and potential internal release from the sediments (Wang et al., 2012), the northern part of Dianchi should be targeted for high resolution of sediment trace metals analysis and potential for remediation (Yang et al., 2017).

5. Conclusions

The metal and metalloid elements were classified into two groups: group I: Al, Ti, Cu, Cr and Ni, and group II: As, Cd, Hg, Pb and Zn. The elemental concentrations in group I were decreased gradually since the 1950s, along with the decrease in clay percentage, which was due to the accelerated coarser soil erosion following land conversion from farmland to construction land and strengthening human perturbation. In contrast, group II elements were increased generally since the 1960s, which was due to the large anthropogenic inputs to the lake. Metal pollution was peaked at the mid-1990s to 2000 and remained at a high level for Cd, Hg, Pb and Zn thereafter, except for As which started to decrease during recent decades. The temporal trends of metal pollution in the sediments of Lake Dianchi were consistent with the watershed economic development and implementation of pollution control measures. The spatial patterns in metal stocks in the sediments were closely associated with the intensity and types of human activities in the watershed. High stocks of anthropogenic As, Cd, Hg, Pb and Zn in the sediments of the northern lake areas were due to the large input of industrial and domestic wastewaters from Kunming district, while low stocks of metals in the southeastern part of the lake were due to the limited input from the agricultural and forested areas. In summary, the spatial and temporal variations of metals in the sediments of Lake Dianchi were the result of a complex interplay between soil erosion, detritus input and pollution.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at…

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Figure captains

Fig. 1. Map showing (a) location of Lake Dianchi in southwest China, (b) land use in the watershed in 2013 (compiled from Huang et al., 2014) and (c) sampling sites of sediment cores.

Fig. 2. Vertical variations of concentrations and enrichment factors (EF) of As and other metals and clay (<4 μm) percentage in core DC2.

Fig. 3. Hierarchical cluster analysis of As and other metals in the sediments of Lake Dianchi (total number of samples = 188).

Fig. 4. Spatial distributions of As and other metals in the surface and pre-industrial sediments of Lake Dianchi.

Fig. 5. Boxplot of EF values of As and other metals in the sediments of Lake Dianchi.

Fig. 6. Temporal variations of mass accumulation fluxes of anthropogenic As, Pb, Cd, Zn and Hg in core DC2, the total industrial production values (TIPV) in Kunming City and the output of chemical fertilizers (OCF) in Yunnan Province.

Fig. 7. Spatial variations in (a) enrichment factor (EF) and (b) anthropogenic concentrations of As, Cd, Hg, Pb and Zn in the surface sediments of Lake Dianchi.

Fig. 8. Spatial variations in stocks of anthropogenic As, Cd, Hg, Pb and Zn during recent one hundred years' sediments of Lake Dianchi.

Table captain

Table 1. Summary statistics of As and other metals in the sediments of Lake Dianchi.

Table 1. Summary statistics of As and other metals in the sediments of Lake Dianchi.

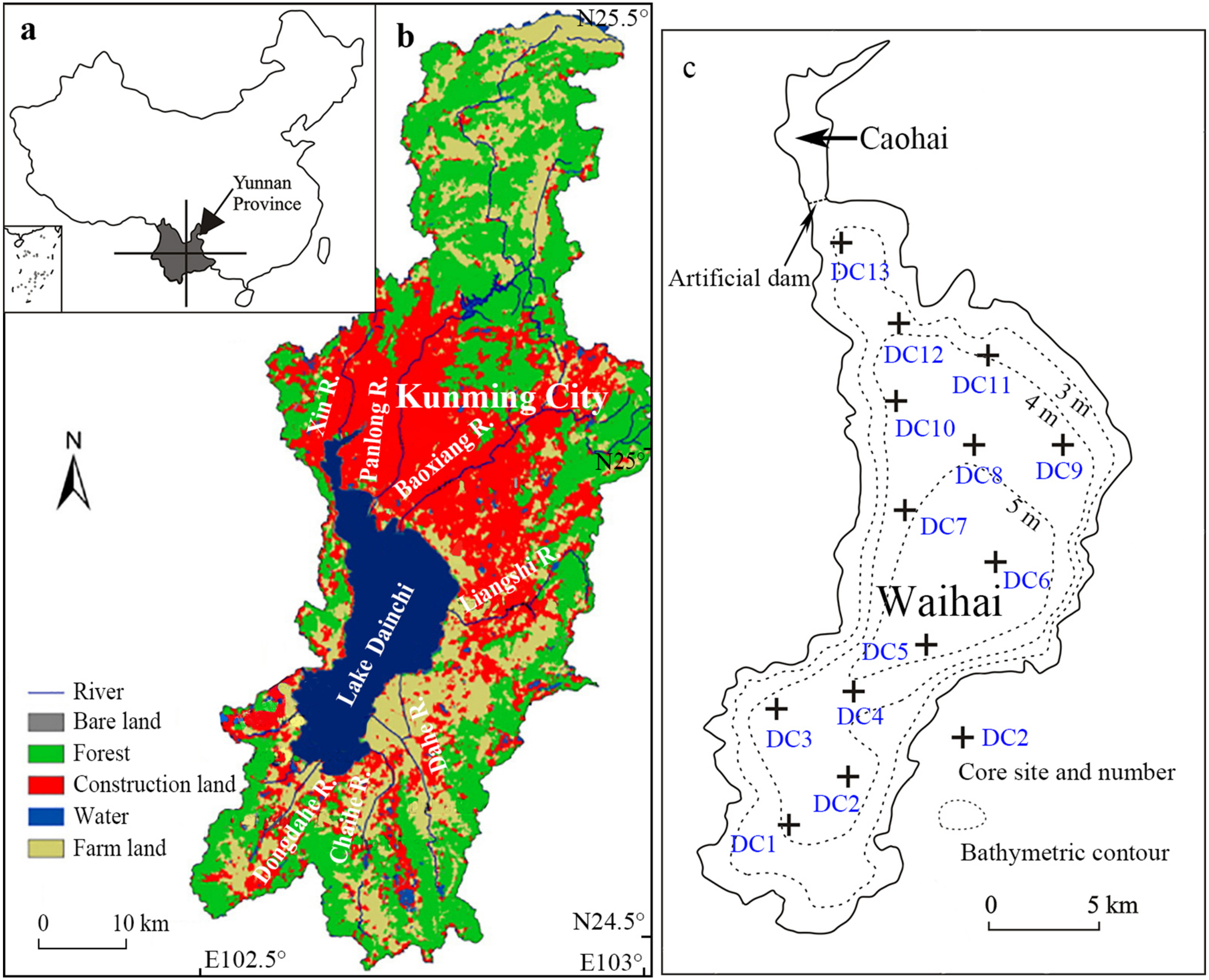
	As (mg kg^{-1})	Al (g kg^{-1})	Ti (g kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Hg (μg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
Range	21.5-64.4	62.7-120	5.4-15.5	0.38-3.07	57.2-113	57.3-114	102-594	33-59.8	44.1-105	132-606
Mean	30.0	85.1	9.7	1.07	81.7	84.9	174	46.1	65.7	195
C.V.	0.22	0.20	0.25	0.52	0.17	0.17	0.43	0.17	0.21	0.40

Note – C.V., coefficient of variation, total number of cores = 13, and total number of samples = 188.

Graphical abstract

Highlights

- Spatio-temporal variations of lithogenic and anthropogenic metals were studied.
- The changes in sedimentary environments were mainly due to land use alterations.
- Temporal variations of metal pollution were associated with economic developments.
- Spatial stocks of anthropogenic metals were regulated by sub-basin human activities.



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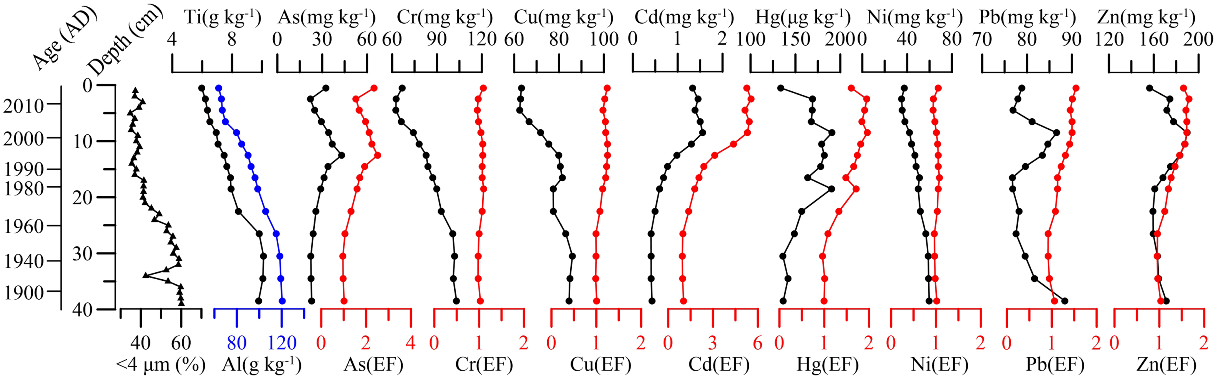
N25°
Liangshu R.
Lake Daichi
Dahe R.
Chaihe R.
Dongdahe R.
N
River
Bare land
Forest
Construction land
Water
Farm land
0
10 km
N24.5°
E102.5°
E103°
c
Caohai
Artificial dam
DC13
DC12
DC11
DC10
3 m
4 m
DC8
DC9
5 m
DC7
DC6
Waihai
DC5
DC4
DC3
DC2
DC2
DC1
Core site and number
Bathymetric contour
0
5 km

Figure 1



Age (AD)
Depth (cm)
Ti(g kg-1)
As(mg kg-1)
Cr(mg kg-1)
Cu(mg kg-1)
Cd(mg kg-1)
Hg(μg kg-1)
Ni(mg kg-1)
Pb(mg kg-1)
Zn(mg kg-1)
<4 μm (%)
Al(g kg-1)
As(EF)
Cr(EF)
Cu(EF)
Cd(EF)
Hg(EF)
Ni(EF)
Pb(EF)
Zn(EF)

Figure 2

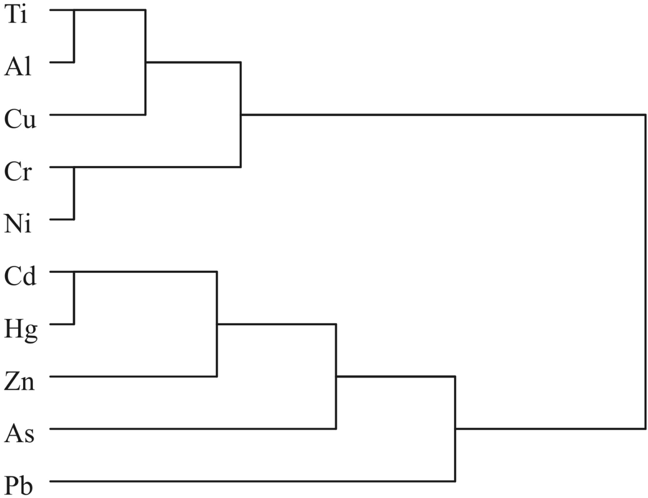
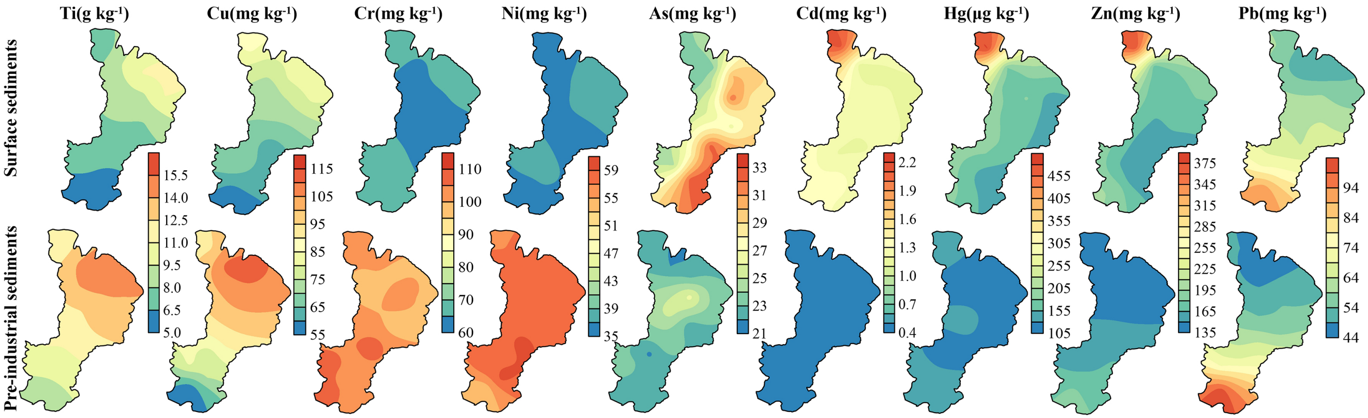


Figure 3



Ti(g kg-1)
Cu(mg kg-1)
Cr(mg kg-1)
Ni(mg kg-1)
As(mg kg-1)
Cd(mg kg-1)
Hg(μg kg-1)
Zn(mg kg-1)
Pb(mg kg-1)
Surface sediments
Pre-industrial sediments
15.5 14.0 12.5 11.0 9.5 8.0 6.5 5.0
115 105 95 85 75 65 55
110 100 90 80 70 60
59 55 51 47 43 39 35
33 31 29 27 25 23 21
2.2 1.9 1.6 1.3 1.0 0.7 0.4
455 405 355 305 255 205 155 105
375 345 315 285 255 225 195 165 135
94 84 74 64 54 44

Figure 4

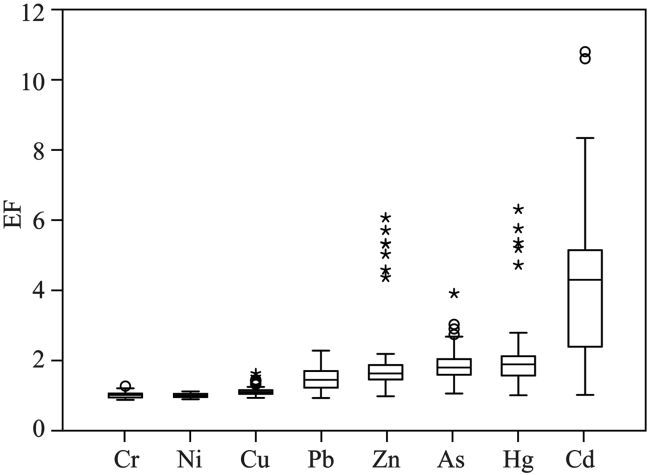
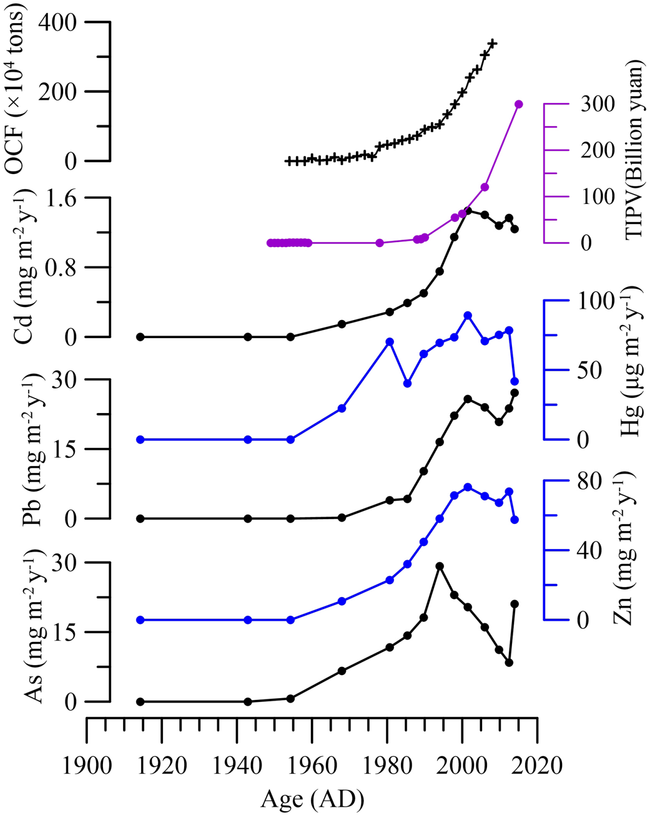


Figure 5



OCF (×10⁴ tons)
400
200
0
TIPV(Billion yuan)
300
200
100
0
Cd (mg m⁻² y⁻¹)
1.6
0.8
0
Hg (μg m⁻² y⁻¹)
100
50
0
Pb (mg m⁻² y⁻¹)
30
15
0
Zn (mg m⁻² y⁻¹)
80
40
0
As (mg m⁻² y⁻¹)
30
15
0
1900
1920
1940
1960
1980
2000
2020
Age (AD)

Figure 6

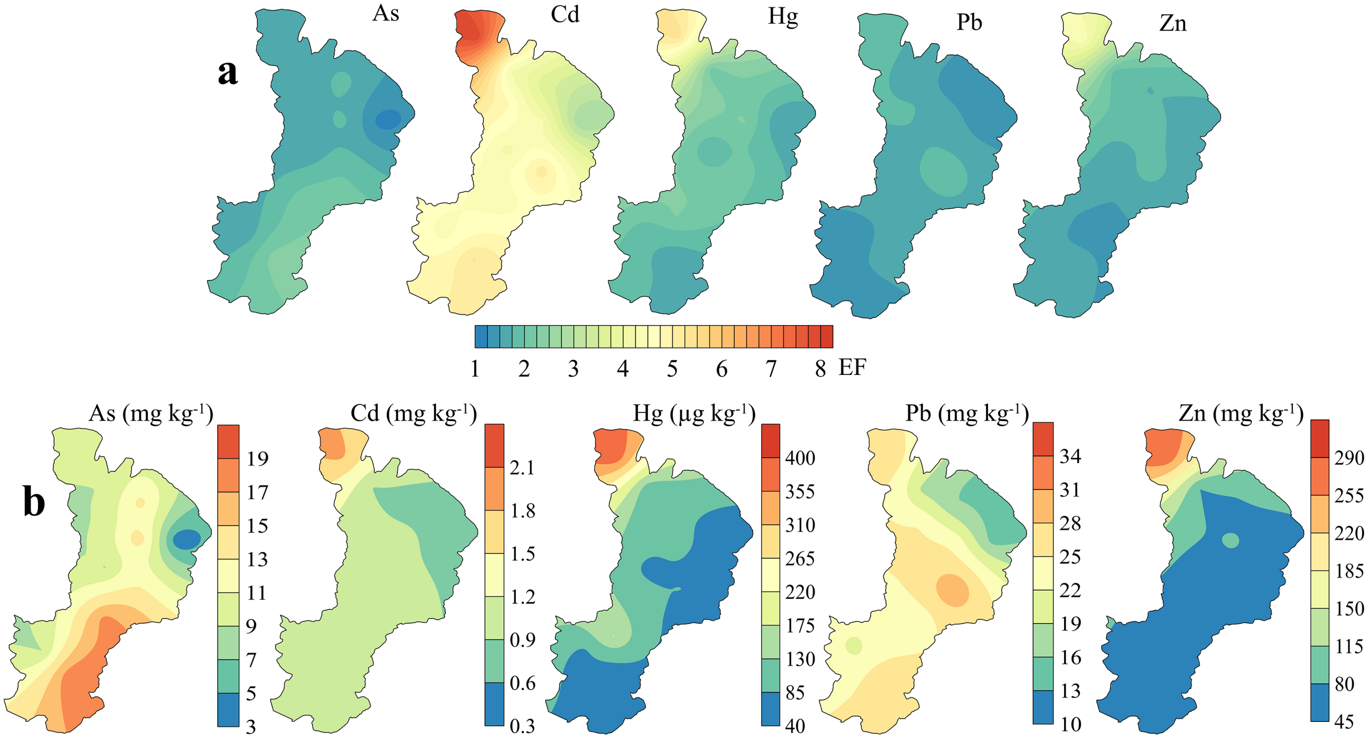
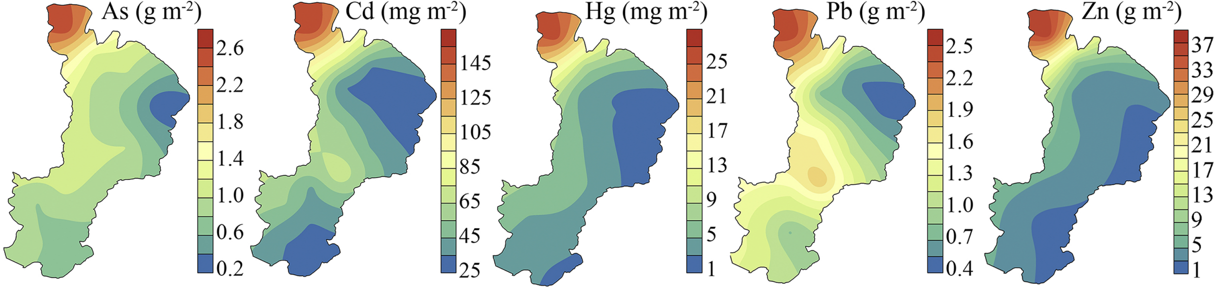

a
As
Cd
Hg
Pb
Zn
1
2
3
4
5
6
7
8
EF
b
As (mg kg-1)
19
17
15
13
11
9
7
5
3
Cd (mg kg-1)
2.1
1.8
1.5
1.2
0.9
0.6
0.3
Hg (µg kg-1)
400
355
310
265
220
175
130
85
40
Pb (mg kg-1)
34
31
28
25
22
19
16
13
10
Zn (mg kg-1)
290
255
220
185
150
115
80
45

Figure 7



As (g m-2)
2.6
2.2
1.8
1.4
1.0
0.6
0.2
Cd (mg m-2)
145
125
105
85
65
45
25
Hg (mg m-2)
25
21
17
13
9
5
1
Pb (g m-2)
2.5
2.2
1.9
1.6
1.3
1.0
0.7
0.4
Zn (g m-2)
37
33
29
25
21
17
13
9
5
1

Figure 8