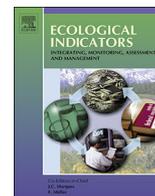




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Original Articles

Accumulation of arsenic, mercury and heavy metals in lacustrine sediment in relation to eutrophication: Impacts of sources and climate change

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ABSTRACT

Information on both the climate change and anthropogenic activities on lacustrine ecosystem is of crucial importance for understanding the current state and future development of lake systems. The sediment profiles of arsenic, mercury, other metals, and nutrients were used to investigate climate change and anthropogenic activities impacts on three lakes located on the Yunnan-Guizhou Plateau (Lake Chenghai, Qionghai) and Northeastern Plain region (Lake Jingpohu) of China. The enrichment factor (EF), geoaccumulation index (I_{geo}) and anthropogenic factor (AF) were used to assess the enrichment degree of metals. The results show that these lakes have been progressively eutrophied since the development of widespread industrialization and urbanization in these areas. The enrichment of heavy metals is generally not serious ($EF < 1.5$, $I_{geo} < 0$), except for Cd, Pb, and Hg in Lakes Chenghai and Qionghai. Correlation analysis shows that generally, the heavy metals characterized had significant correlations with nutrient concentrations (TOC, $\delta^{13}C$, TP), which implied the establishment of geochemical associations during transport, that they had similar anthropogenic sources (such as fertilizers), or both. Cluster analysis grouped nutrients, As, and most other metals (except Ca, Mg, Fe, Al), the annual average temperature, and annual precipitation into one category. Increases in both average annual air temperatures and total precipitation are likely influencing the input of heavy metals and nutrients to these lakes.

1. Introduction

Various anthropogenic activities affect lacustrine water quality in many parts of the world, and are likely to continue to for a long period into the future, however, it is anticipated that climatic changes will further aggravate the deterioration of water quality (Helbling et al., 2015; Xu et al., 2017; Laura et al., 2017). The quality of water, and aquatic environments generally, are influenced by climate change, but these relationships are complicated in part due to variations of associated meteorological factors, including precipitation, temperature, radiation, and wind speed/direction. For example, changes in precipitation frequency and intensity can directly impact the input of non-point source pollutants to lakes by regulating surface runoff (Prowse et al., 2006; Karim and Mimura, 2008; Horn et al., 2015). Also, global warming impacts the thermal characteristics of lakes, changing water temperatures, which can extend stratification periods, decreasing the depths of mixed layers and thermoclines, which can reduce convective mixing (Fan and Kao, 2008; Kraemer et al., 2015; Ma et al., 2015). Lacustrine algal community structures can also be altered by

climate change, which in some cases can promote algal productivity and increase the production of algal toxins (Hayes et al., 2015; Reavie et al., 2016). O'Beirne et al. (2017) showed that global warming caused an increase in surface water temperatures and longer ice-free periods, generating longer seasonal stratification, resulting in a rapid increase in primary productivity in Lake Superior, USA. Climate change has facilitated salinization, eutrophication, shrinkage, and even the total desiccation of some lakes (Hayes et al., 2015; Horn et al., 2015; Wu et al., 2017), and so it is urgent to conduct research on the impacts of climate change on lacustrine environments.

Heavy metal contamination of aquatic ecosystems is a major concern due to their toxicity, frequent bioaccumulation, environment persistence, and resulting potential ecological risks (e.g., Atici et al., 2008; Guo et al., 2015). Arsenic (As) is a carcinogenic metalloid that is widely distributed in aquatic environments in various forms, and is recognized as a major pollutant (e.g., Jain and Ali, 2000; Hasegawa et al., 2009). Heavy metals, including As, are derived from a variety of sources, including natural weathering of rocks and sediments, atmospheric deposition, soil erosion, and various anthropogenic activities,

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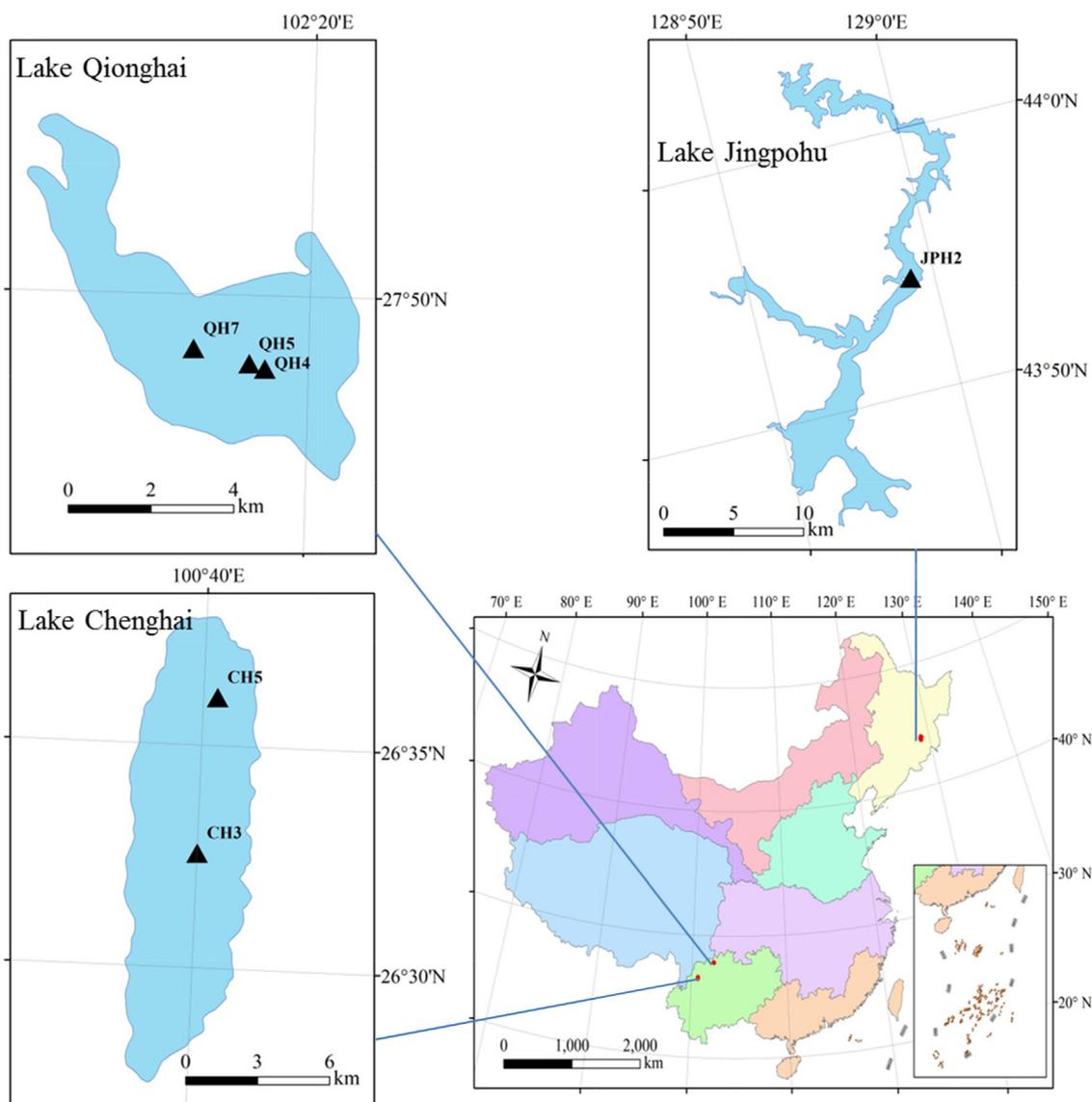


Fig. 1. Maps showing locations of sampling sites.

and they can be transported to and deposited in lacustrine sediments temporarily or permanently (Zhang et al., 2014; Guo et al., 2015a). Lake sediments often serve as effective archives of pollutants, and can provide reliable records of water quality variations over time (e.g., Thevenon et al., 2011; Lintern et al., 2016; Zan et al., 2012a,b; Zan et al., 2014). Stratified sediment cores, dated by stable isotopes, are used extensively to track the past accumulation of heavy metals and persistent organics pollutants (POPs), and reconstruct lake and coupled watershed pollution histories (e.g. Zhang et al., 2014; Li et al., 2015; Guo et al., 2015a,b; Qi et al., 2015). A body of study has focused on the spatial distributions, bioavailability, risk assessment, and source identification of heavy metals in lake sediment (e.g., Atici et al., 2008; Guo et al., 2015). However, less attention has been paid to heavy metal deposition in relation to changing nutrient conditions and/or the dual impacts of anthropogenic activities and climate change (Wu et al., 2017). For instance, trivalent arsenic (As^{3+}) and pentavalent arsenic (As^{5+}) are converted to organoarsenic compounds more frequently in eutrophic lakes than in mesotrophic lakes, which differentially affects biological activity in the water column (Hasegawa et al., 2009). Recent research has shown that the deposition of As, cadmium (Cd), cuprum (Cu), zinc (Zn), nickel (Ni), chromium (Cr), cobalt (Co), and argentum (Ag) was strongly affected and/or controlled by algal organic matter

(AOM) in eutrophic, non-point source polluted lakes, suggesting that the abundance of AOM is an important factor in controlling trace metal accumulation in lake sediments (Duan et al., 2014).

Climate change can affect heavy metal deposition in lakes by modifying their input from surface sources in the watershed, by changing atmospheric wet and dry deposition via changes in precipitation, and by impacting mixing and stratification processes, or by changing water chemistry, resulting in some cases in the release of metals from bottom sediments (Visser et al., 2012; Xu et al., 2017). Increases in the amount or intensity of precipitation can drive dissolution of metal carbonates and metal sulfides in sediments, which can then increase the release of heavy metals (e.g., Nedrich and Burton, 2017). Changes in lake water levels caused by extreme rainfall or extreme heat can intensify heavy metal cycling in lake sediment (Nedrich and Burton, 2017). Furthermore, changing climate patterns can enhance the mobilization of natural metal sources in high altitude environments, as shown at Lake Bubal (Zaharescu et al., 2016). However, few investigations have focused on unraveling the mechanisms of heavy metal deposition in lakes with respect to climate change factors, explicitly. In this research, three lakes (Jingpohu, Qionghai, Chenghai) on the Northeastern Plain, and Yunnan-Guizhou Plateau regions of China were sampled to examine various metals (iron (Fe), aluminum (Al), Cu, Zn,

calcium (Ca), magnesium (Mg), manganese (Mn), titanium (Ti), vanadium (V), Co, Ni, Cd, plumbum (Pb), Cr, mercury (Hg), As) and nutrients (total organic carbon (TOC), $\delta^{13}\text{C}$, and total phosphorus (TP)) in bottom sediments over time, while also considering meteorological factors (temperature and precipitation) in an effort to reveal contributions of climate change and human activities to the deposition of these pollutants.

2. Materials and methods

2.1. Study areas

Lake Chenghai (26°27'N–26°38'N, 100°38'E–100°41'E) is located in the Yunnan-Guizhou Plateau region, Yunnan Province, China. The lake covers an area of 74.6 km², with an average depth of 25.7 m (Bai et al., 2005), and serves as a host to aquaculture, and as a water source for regional agricultural irrigation (Zhang et al., 2014). In recent years, water pollution and the severity of eutrophication in Lake Chenghai have increased significantly, with increasing salinity and Fluorine ion concentrations (Zhang et al., 2014). Lake Qionghai (27°42'N–27°55'N, 102°15'E–102°28'E) is a plateau freshwater lake, and is also located in the Guizhou Plateau Region, Sichuan Province, China. Lake Qionghai has an average depth of 10.3 m, and covers an area of 27.9 km² (Huo et al., 2011). The lake is surrounded by mountains on three sides, and borders the city of Xichang to the north. It is a vital water source (drinking water, irrigation), but also hosts aquaculture and provides resources that support tourism (Zan et al., 2014). Lake Jingpohu (43°30'N–44°20'N, 128°07'E–129°06'E) is located in the Northeastern Plain Region, Heilongjiang Province, China. The eruption of volcanic lava dammed the Mudanjiang River ~10,000 years ago, forming Lake Jingpohu, which is the largest channel-type deepwater lake in Asia (Huo et al., 2011). It is also the largest alpine barrier lake in China, with an average depth of 13.8 m, covering an area of 79.3 km² (Huo et al., 2011).

2.2. Sediment sampling and analysis

The sampling sites (JPH2 – Lake Jingpohu; CH3 and CH5 – Lake Chenghai; and QH4, QH5 and QH7 – Lake Qionghai) were distributed in the central lake areas, where relatively stable depositional conditions were expected, lessening the likelihood that sediments have been disturbed (Fig. 1). The sampling locations away from lake banks, stream inlets and lake outlet were carefully selected to reflect the pollution level in the studied lakes. All sediment cores were collected by gravity corer equipped with a PMMA (acrylic) tube (100 cm long, 8 cm i.d.) in July 2010. The cores were sectioned at 1 cm intervals, with sample aliquots stored in polyethylene bags. All samples were stored in a freezer at –20 °C prior to analyses. Samples were then freeze-dried at –50 °C using FD-1D-50 freeze dryers, ground, and passed through a 100 mesh sieve.

The fallout radionuclide ¹³⁷Cs was used to date the sediment cores collected at stations QH4, QH5, QH7 and JPH2 (Fig. 1; Zan et al., 2012a). ¹³⁷Cs activities (at 661 KeV) were determined directly using a GCW3022 H-P Ge coaxial probe gamma spectrometer (S-100 multi-spectral spectrometer, Canberra, USA). A ¹³⁷Cs sediment standard (Catalog No.: 7137, Source No.: 586-26-2) was used, provided by the Institute of Atomic Energy, Chinese Academy of Sciences. Previous research that describes the chronology of cores CH3 and CH5 from Lake Chenghai is included in Zan et al., 2012a.

TP concentrations were determined by the alkali fusion-Mo-Sb Antispectrophotometric method (ECAMWWM, HJ 632-2011). TOC concentrations were determined using a TOC/TN analyzer (Multi-N/C2100TOC/TN, Jena, Germany) after samples were pretreated with HCl (1N) to remove inorganic carbon. Stable carbon isotopes ($\delta^{13}\text{C}$) were determined by isotope ratio mass spectrometry (IRMS) (Finnigan Delta^{plus} XP), with an accuracy of < 0.1‰. Prior to IRMS analyses, the

samples were pretreated with 1M HCl to remove inorganic carbon. Glycine and cellulose standards were used to detect and correct for instrument drift (Zan et al., 2012b).

Concentrations of metals (Fe, Al, Cu, Zn, Ca, Mg, Mn, Ti, V, Co, Ni, Cd, Cr) in sediments were determined by ICP-MS (Agilent 7500 Series, USA) after ~0.2 g of sediment was digested in a mixture of concentrated HNO₃-HCl-HF (1:3:6, v:v) under microwave condition (Zan et al., 2012b). The sediment reference material of SUD-1 (National Water Research Institute, Canada) was used to evaluate the accuracy of analytical method with recoveries (%) of between 85% and 110%. Quality control was assured by the analysis of duplicate samples, blanks, and standard material (SUD-1). Measurement errors were less than 9%.

As and Hg in samples and blanks were measured by cold vapor atomic fluorescence spectrometry. Quality assurance and quality control procedures included the use of certified reference materials (soil GBGSS-2), procedural blanks, standard-spiked blanks, and replicates (every 12 samples) (Guo et al., 2015a). The average recoveries of Hg and As were 98.3% and 97.9%.

2.3. Sediment background metal concentrations and pollution indices

Background metal concentrations in each sediment core were calculated using the Paleocological Investigation of Recent Lake Acidification (PIRLA) method (Binford, 1990). In this method, the mean (\bar{x}) and standard deviation (δ) of a set of apparently constant values found at the bottom of the core were calculated. If the next concentration value was less than the mean value plus one standard deviation ($\bar{x} + \delta$), the concentration value would be included in this set of constant values, and the mean and standard deviation would be recalculated. The procedure continued until the next concentration level was greater than ($\bar{x} + \delta$) (Zan et al., 2011).

Enrichment factors (EF), the geoaccumulation index (I_{geo}) and anthropogenic factor (AF) were used to evaluate metal pollution in these sediments, similar to other studies (Chabukdhara and Nema, 2012; Chakravarty and Patgiri, 2009; Guo et al., 2015a; Barik et al., 2017). The EF is calculated by the following formula:

$$EF = \frac{[Me/Ti]_{sample}}{[Me/Ti]_{reference}}$$

where $[Me/Ti]_{sample}$ is the ratio of the concentration of metal to the reference element (Ti) in the sediment; and $[Me/Ti]_{reference}$ is the ratio of the background concentration of metal to the background value of Ti.

The I_{geo} is another assessment method used to evaluate soil metal pollution and calculated as follows:

$$I_{geo} = \log_2 \frac{C_n}{K \times C_b}$$

where: C_n is the measured concentration of the element n in the sedimentary core, C_b is the background concentration of the element n ; and the constant K is a coefficient used to eliminate the change of background values caused by regional differences (usually assumed at 1.5) (Guo et al., 2015a).

The AF was used to estimate anthropogenic input of metals to the sediment of the aquatic ecosystem (Barik et al., 2017). The AF value of a particular metal is equal to the ratio of the concentration in the surface sediment to the concentration in the deepest part of the sediment core of the metal.

2.4. Data processing

Meteorology data were collected from the CN05.1 dataset, which was constructed using the anomaly approach during the interpolation with more station observations (~2400) in China (Xu et al., 2009). Relationship between metals, nutrients and climate factors of three

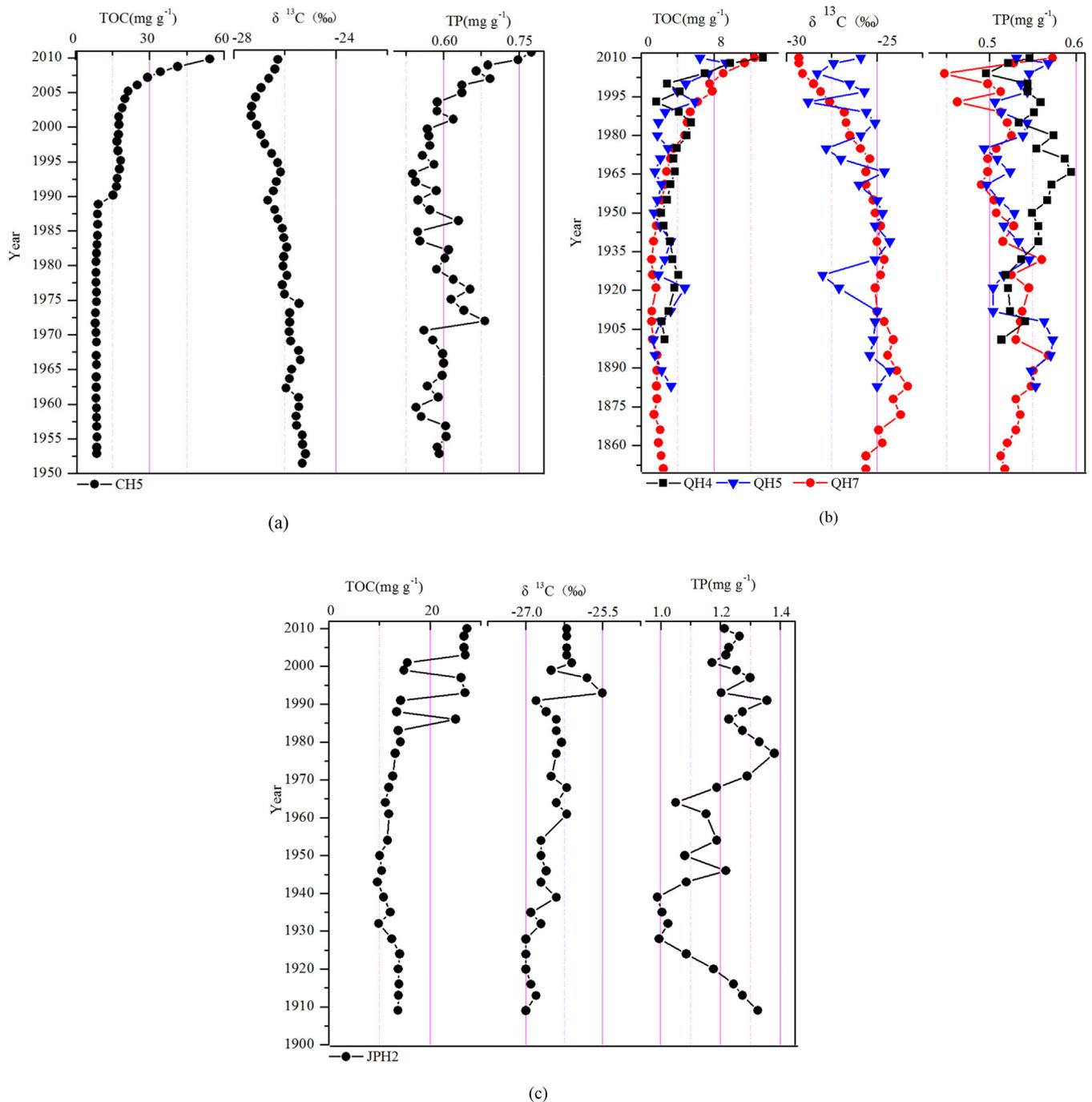


Fig. 2. Vertical concentration profiles of TOC, $\delta^{13}\text{C}$ and TP in Lake Chenghai (a), Lake Qionghai (b), and Lake Jingpohu (c) sediment cores.

studied lakes was identified by Spearman correlation analysis with 2-tailed test of significance and cluster analysis (Squared Euclidean distance, Between-groups linkage) using the software packages SPSS 16.0 for Windows. All data in this study was plotted by the software packages Origin 8.

3. Results and discussion

3.1. Vertical profiles of TOC, $\delta^{13}\text{C}$ and TP

The variables TOC, $\delta^{13}\text{C}$ and TP in lake sediments have been used to deduce long-term variations in trophic status, and to distinguish sources of organic matter (e.g., Zan et al., 2012a; Guo et al., 2015; Mays et al., 2017). In core CH5 from Lake Chenghai, concentrations of TOC, $\delta^{13}\text{C}$

and TP varied in the ranges of 8.16–54.29 mg g^{-1} , -27.31 to -25.20‰ , and 0.54–0.77 mg g^{-1} , respectively (Fig. 2a). The trends of TOC and TP showed a positive excursion after the 1990s, corresponding to the beginning of large-scale cultivation of spirulina here in 1994 (Huo et al., 2011; Zan et al., 2012a). The increasing quantities of AOM derived from spirulina cultivation caused more serious eutrophication of the lake (Posch et al., 2012; Shi et al., 2017). Sedimentary $\delta^{13}\text{C}$ signatures have often been used to deduce changes in the flux of organic matter to aquatic systems over time, based on the different carbon isotopic ratios characteristic of different organic matter types (e.g., Meyers, 1997; Lücke et al. 2003; Mays et al., 2017). C3 and C4 land plants use atmospheric CO_2 ($\delta^{13}\text{C} \sim -7\text{‰}$) to produce average $\delta^{13}\text{C}$ values of -27 and -14‰ , respectively, while $\delta^{13}\text{C}$ values in lake algae are generally below -25‰ (Lücke et al., 2003; Mays et al., 2017).

Table 1
Geographic and limnological features of the studied lakes.

	Lakes	Sample sites	Positions	Depth (m)	Lake area (km ²)	Trophic status	
Yunnan-Guizhou Plateau	Chenghai	CH3	26°32.566'N	100°40.093'E	28	74.6	Mesotrophic
		CH5	26°36.073'N	100°40.352'E	31		
	Qionghai	QH4	27°29.159'N	102°12.037'E	15	27.9	Eutrophic
		QH5	27°29.221'N	102°11.804'E	16		
		QH7	27°29.403'N	102°10.976'E	15		
North-eastern Plain	Jingpohu	JPH2	43°54.368'N	128°58.724'E	11	79.3	Mesotrophic

Based on the data (Fig. 2a), it appears that organic carbon in Lake Chenghai was likely sourced primarily from a mixture of C3 plants and phytoplankton. Therefore, the influence of agriculture and aquaculture on nutrient loading and lake productivity at Lake Chenghai comes from either terrestrial or endogenous sources since 1990s (Table 1).

TOC concentrations in cores QH4, QH5, QH7 from Lake Qionghai ranged between 1.69 and 13.33, 1.35 and 9.30, and 1.18 and 12.42 mg g⁻¹, respectively, and TP ranged between 0.50 and 0.59, 0.49 and 0.57, and 0.44 and 0.57 mg g⁻¹, respectively (Fig. 2b). The $\delta^{13}\text{C}$ values in cores QH5 and QH7 ranged from -28.8 to -24.3‰, and -29.3 to -23.3‰, respectively, and general trends of decreasing $\delta^{13}\text{C}$ values over time were observed, despite some oscillation (Fig. 2b). The trends of TOC concentrations in the three cores from Lake Qionghai are similar, with significant increases after ~1980, which is most likely due to progressively greater discharges of untreated domestic and industrial waste water, and increasing non-point source pollution (especially from agriculture and soil erosion) in the Lake Qionghai watershed (Zan et al., 2014). TOC concentration profiles in Lake Qionghai are similar in form with those from Lake Chenghai, but at much lower mean concentrations. Because industry is relatively underdeveloped in the Lake Qionghai watershed as compared to the Lake Chenghai watershed, wastewater discharges are much lower (Zan et al., 2014).

The profiles of TOC, $\delta^{13}\text{C}$ and TP concentrations in core JPH2 varied over the ranges of 9.62–27.3 mg g⁻¹, -27 to -25.5‰, and 0.99–1.38 mg g⁻¹, respectively (Fig. 2c). All three lakes have been progressively eutrophied by both industrialization and urbanization (Zan et al., 2012a; Huo et al., 2014). Concentrations of TP, the most critical nutrient limiting lake primary productivity on longer time-scales, were much higher in Lake Jingpohu than either Lake Chenghai or Qionghai, due to the heavy use of fertilizers (Huo et al., 2011).

3.2. Metals and their enrichment

The PIRLA procedure was used to deduce metal background concentrations. Background concentrations of Ti, Co, Ni, Cu, Zn and Fe in Lake Chenghai were higher than those in Lakes Qionghai or Jingpohu, while background concentrations of Pb, Ca and Mg in Lake Qionghai were higher than both other lakes (Table 2). Background concentrations of Hg, V, Cr, Co, Ni, Cu, Zn, Fe, Al, and Mg at station QH4 were higher than those at stations QH5 and QH7 (Table 2).

The metal concentration profiles in sediment cores from Lake Qionghai exhibit no significant increases, and show similar ranges in concentration fluctuations in all three sediment cores (Fig. 3b). Concentrations of Cd and Pb show increasing concentrations after ~1980 at stations QH4 and QH7. Concentrations of Co, Ni and Cr at stations QH4, QH5 and QH7 were not enriched, expressed as $EF \approx 1$ (Fig. 4a), and $I_{geo} < 0$ (Fig. 4b). Concentrations of Cd and Pb at stations QH4 and QH7 indicate enrichment since ~1980 ($EF > 1.5$), with the I_{geo} of Cd close to 1 (Fig. 4a, b). AF of Cd at station QH4 and QH7 were 3.07 and 5.44 (Table 3), which greater than 1 significantly showed anthropogenic origin as a source to the lacustrine sediments (Barik et al., 2017). Concentrations of Cd and Pb showed significant correlations with TOC, $\delta^{13}\text{C}$ and inorganic phosphorus ($p < 0.01$) using mean data derived from all three stations in Lake Qionghai (Supplementary information, SI). The correlation coefficients of Cd with TOC, $\delta^{13}\text{C}$, and

inorganic phosphorus are 0.843, -0.78, and -0.435 (all with $p < 0.01$), respectively (SI Table 1). The correlation coefficients of Pb with TOC, $\delta^{13}\text{C}$, and inorganic phosphorus are 0.826, -0.749, and -0.602 (all with $p < 0.01$), respectively (SI Table 1). The primary source of Cd in soils and aquatic environments is phosphatic fertilizers, which explains the connection between Cd and inorganic phosphorus in Lake Qionghai sediments (De et al., 2002; Mirlean and Roisenberg, 2006; Liu et al., 2012). Coal-fired power plants and petrol combustion are important sources of anthropogenic Pb to the atmosphere (Cheng and Hu, 2010; Zhang et al., 2014). Therefore, the most likely explanation of these results is the co-sourcing of Cd, Pb and nutrients, derived from agricultural non-point source pollution, and the proliferation of coal-fired power plants and automobiles in China over the last ~30 years (Mirlean and Roisenberg, 2006; Cheng and Hu, 2010; Shindell and Faluvegi, 2010).

The concentrations of Cu, Zn, Mn, V and Pb in Lake Jingpohu increased after ~1990 (Fig. 3c). Concentrations of Co, Ni, Cr, Pb, and Cd are enriched, but not strongly, with $EF < 1.5$, $I_{geo} < 0$ (Fig. 4c), and $AF > 1$ (Table 3). TOC concentrations are significantly and positively correlated with the concentrations of Mn, V, Cu, Zn, Cd, Pb, Fe, and Al (all with $p < 0.01$), and significantly negatively correlated with the concentrations of Ti and Ca (all with $p < 0.01$) in Lake Jingpohu (SI Table 3). Also, the concentrations of Fe and Mn in Lake Jingpohu are significantly correlated with most of the metals, including V, Co, Cu, Zn, Pb, Al, and Ca (all with $p < 0.01$ SI Table 3). These results indicate that the deposition of most metals, such as V, Co, Ni, and Cu, have been influenced by organic matter and Fe-Mn oxides (Guo et al., 2015).

3.3. Pollution intensity of As and Hg

Background concentrations of As were 6.98 ± 0.47 and $7.21 \pm 0.31 \mu\text{g g}^{-1}$ in cores CH3 and CH5, respectively, 8.13 ± 0.04 , 7.41 ± 0.91 and $8.75 \pm 0.32 \mu\text{g g}^{-1}$ in cores QH4, QH5 and QH7, respectively, and $8.08 \pm 0.08 \mu\text{g g}^{-1}$ in core JPH2 (Table 2). Arsenic was not enriched seriously in sediments of Lakes Chenghai or Qionghai, with $EF < 1.5$, $I_{geo} < 0$ (Fig. 5a, b), and $AF \approx 1$ (Table 3). However, As was enriched in surface sediment of Lake Jingpohu, with $EF = 1.65$, $I_{geo} = 0.11$ (Fig. 5c), and $AF = 1.61$ (Table 3). The concentrations of As and TOC, and TP were significantly and positively correlated in all three lakes (SI Tables 1–3), indicating that increasing phosphorus loading may drive deposition of As (Martin and Pedersen, 2004; Barringer et al., 2007). The migration mechanisms of As at the sediment-water interface are rather complicated. Previous studies have shown that the application of nitrogen fertilizers could accelerate the release of As from bottom sediment to overlying waters under reducing conditions (Uddin and Kurosawa, 2011). While, the predominant mechanism of As release is considered to be the conversion of As^{3+} and As^{5+} into biosynthetic organoarsenic compounds a process that is enhanced via eutrophication, especially by increases in TP (Martin and Pedersen, 2004; Nikolaidis et al., 2004; Mirlean and Roisenberg, 2006; Hasegawa et al., 2009).

Background concentrations of Hg were 43.60 ± 7.67 and $62.00 \pm 6.01 \text{ ng g}^{-1}$ in cores CH3 and CH5, respectively, 56.91 ± 10.59 , 23.25 ± 3.16 and $34.23 \pm 5.62 \text{ ng g}^{-1}$ in cores QH4, QH5 and QH7, respectively, and $76.00 \pm 4.31 \text{ ng g}^{-1}$ in core JPH2.

Table 2
Background concentrations of metals in the three studied lakes.

Elements	Sampling Sites					
	CH3	CH5	QH4	QH5	QH7	JPH2
As ($\mu\text{g g}^{-1}$)	6.98 ± 0.47	7.21 ± 0.31	8.13 ± 0.04	7.41 ± 0.91	8.75 ± 0.32	8.08 ± 0.08
Hg (ng g^{-1})	43.60 ± 7.67	62.00 ± 6.01	56.91 ± 10.59	23.25 ± 3.16	34.23 ± 5.62	76.00 ± 4.31
Ti (mg g^{-1})	6.04 ± 0.24	6.10 ± 0.40	4.65 ± 0.11	4.46 ± 0.24	3.87 ± 0.44	5.53 ± 0.30
Mn (mg g^{-1})	0.85 ± 0.05	0.94 ± 0.06	0.97 ± 0.01	1.01 ± 0.06	0.94 ± 0.02	1.06 ± 0.05
V ($\mu\text{g g}^{-1}$)	188.14 ± 9.39	173.33 ± 10.08	153.86 ± 10.09	131.50 ± 4.80	141.00 ± 8.19	104.12 ± 5.21
Cr ($\mu\text{g g}^{-1}$)	90.34 ± 7.50	100.23 ± 5.07	100.33 ± 10.04	87.83 ± 4.81	92.14 ± 4.39	86.74 ± 4.57
Co ($\mu\text{g g}^{-1}$)	22.47 ± 0.95	23.50 ± 1.34	21.27 ± 1.12	20.20 ± 1.02	20.93 ± 0.51	21.6 ± 0.90
Ni ($\mu\text{g g}^{-1}$)	61.71 ± 4.17	62.87 ± 3.83	53.80 ± 1.92	49.10 ± 2.43	50.11 ± 2.30	44.16 ± 2.97
Cu ($\mu\text{g g}^{-1}$)	64.91 ± 3.16	62.26 ± 6.37	37.50 ± 1.00	33.93 ± 5.21	33.94 ± 1.24	34.13 ± 2.17
Zn ($\mu\text{g g}^{-1}$)	128.86 ± 6.69	128.64 ± 7.69	126.92 ± 4.83	120.17 ± 10.25	122.00 ± 3.00	122.50 ± 6.28
Cd ($\mu\text{g g}^{-1}$)	0.39 ± 0.08	0.28 ± 0.05	0.31 ± 0.04	0.32 ± 0.01	0.25 ± 0.05	0.28 ± 0.06
Pb ($\mu\text{g g}^{-1}$)	24.14 ± 2.15	26.80 ± 1.69	30.83 ± 0.55	30.53 ± 1.71	30.21 ± 1.76	20.49 ± 1.68
Fe (mg g^{-1})	47.53 ± 2.25	48.99 ± 2.02	46.96 ± 1.58	44.30 ± 1.97	43.63 ± 0.75	46.07 ± 2.05
Al (mg g^{-1})	94.30 ± 6.38	101.30 ± 5.63	102.60 ± 3.68	92.24 ± 4.11	89.88 ± 7.90	85.01 ± 4.51
Ca (mg g^{-1})	27.56 ± 2.01	18.72 ± 2.48	28.82 ± 1.26	25.29 ± 3.77	19.75 ± 0.47	9.97 ± 0.61
Mg (mg g^{-1})	18.52 ± 0.79	19.48 ± 1.11	29.91 ± 0.82	27.19 ± 3.54	24.46 ± 3.26	14.18 ± 0.84

The concentrations of Hg in sediment cores from Lake Chenghai fluctuated in the deeper sections without significant enrichment, $EF < 1.5$, $I_{geo} < 0$ (Fig. 5a). After ~2007, concentrations of Hg increased sharply in Lake Chenghai, with $EF = 2.0$, and $I_{geo} = 0.6$. AF of Hg at station CH4 and CH5 were 1.80 and 2.18 respectively (Table 3), representing moderately anthropogenic polluted condition. Enrichment of Hg in sediments from Lake Qionghai began in the 1970s, with $EF > 1.5$, $I_{geo} > 0$ (Fig. 5b). Mercury is different from other heavy metals, in part because of its volatility, which allows it to be transported

over long distances in the atmosphere (e.g., Covelli et al., 2016; Ramasamy et al., 2017). Therefore, watersheds located far from Hg sources can be contaminated with Hg through atmospheric wet-dry deposition (Covelli et al., 2016; Ramasamy et al., 2017).

3.4. Impacts of climate change on metals and nutrient deposition

Climate change can have a significant impact on the historical deposition of various elements in lake sediments, especially so in high-

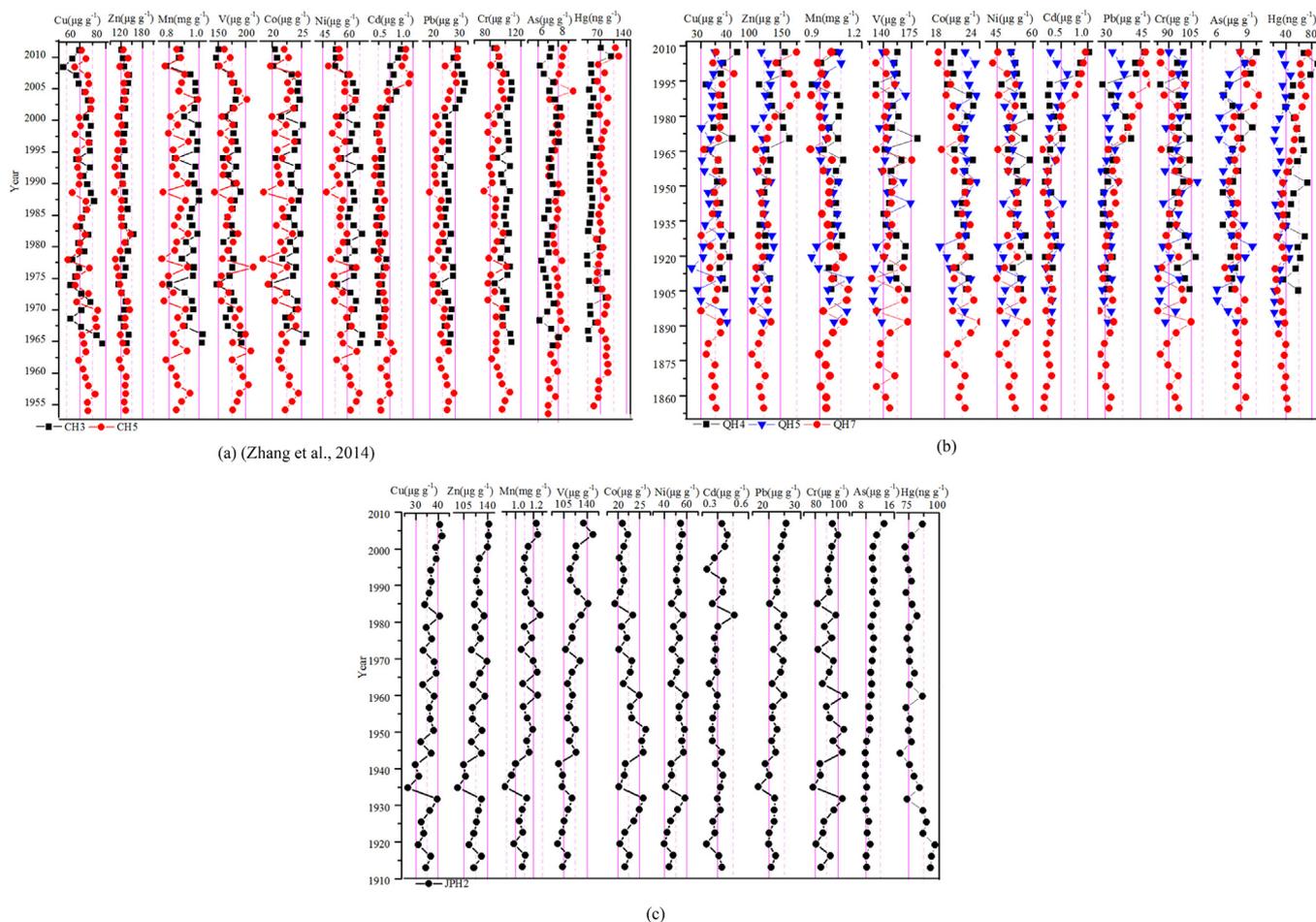


Fig. 3. Vertical profiles of metal concentrations in Lake Chenghai (a), Lake Qionghai (b) and Lake Jingpohu (c) sediment cores.

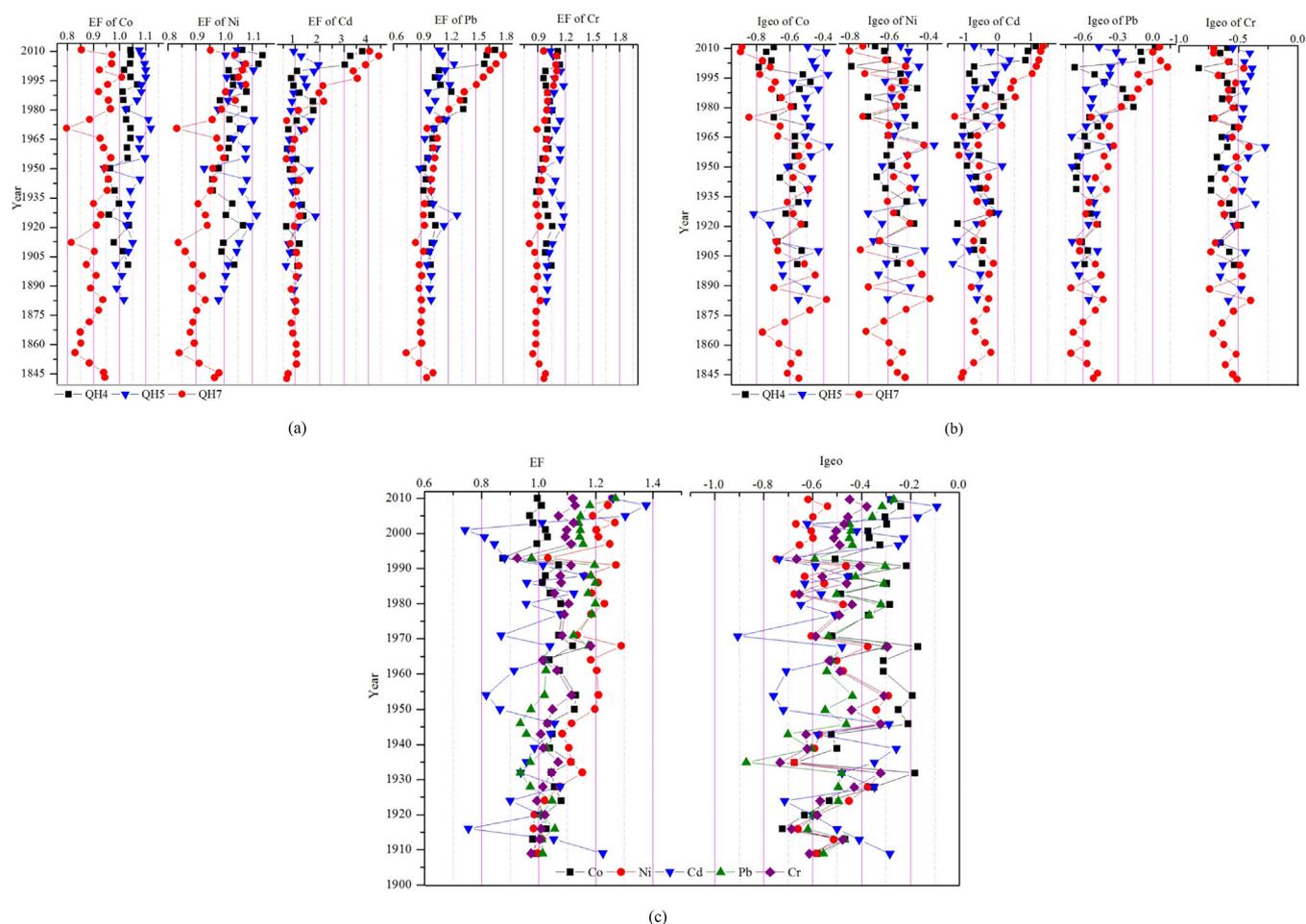


Fig. 4. EF and I_{geo} values for heavy metals in Lake Qionghai (a and b), and Lake Jingpohu (c) sediment cores.

Table 3
Anthropogenic factor of metals in the three studied lakes.

Elements	Sampling Sites					
	CH3	CH5	QH4	QH5	QH7	JPH2
As	0.98	1.22	1.30	1.04	1.01	1.61
Hg	1.80	2.18	1.15	1.18	1.76	0.93
Ti	0.80	0.95	0.90	0.99	0.87	0.98
Mn	1.07	1.00	1.03	1.04	1.04	1.14
V	0.78	0.92	0.92	1.00	0.97	1.30
Cr	0.80	0.93	0.96	1.03	0.87	1.12
Co	0.81	0.99	0.91	1.04	0.79	0.98
Ni	0.78	0.88	0.92	1.05	0.86	1.23
Cu	0.77	0.93	1.10	0.89	1.00	1.18
Zn	0.88	0.95	1.20	0.98	1.72	1.18
Cd	3.03	2.71	3.07	0.94	5.44	1.00
Pb	1.13	1.15	1.52	1.06	1.48	1.22
Fe	0.83	0.99	0.97	0.97	0.94	1.08
Al	0.82	0.94	0.95	1.04	0.91	1.01
Ca	1.07	1.16	1.22	0.70	1.61	0.79
Mg	1.05	1.35	0.79	0.88	0.91	1.10

altitude (plateau) closed, or semi-enclosed lakes (O’Beirne et al., 2017; Xu et al., 2017). According to meteorological data from the CN05.1 dataset (Xu et al., 2009), the average annual air temperature increased by 1.031, 0.619, and 1.472 °C in the watersheds of Lakes Chenghai, Qionghai, and Jingpohu from 1961 to 2016 (Fig. 6a). Annual average air temperatures and TOC concentrations were strongly and positively correlated (all with $p < 0.01$) in Lakes Chenghai and Qionghai (SI Tables 1 and 2), suggesting that increasing average air temperatures

drove increased primary productivity in those lakes (Posch et al., 2012; Carey et al., 2012; Chen et al., 2016; Xu et al., 2017). However $\delta^{13}C$ concentrations had a significant negative correlation ($p < 0.05$) with annual average air temperature at Lake Chenghai (SI Table 2). This suggests that global warming has enhanced algal productivity, resulting in increased production and deposition of endogenous organic matter (Yang et al., 2016; O’Beirne et al., 2017). The same conclusion was demonstrated by the study in Lake Taihu, China, that sedimentary nutrient enrichment was contributed to extreme high temperature by accelerating cyanobacterial bloom formation (Yang et al., 2016). Warming temperature is expected to reinforce the problem of lake eutrophication and the risk of harmful algae blooms, which is a major challenge for sound water resource management (Carey et al., 2012).

Climate change can affect the transport, enrichment, speciation, and bioavailability of metals in the environment (Rothwell et al., 2007; Monteiro et al., 2012; Visser et al., 2012; Schroth et al., 2015). Annual average air temperatures were significantly and positively correlated with Cd and Pb (all with $p < 0.05$) in Lakes Chenghai and Qionghai (SI Tables 1 and 2). Generally, Cd and Pb are primarily supplied to the environment from anthropogenic sources, including phosphatic fertilizers and the combustion of fossil fuels (Mar and Okazaki, 2012; García-Ordiales et al., 2016). Increased average temperatures and precipitation may result in increased leaching of heavy metals (including Cd and Pb) from watershed rocks, sediments and soils, and fluxes to receiving waters (e.g., Visser et al., 2012; García-Ordiales et al., 2016). Due to the potential mobility of Cd and Pb, climate change that produces higher average temperatures and precipitation may increase their transport from agricultural lands (Ockenden et al., 2016; Saleem et al., 2018). Also warming temperature accelerated the growth of aquatic plants,

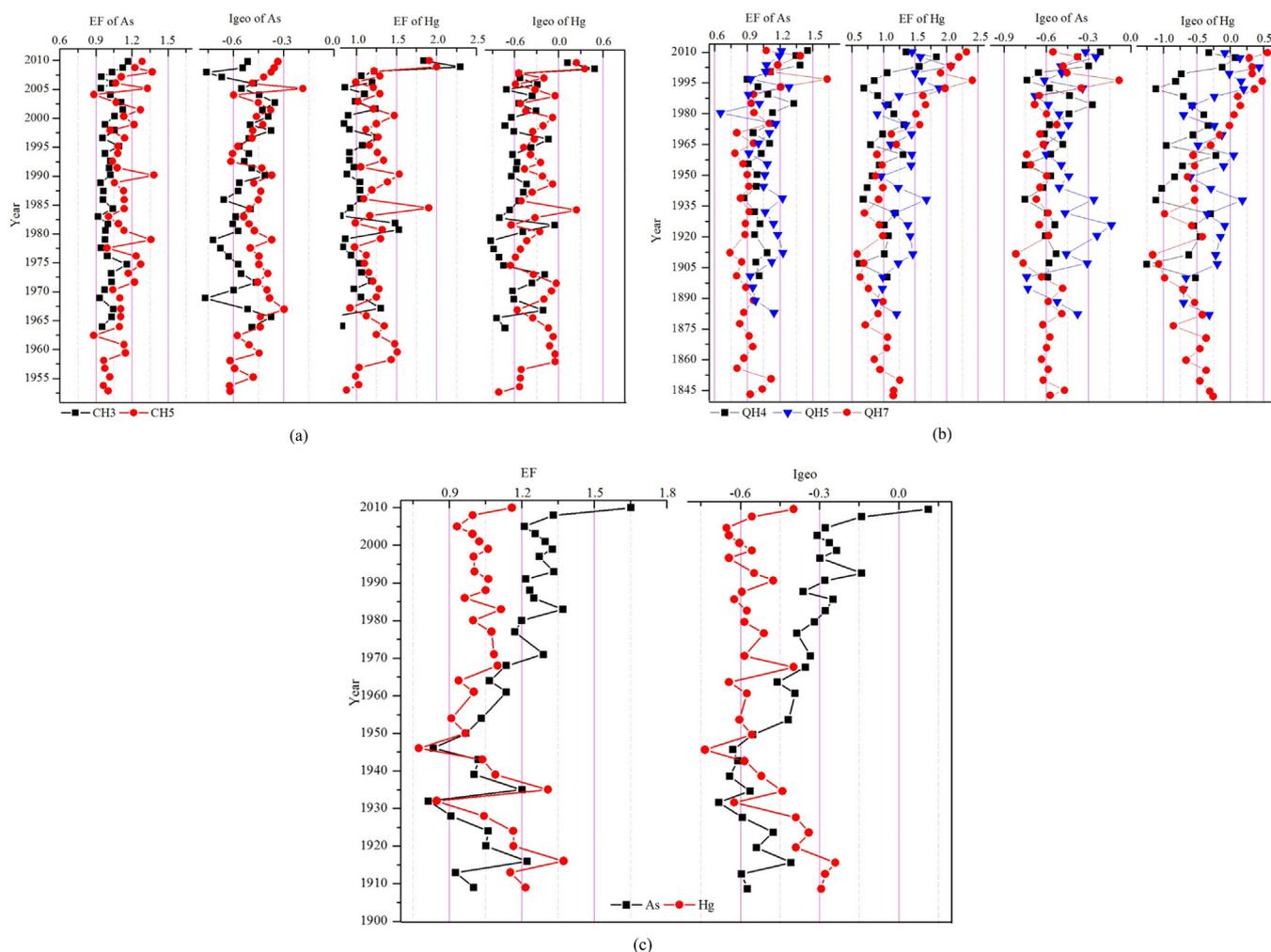


Fig. 5. EF and I_{geo} of As and Hg in Lake Chenghai (a), Lake Qionghai (b) and Lake Jingpohu (c) sediment cores.

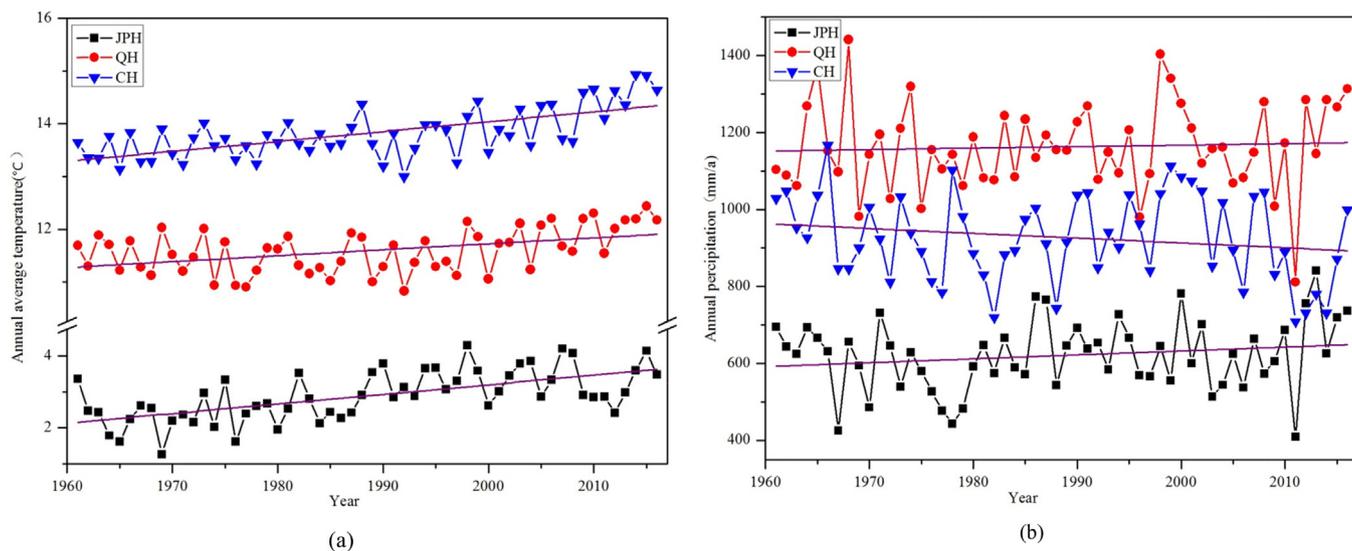
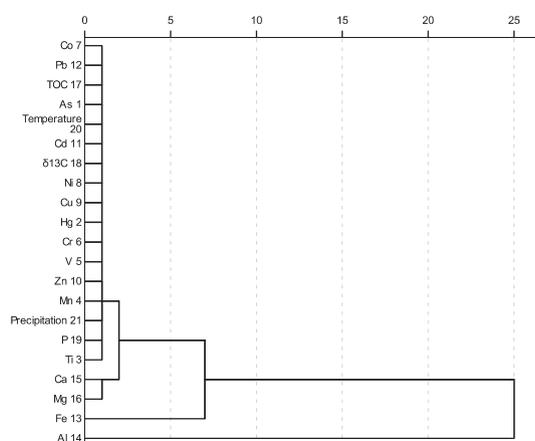


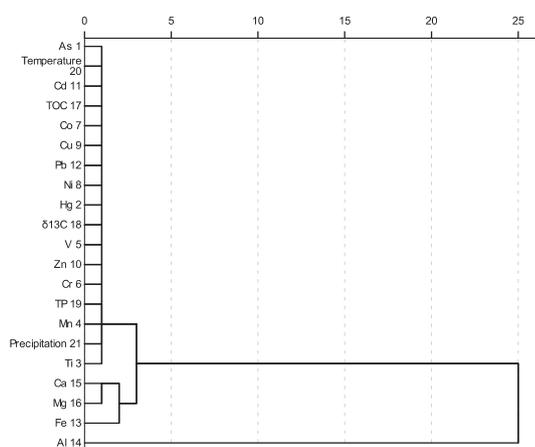
Fig. 6. Variations of annual average temperature (a) and annual precipitation (b) in the Lake Chenghai, Lake Qionghai and Lake Jingpohu watersheds from 1961 to 2016 (CN05.1 dataset; Xu et al., 2009).

which could affect the enrichment of metals in the sediment by influencing binding capacity of metals with organic matters (Duan et al., 2014). The average annual precipitation varied by -68.81, 21.41, and 55.59 mm at Lakes Chenghai, Qionghai, and Jingpohu, respectively,

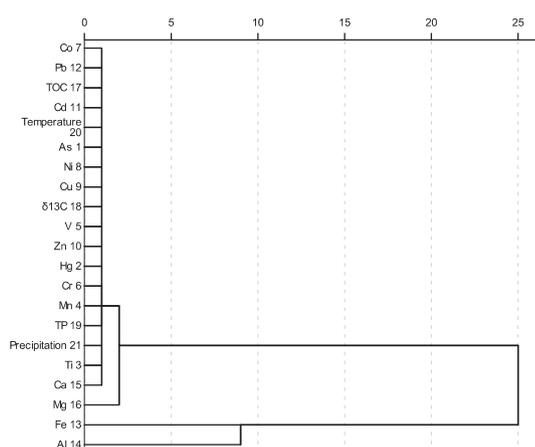
from 1961 to 2016 (Fig. 6b). Previous studies showed that the transport of dissolved metals (e.g. Pb and V) could be promoted by strong rainfall through modulate baseflow and stormflow metal concentrations in streams of UK (Rothwell et al., 2007). Future climate change with rising



(a)



(b)



(c)

Fig. 7. Dendrograms derived from the average linkage hierarchical cluster analysis (between groups) for Lake Chenghai (a), Lake Qionghai (b) and Lake Jingpohu (c).

temperature, strong rainfall and extreme weather may have adverse impacts on the distribution and toxicity of metals in the aquatic ecosystem (Wu et al., 2017).

The results of cluster analysis show that the variables temperature,

precipitation, nutrient concentrations (TOC, $\delta^{13}\text{C}$, TP), and the concentrations of As, and heavy metals (except Ca, Mg, Fe, Al) were classified into one category at Lakes Chenghai and Qionghai (Fig. 7a, b). This indicates that heavy metals, As, and nutrients have similar sources (terrestrial inputs), and are influenced by temperature and precipitation. Calcium and Mg were classified into another category at Lakes Chenghai and Qionghai (Fig. 7a, b). This is likely because Ca and Mg are major components of rocks, and are released by natural weathering processes, and so are derived from sources different from the other metals (Wu and Xia, 2014). Iron and Al were classified into third and fourth categories, respectively, in all three lakes (Fig. 7). As constant elements, Fe and Al are distinguished from heavy metals in terms of their geochemical behavior (García-Ordiales et al., 2016).

4. Conclusions

As nutrient supplies to these lakes have changed, the enrichment of heavy metals has increased to different degrees since ~1980 in Lakes Chenghai, Qionghai, and Jingpohu. Most heavy metals characterized were minimally enriched as assessed by EF, I_{geo} and AF, except for Cd, Pb and Hg, which were moderately enriched in sediments from Lakes Chenghai and Qionghai. The significant correlations between heavy metals and nutrients indicate that organic matter has a strong influence on the processes of adsorption and deposition of heavy metals in the bottom sediments of these lakes, or alternatively, that the nutrients and heavy metals have similar anthropogenic sources. Cluster analysis showed that average temperature and precipitation affected the deposition of both heavy metals and nutrients. The higher average temperatures led to higher TOC concentrations, influencing the deposition of heavy metals. The increased average temperatures may also drive secondary emissions of Hg. Also, it is likely that increasing average annual precipitation is driving both increasing agricultural non-point source pollution and soil erosion, further increasing the inputs of heavy metals and nutrients.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.ecolind.2018.05.059>.

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