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Huguangyan Maar Lake (SE China): A solid record of atmospheric mercury pollution history in a non-remote region

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ABSTRACT

Mercury is a highly toxic metal that can cause harm to environment and human health. As atmospheric deposition is the main source of total Hg input to aquatic system in remote and pristine regions, almost all the studies on atmospheric Hg pollution history concentrated in these areas, while the studies in non-remote areas are much limited, especially for the long history records. In this study, Huguangyan Maar Lake, an undisturbed lake system at low altitude in China, was selected to reconstruct the atmospheric mercury pollution history. Variation patterns of TOC, Hg and non-residual Sr in the sediment core indicated that, compared to the direct atmospheric Hg deposition, the effect of either Hg scavenging from water column by algae or the catchment inputs of previously deposited Hg on the Hg accumulation in the lake sediment was limited. The sediment Hg content in Huguangyan Lake was mainly controlled by the atmospheric Hg deposition, and thus accurately reflected the atmospheric Hg pollution history. The Hg_a (Hg content from atmospheric deposition) in Huguangyan Lake presented a comparable variation pattern to that in remote sites. It had the same variation trend as the global atmospheric Hg before 1950 CE, which could be attributed to the Industrial Revolution. After that, it was mainly controlled by Hg emissions from Asian countries. The variation of Hg_a also indicated that atmospheric Hg deposition accelerated significantly since 2000 CE. This study, along with other investigations in remote sites in China, showed that the sediment Hg in Huguangyan Lake responded to the atmospheric Hg pollution more sensitively than in the alpine regions. It should be noted that, the more intensive acceleration of Hg deposition in Huguangyan Lake may imply that the South of China suffered from much more serious atmospheric Hg pollution than previous studies revealed.

1. Introduction

Mercury (Hg) is a highly toxic metal that can cause harm to environment and human health. It is well known that Hg as a gas phase can travel for a long distance in the atmosphere, so aquatic systems even in pristine and remote regions can be impacted by Hg pollution through wet and dry deposition from the atmosphere (Feng et al., 2011; Lindqvist et al., 1991). Now increasing evidences indicate that Hg has deposited in the Arctic and highly affected the ecosystems (Lindeberg et al., 2006). As the atmospheric deposition is the main source of total Hg input to aquatic system in these remote and pristine regions (Hines and Brezonik, 2007), most studies on atmospheric Hg pollution history concentrated in these areas, while the studies in non-remote areas are relatively limited, especially for the long history records. How the atmospheric Hg pollution varied in the past in non-remote areas needs further illumination, because it is more closely related to human health.

Lake sediments are natural archives that provide a history record of environmental change within a lake and its catchment as well as trends in atmospheric deposition to the lake surface (Yang et al., 2010). Meanwhile, it can tell us the natural background levels of elements in the catchment in addition to information about the impact of human activity on the environment. Therefore, lake sediments provide a key to reconstruct the history of climate and environment change, including pollutant history and evolution (Hao et al., 2013). Up to now, numerous scholars have successfully used lake sediments to reconstruct the history of Hg pollution (Hermanns and Biester, 2013; Phillips et al., 2011; Yang et al., 2010; Fitzgerald et al., 2005; Perry et al., 2005). And almost all of the studies showed a rise in atmospheric Hg fluxes due to the Industrial Revolution and economic growth after 1850s CE. There are some studies concerning continuous Hg record by lake sediments from non-remote areas (e.g., Kading et al., 2009; Li et al., 2013; Shi et al., 2010; Yang and Rose, 2003; Zhang et al., 2011), but these lakes are not closed, which may result in that the effect of the inflow and outflow on the accumulation rate of atmospheric deposited Hg in the past is hard to

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evaluate. Moreover, some inflows have run through the area with intense human activity, which makes the Hg source of the lakes more complicated.

Huguangyan Lake is situated approximately 10 km south-west of Zhanjiang City in the Lei-Qiong volcanic field. It is a closed maar lake with no surface inflow or outflow, and considered as a reliable and high-resolution natural archive in the paleoclimate/paleoenvironment studies (Zeng et al., 2012; Mingram et al., 2004; Fuhrmann et al., 2003; Chu et al., 2002). The area ratio of the catchment and lake surface is only 1.5. The catchment comprises the inner slope of crater rim and is well covered by the evergreen sub-tropical forest. The human activities in the catchment are much limited. Hg inputs to an undisturbed lake system are from atmospheric deposition and its catchment (Yang and Smyntek, 2014). Therefore, Huguangyan Lake was selected to reconstruct the history of atmospheric mercury pollution in non-remote regions in China.

2. Material and methods

2.1. Regional setting

Huguangyan Lake (21 °9′N, 110 °17′E) is located on the low-lying Leizhou Peninsula in the tropical region of South China (Fig. 1), 23 m a.s.l. and only 4 km off the present coastline. It is mainly controlled by the East Asian monsoonal system (Fuhrmann et al., 2003). Seasonal reversals in the wind direction between summer and winter steer warm and humid air from the southwest and southeast and cold and dry winds from the northeast (Fuhrmann et al., 2003), with 90% of the total mean annual precipitation of 1567 mm between April and October (Chu et al., 2002). The dry season is from November to March. The annual mean temperature for many years is 23 °C. The lake is meromictic with a sharp temperature gradient (thermocline) between 6 and 13 m depth.

Huguangyan Lake is a closed maar lake and its crater basin was created from basaltic phreatomagmatic eruptions (Chu et al., 2002). The tephra ring is 10.58 m above the lake surface and consists of pyroclastics. The lake has a surface area of 2.3 km^2 and a catchment area of 3.5 km^2. The catchment comprises only the inner slopes of the crater rim and is well covered by the evergreen sub-tropical forest. The lake has no surface inflow or outflow. The maximum water depth is 22 m. Hydrochemical data of Huguangyan Lake (Mingram et al., 2004) (Table 1) demonstrate its low salinity, which implies a high ratio of direct precipitation into the lake and the inflow of mineralized ground water. The lake water is weakly alkaline with a pH of 7.6. Primary production of the lake is likely limited by the availability of soluble reactive phosphorus (SRP).

2.2. Material and analysis

Sediment core F was retrieved from the deep water part of Huguangyan Lake in December 2004 using a gravitational sediment sampler and a polyethylene tube with a diameter of 59 mm. The core with a length of 117.5 cm was sectioned at approximately 1 cm intervals, and 106 samples were collected in total. The dating of the sediment core was based on the analysis of ^{14}C, ^{210}Pb, and ^{137}Cs. Total carbon (TC) and total nitrogen (TN) were measured by the element analyzer. Total organic carbon (TOC) was calculated as TC minus inorganic carbon (IC). The details are described in Ref Zeng et al. (2012).

The upper 80 samples were used for Hg analysis. For total Hg analysis, 0.2–0.3 g dry sediment samples were digested at 95 °C in a water bath, with a mixture acid (1:3 HCl + HNO_3) (Qiu et al., 2006). Then a suitable aliquot of digested sample solution was measured using cold-vapor atomic absorption spectrometry (CV-AAS), with a detection limit of 0.01 ng g^{-1}. Geogenic element zirconium (Zr) in the sediment samples were analyzed by a Spectra XLAB2000 X-ray fluorescence (XRF) spectrometer.

2.3. Calculation of atmospheric Hg

Hg in lake sediment is from atmospheric deposition and catchment inputs, including the anthropogenic and natural source. In Huguangyan Lake, the human activity in the catchment is much limited, and the anthropogenic source is almost the same as the atmospheric deposition. However, the changing fluxes of terrestrial material could influence the

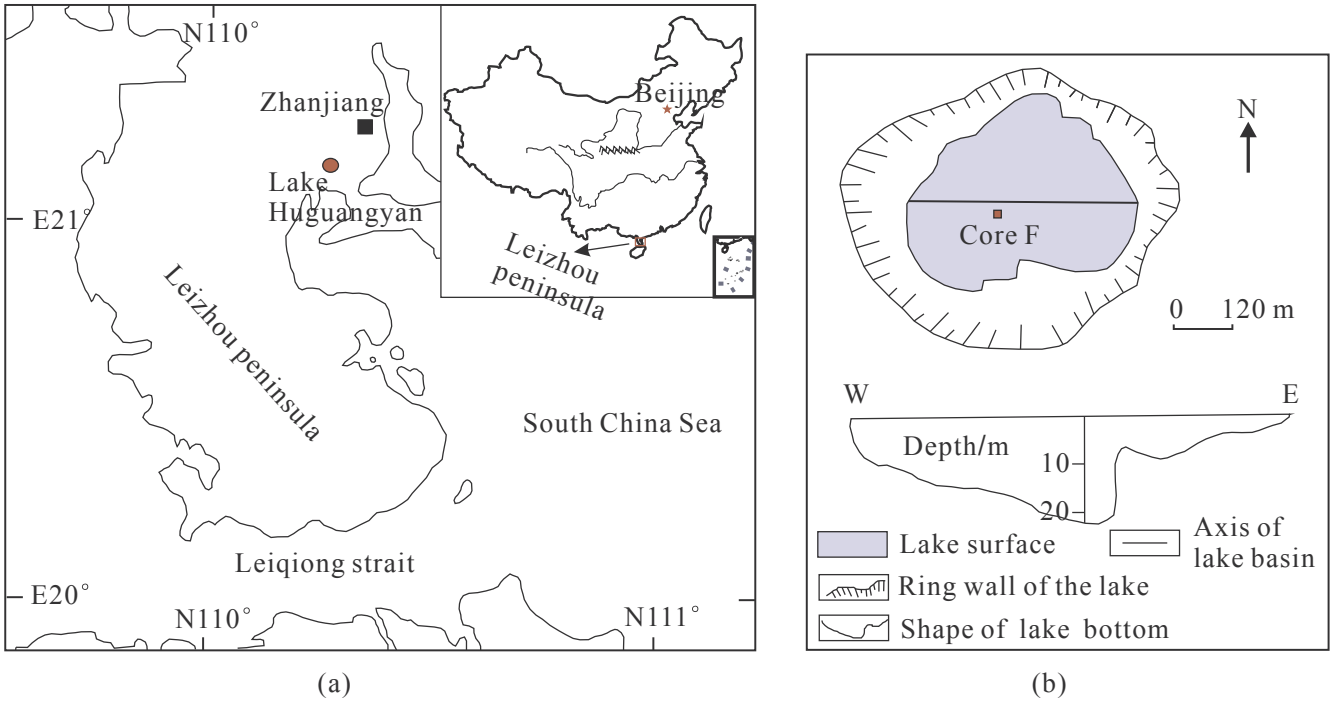

Fig. 1. The location of sample site. (a) The location of Huguangyan Lake. (b) The shape of Huguangyan Lake. The small red block in (b) shows the position of sediment core F. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Surface water composition of Huguangyan Lake (October 10, 2001)(Mingram et al., 2004).

Cations	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Fe^{2+} (mg/L)	Mn^{2+} (mg/L)	Sr^{2+} (mg/L)	Ba^{2+} (mg/L)	Total cations (mEq/L)
	5.8	2.3	6.1	6.1	0.006	0.001	0.047	0.004	1.12
Anions	F^- (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	DIC (mg/L)	Nutrients	Si (mg/L)	SRP (mg/L)	Total anions (mEq/L)
	0.15	7.7	0.7	9.6	8.3		0.5	< 0.01	1.13

total flux of Hg into lakes and sediments (Fitzgerald et al., 2005; Perry et al., 2005). In this case, the evaluation of atmospheric Hg records is challenging, as the signals of atmospheric Hg can be masked by terrestrial Hg fluxes and changing erosion rates (Bookman et al., 2010; Lindeberg et al., 2006). For tracing Hg fluxes from natural sources to the sediments, Zr has been widely used, since Zr is an inert lithogenic reference element and forms mineral components which are resistant against weathering. Therefore, Zr was employed to calculate the natural contribution to the Hg from the catchment in this study.

In a sediment core, the sediment natural contribution fraction is Zr_s/Zr_b, where Zr_s and Zr_b are the concentrations of Zr in the sample and in the background with no anthropogenic impact in the core, respectively. The natural contribution to the Hg concentration in a sample is as follows (Yang and Smyntek, 2014):

$$Hg_{bc} = (Zr_s/Zr_b) \times Hg_b \quad (1)$$

where Hg_b is the Hg concentration in the background sediments. Therefore, the contribution of atmospheric deposition to the total Hg concentration of the sample is as follows:

$$Hg_a = Hg_t - (Zr_s/Zr_b) \times Hg_b \quad (2)$$

where Hg_t is the total concentration in the sample.

3. Results

3.1. Chronologies and sedimentation rates of the core

The cored sediment in Huguangyan Lake consists of homogeneous greenish-grey gyttja without clear lamination. ^{14}C, ^{210}Pb and ^{137}Cs were used to date the sediment core (refer to Zeng et al. (2012) for detail). The ^{210}Pb dating result was confirmed by the ^{137}Cs data, which also indicated the stable sediment accumulation and good preservation conditions in Huguangyan Lake. Linear interpolation between radiocarbon measurements from six terrestrial plant macrofossils is used to calculate sediment age by assuming that the sediment accumulation rate between the dated levels was linear. The samples analyzed in this study recorded the deposition history of the past over 600 years.

3.2. Mercury, Zr, and TOC records in the sediments

It appears that Hg_t concentrations in the sediment core were relatively constant and kept low values before the middle of 19th century, especially before 1700 CE. From 1350 to 1700 CE, Hg_t concentration varied from 15 to 45 ng g^{-1}, with an average value of 26.7 ng g^{-1}. From 1700 to 1850 CE, Hg_t concentration increased gently and varied between 38 and 78 ng g^{-1}, with an average value of 54.2 ng g^{-1}. Around 1850 CE, there was an abrupt increase in Hg_t concentration, and then it increased gradually and continuously until about 2000 CE. During this period, Hg_t concentration ranged from 104 to 216 ng g^{-1}, with an average value of 144.5 ng g^{-1}. After 2000 CE, Hg_t concentration increased sharply, as shown in Fig. 2a.

The concentrations of Zr were low and fluctuated around 146 μg g^{-1} before 1700 CE, and then gradually increased (Fig. 2b). The relatively high values occurred after 1800 CE.

In this study, as the Hg_t concentrations were relatively constant and kept low values before 1700 CE, the mass weighted average concentration of Hg_t and Zr were considered as background concentration of them, respectively. Based on the Eqs. (1) and (2), Hg_a was obtained. Hg_a concentrations varied from 6.3 to 356 ng g^{-1} and showed a very similar variation trend with Hg_t, as shown in Fig. 3. The Hg_a accumulation flux for the lake basin was achieved based on the sedimentation rate and the ratio of the lake area and catchment area. As the sedimentation was relatively constant since 1650 CE (Zeng et al., 2012), the Hg_a accumulation flux varied as the same as Hg_a.

Vertical profiles of TOC and TN are similar to each other, with the contents in the range of 0.86–5.48% and 0.15–0.65%, respectively (Fig. 2C). Relatively low levels of TOC and TN were found before 1500 CE and in the period of 1750–1940 CE. TOC/TN ratios in sediments are generally low, most of which are less than 9.

4. Discussion

4.1. Influence of organic matter accumulation

Many studies have proposed that, besides atmospheric deposition and soil erosion, the accumulation of organic matter could significantly influence Hg accumulation records and possibly mask atmospheric deposited Hg signals (Hermanns and Biester, 2013; Teisserenc et al., 2011; Bookman et al., 2010; Rydberg et al., 2010; Perry et al., 2005). Significant associations between TOC and the distribution of Hg have been observed in sediments (Wu et al., 2013; Kainz and Lucotte, 2006; Kainz et al., 2003; Mirlean et al., 2003). These correlations led to the hypothesis that recent records of Hg in sediments of higher latitude lakes could have been confounded by scavenging of Hg from the water column by algae so that Hg concentrations or fluxes observed in sediments might not accurately represent a historical deposition of Hg (Stern et al., 2009). However, a recent comparative study in 14 Canadian Arctic and sub-Arctic lakes (Kirk et al., 2011) suggested that scavenging by algae was not an important process governing Hg fluxes to sediments because some Arctic lakes were simultaneously experiencing greater algal abundance and lesser deposition of Hg. To verify whether Hg variation in the sediments of Huguangyan Lake could reflect the atmospheric Hg deposition history, the influence of organic matter was discussed.

TOC and TN in lacustrine sediments are indicative of the productivity (Meyers, 1997). The atomic TOC/TN ratio can roughly reflect the proportion of allochthonous (terrestrial) vs. autochthonous (algal) organic matter, while the former has a ratio of greater than 20, and the latter is typically 4–10 (Meyers, 1997). TOC and TN in Huguangyan Lake varied in almost the same pattern (Fig. 2c) and significantly positively correlated with each other ($R^2 = 0.95$, $p < 0.001$, $n = 80$), which may suggest that both TOC and TN are bond on organic matter. TOC/TN ratios in the sediments of Huguangyan Lake are low, varying between 5 and 11. Some processes, such as diagenetic alteration of organic matter and the sorption of ammonia by clays, may change the TOC/TN ratio and accordingly influence the validity of using TOC/TN ratio to reflect organic matter source (Meyers, 1997). However, our previous work showed that TOC and the content of biogenic silica varied with broad similarities and positively correlated with each other ($R^2 = 0.527$, $p < 0.001$, $n = 109$) (Chen et al., 2012). Therefore, we concluded that the organic matter were derived largely from planktonic algae in Huguangyan Lake.

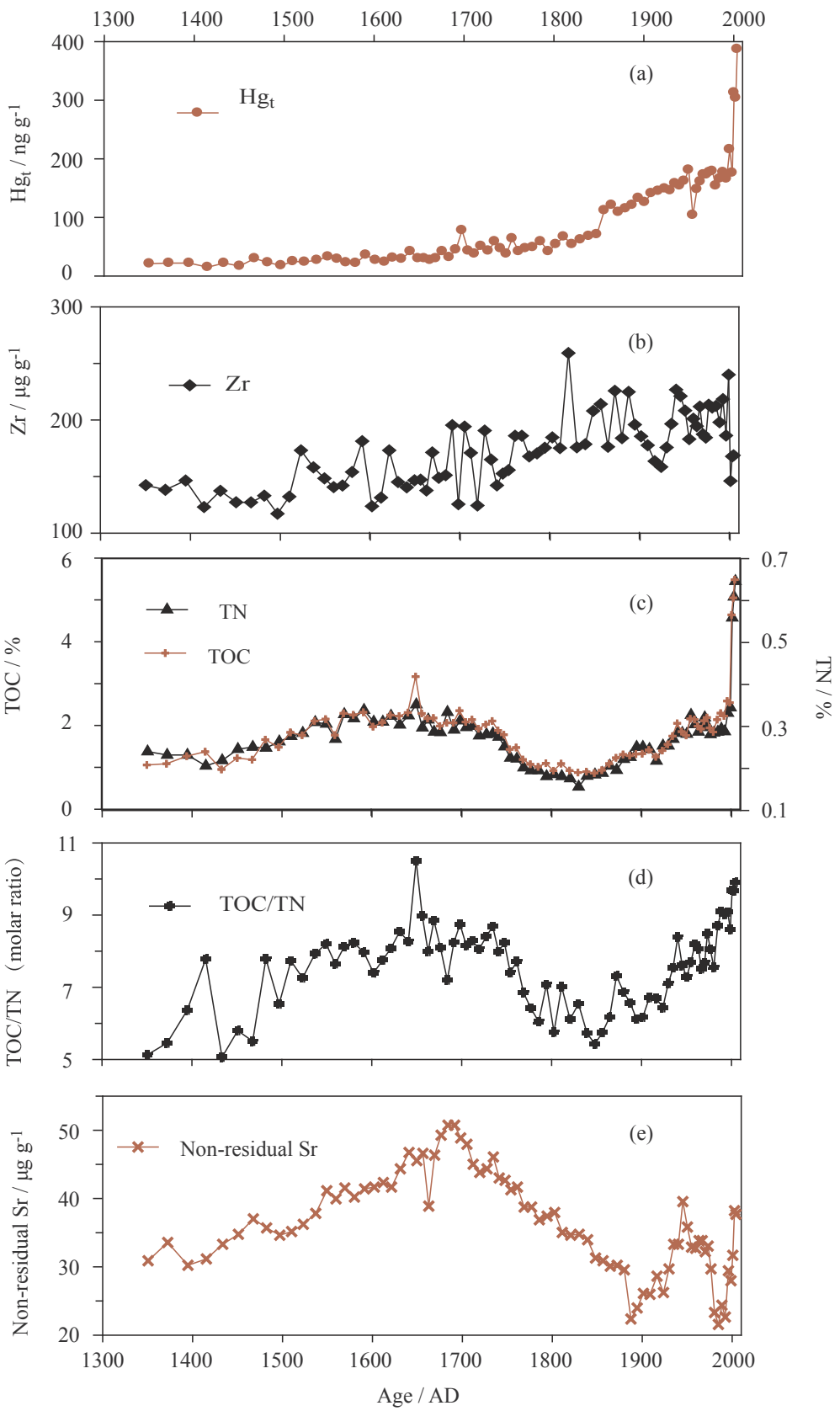

Fig. 2. Variations of Hg_t, Zr, TOC, TN, TOC/TN and non-residual Sr (Non-residual Sr data was from Zeng et al. (2012)).

In Huguangyan Lake, TOC and Hg_t did not vary in a similar trend (as shown in Fig. 2). Hg_t kept low values before 1700 CE, and then gently increased until 1850 CE. After 1850 CE, Hg accumulation rate increased significantly. While TOC contents showed a variation trend from 1300 CE to present as "increase-decrease-increase". TOC contents in Huguangyan Lake were dominated mainly by rainfall (Zeng et al., 2012). Both Hg_t and TOC contents increased sharply after 2000 CE, but this does not mean that the increased TOC caused the high accumulation

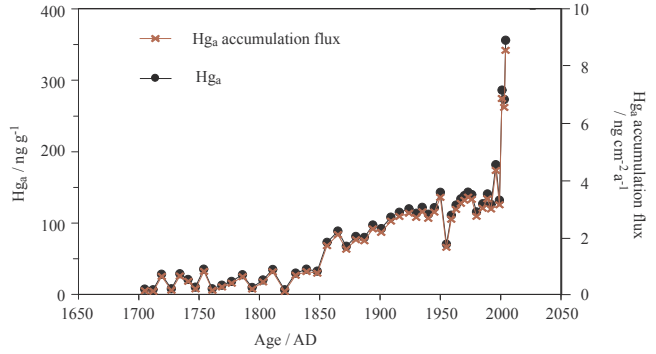

Fig. 3. Variation of Hg_a in the sediments of Huguangyan Lake and corrected Hg_a accumulation flux for the lake basin.

rate of Hg_t. The relatively high TOC content in surface sediments may be caused by the incompletely degradation of newly deposited organic matter. And a recent study showed that degradation of organic matter could not affect Hg accumulation (Outridge and Sanei, 2010).

In addition, the CV (Coefficient of Variation) of Hg_t was 85, while that of TOC was 41.9. Furthermore, before 2000 CE, the CV of Hg_t was 73.6, while that of TOC was just 21.4. In Huguangyan Lake, the limited variation of TOC contents was impossible to lead to the continuous increase of Hg contents in the sediments. The correlation analysis between TOC and Hg_t also reflected that they were not significantly correlated with each other, as shown in Fig. 4. Thus, the effect of Hg scavenging from water column by algae on accumulation is limited in Huguangyan Lake.

4.2. Influence of precipitation/catchment erosion

Some scholars suggested that lake sediment records had been affected by catchment inputs that brought previously deposited and stored Hg in the catchment into lakes (Rose et al., 2012; Yang et al., 2002). In addition, with the increase of extreme weather events in recent years, catchments erosion might have increased, which could affect the use of lake sediments to reconstruct Hg deposition in the past even further and might also change the pollution level in lakes (Yang and Smyntek, 2014). However, the extent of the impact of catchment inputs on the use of lake sediment records to reveal the atmospheric deposition history is not well known (Yang and Smyntek, 2014).

Our previous study (Zeng et al., 2012) has shown that non-residual Sr in the sediments of Huguangyan Lake could be used as an indicator of local paleoprecipitation. Increased precipitation causes elevated surface runoff in the catchments and enlarges the catchment erosion, accordingly may in turn bring more terrigenous materials into lakes.

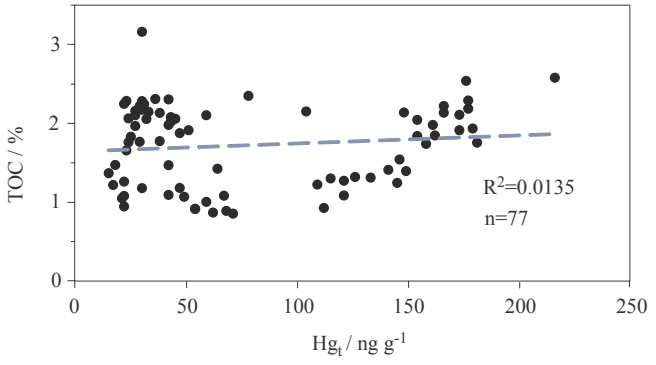

Fig. 4. The correlation between TOC and Hg_t (n = 77). As the relatively high TOC content in the three surface sediments may be caused by the incompletely degradation of newly deposited organic matter, the correlation coefficient between TOC and Hg_t was analyzed without the data of the three surface sediments.

As shown in Fig. 2, non-residual Sr and Hg_t show obviously different variation patterns. The non-residual Sr showed relatively high values between 1500 and 1750 CE, while Hg_t still kept low concentration during this period. After 1900 CE, non-residual Sr showed a small peak around 1900 CE, and then decreased to the lowest value around 1990 CE, which was followed by a rapid increase. During the same period, Hg_t showed a gradual increase until 2000 CE, and then a steep increase occurred. Therefore, the influence of the catchment inputs of previously deposited and stored Hg on Hg accumulation in the lake sediments can be ignored, compared to the direct atmospheric deposition.

Variation patterns of Hg, TOC and non-residual Sr in the sediment core indicated that, compared to the direct atmospheric Hg deposition, the effect of either Hg scavenging from water column by algae or the catchment inputs on the Hg accumulation in the lake sediment was limited. The sediment Hg content in Huguangyan Lake was mainly controlled by the atmospheric Hg deposition.

4.3. Atmospheric Hg deposition history

The history of environmental pollution associated with Hg is linked to temporal and spatial patterns of Hg use and atmospheric emissions (Schroeder and Munthe, 1998). Atmospheric Hg reaches the surface of lakes and watersheds by dry and wet deposition (Bookman et al., 2010). In the water column of lakes, Hg follows four main pathways: reduction and subsequent evasion back to the atmosphere, methylation and/or demethylation, loss with outflow water, and particle scavenging and sediment deposition (Watras et al., 1994). Sedimentation is an effective removal mechanism from the water, and after deposition and burial, remobilization is very limited (Fitzgerald et al., 1998). Therefore, Hg in lake sediments can be used to reconstruct the Hg deposition history.

Besides, Huguangyan Lake is a closed maar Lake with no surface inflow and outflow. The catchment comprises only the inner slopes of the crater rim. No industry ever occurred in the catchment, and other human activities are much limited. Therefore, anthropogenic Hg in the site is solely from atmospheric deposition. The Hg_a can be used to reflect the Hg air pollution history in the region.

Emission of Hg from anthropogenic sources started around 5000 years ago when human began to extract gold, silver, copper, coal and other materials. However, it increased substantially since the onset of industrial period in Europe and resulted in increased contamination in lake sediments and peat logs (Fitzgerald et al., 1998). Increase of two to seven times above background levels has been recorded in various studies in both hemisphere (Yang and Smyntek, 2014; Hermanns and Biester, 2013; Phillips et al., 2011; Yang et al., 2010; Lamborg et al., 2002; Lorey and Driscoll, 1999; Swain et al., 1992). As most remote sites did not show a signal of Hg increase in lake sediments before 1850 CE, Hg in sediments formed before 1850 CE was considered as background in many studies (Yang and Smyntek, 2014; Fitzgerald et al., 1998). However, anthropogenic Hg in the sediments formed before 1850 CE cannot be ignored. The Industrial Revolution started from the mid-19th century on a global scale, but the Industrial Revolution might have started as early as the 16th century in the UK as a result of economic expansion (Yang and Smyntek, 2014; Allen, 2011). Maybe that is why Hg_a concentration became higher from 1700 CE. The study in Red Tarn also found that anthropogenic Hg in the sediments formed before 1850 CE indicated an increase (Yang and Smyntek, 2014).

Similar to many remote regions, rapid increase of Hg_a content in the sediment of Huguangyan Lake occurred after 1850 CE, which revealed a further increase in air pollution in the region in modern times. The rapid increase of Hg emission that started from the middle of the 19th century has been recorded not only by European lake sediments and peat bogs from relatively remote sites (Yang and Smyntek, 2014; Farmer et al., 2009; Yang and Rose, 2003), but also by the records from other regions, like Asia (Yang et al., 2010), North America (Hylander and Meili, 2005) and even the Southern Hemisphere (Hermanns and Biester, 2013; Lamborg et al., 2002). The timing of the beginning of Hg

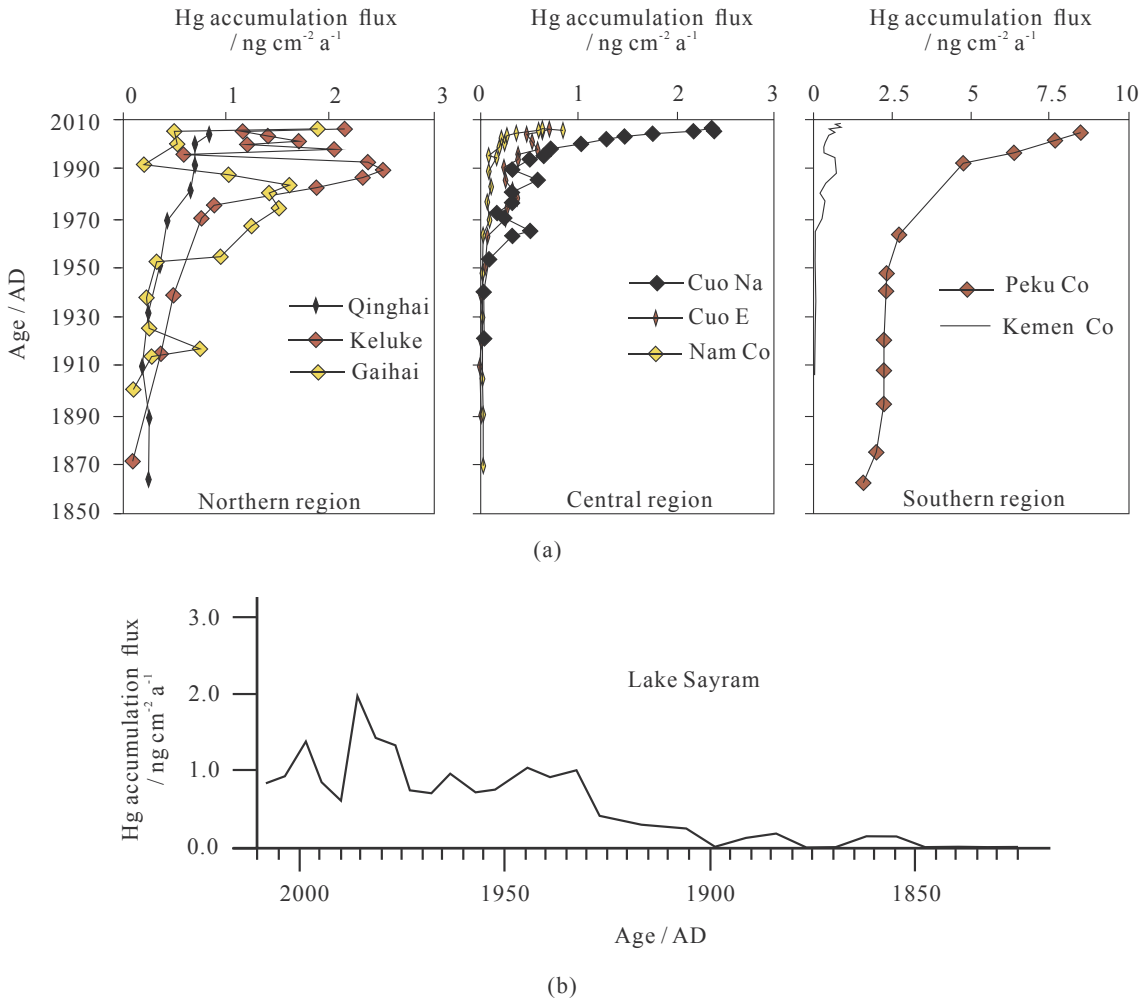

Fig. 5. The accumulation flux of atmospheric deposited Hg of Tibetan Plateau (a) (Yang et al., 2010) and Tianshan (b) (Zeng et al., 2014).

deposition rate increase agrees with other records from the sites in different regions. The similar shape of Hg accumulation from different regions of both hemisphere can be ascribed to the long range transport of Hg (Schroeder and Munthe, 1998) and an active cycling between the atmosphere and land and ocean's surface, respectively, promoting interhemispheric mixing (Hermanns and Biester, 2013). Since the onset of the Industrial Revolution in Western Europe, human activities have significantly increased atmospheric Hg emissions, deposition and global Hg contamination (Hylander and Meili, 2005). The estimated data of gross domestic product (GDP) of Western Europe and America increased rapidly and constantly from 1820 to 1950 CE, while the estimated GDP of China almost did not increase during this period, and even a weak decrease occurred around 1870 CE (Maddison, 2001). Therefore, this rapid and constant increase of atmospheric Hg pollution in the region of Huguangyan Lake could be mainly attributed to the global mercury change, which was resulted from the Industrial Revolution, but not local emission.

An abrupt decline of Hg_a in Huguangyan Lake occurred around 1950 CE. The decline might be caused by the World War II and the Civil War in China, which caused the economic depression and the corresponding relatively low Hg emission (Liu et al., 2012).

As emissions from industrial countries dramatically decreased since 1970 CE in EU and later in North America as a result of emission reduction policies implemented due to the wide concerns about Hg toxicity (Hylander and Meili, 2005), Hg_a in Huguangyan Lake still kept high values without any decline and sharply increased since 2000 CE. Hg emissions in Asia have increased due to the increase in local combustion in the region (Jiang et al., 2006; Hylander and Meili, 2005) related to rapid economic development since the 1970s CE (Hylander and Meili, 2005). The modeling calculation of Hg cycling presented that North America and Europe were the dominant emitting regions in the 19th century, but emphasis shifted initially to Russia and then sharply to Asia after 1950 CE (Streets et al., 2011). It is estimated that Hg contribution from Asian countries to worldwide total emissions in 2008 CE was 64% (Streets et al., 2011), increased from 54% in 2000 CE (Pacyna et al., 2006, 2003). China is assumed one of the largest contributors (Li et al., 2013). A study from several lakes in Shanghai also revealed that total Hg content in surface sediments showed a clear urbanization pattern (Li et al., 2013). Hg fluxes accelerated since 1990 CE when China's economy and urbanization booms started, and the coal combustion was a major source of Hg emission (Li et al., 2013). Furthermore, Streets et al. (2005) has calculated that 32% of emitted Hg in China is released as Hg^{2+} and 12% as particulate Hg. These emissions tend to be deposited locally and regionally. These parts may accelerate the Hg deposition rate in Huguangyan Lake.

4.4. Comparison with other studies in remote sites at higher altitude in China

As shown in Fig. 5, the increase in the atmospheric Hg flux rate in the lakes from Tibetan Plateau (over 4000 m a.s.l.) from 1850s to 1950s CE was not much notable (Yang et al., 2010), and the increase of the anthropogenic Hg flux in lake Sayram (2072 m a.s.l.) located in the central Tianshan before 1930s CE was also slow compared to that of

Huguangyan Lake (Zeng et al., 2014). The increase in Huguangyan Lake was obvious since 1850s CE (Fig. 3). Two main factors may contribute to this difference: (1) The dry and wet deposition of Hg^0 is much larger in Lake Huguangyan than in the lakes in Tibetan Plateau and Tianshan Mountain. A recent study revealed that approximately 70% of global Hg^0 dry deposition occurres in the tropical and subtropical regions (Wang et al., 2016). The Hg deposition flux through litterfall decreases spatially from tropical to temperature and boreal regions. In addition, the mean annual precipitation in Huguangyan Lake is several times of that of the alpine lakes, which may also result in more atmospheric Hg deposition. (2) The local released Hg^{2+} and particulate Hg may also increase the atmospheric Hg accumulation much more in Huguangyan Lake than in the remote lakes, corresponding to the local economic growth. Before 1970 CE, the Hg_a in Huguangyan Lake presented a comparable variation pattern to the records from EU and North America. As the industrial revolution evolved, the industry in China also developed to some extent, companied by increased atmospheric Hg concentration. Since 1970 CE, China and other Asian countries became the largest contributor to the global Hg emission due to the economic growth of Asian countries and emission decline of developed countries, which made the atmospheric Hg pollution in China became worsening. Although alpine regions were considered as convergence zones for Hg (the 'mountain trapping effect') due to its high surface roughness and low temperature (Zhang et al., 2013), our study revealed that the sediment Hg content in Huguangyan Lake responded to the atmospheric Hg pollution more sensitively than in the alpine regions in China.

5. Conclusions

The sediments of Huguangyan Lake truly recorded the atmospheric Hg deposition in the catchment with almost no effect of TOC or catchment erosion. Hg_a is relatively low before 1850 CE, and then increased until 1950 CE. The variation shaped as the same as the global atmospheric Hg pollution pattern, which could be attributed to the Industrial Revolution in EU and North America. After an abrupt decline around 1950 CE, Hg_a increased again and kept relatively high values without any decline, which was followed by the most significant pollution increase from 2000 CE. As emissions from industrial countries dramatically decreased since 1970 CE, Hg emissions from Asian countries have increased due to the increase in coal combustion related to rapid economic development. Besides the increased gaseous elemental mercury, the local deposited Hg^{2+} and particulate Hg may also accelerate the Hg deposition flux. All of the above indicate that Huguangyan Lake is a rare and reliable natural record for the atmospheric Hg pollution history in the region with strong human activity.

Compared with other studies in remote sites in China, it is also revealed that the records in Huguangyan Lake responded to the atmospheric Hg pollution more actively than in the alpine regions. The more intensive acceleration of Hg deposition flux may imply that South China suffered from much more serious atmospheric Hg pollution than previous studies revealed. The relative research in non-remote areas should be strengthened in the future.

Acknowledgements

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References

Allen, R.C., 2011. Why the industrial revolution was British: commerce, induced invention, and the scientific revolution. Econ. History Rev. 64, 357–384.

Bookman, R., Driscoll, C.T., Effler, S.W., Engstrom, D.R., 2010. Anthropogenic impacts recorded in recent sediments from Otisco Lake, New York, USA. J. Paleolimnol. 43, 449–462.

Chen, J.A., Li, J., Tian, S.H., Kalugin, I., Darin, A., Xu, S., 2012. Silicon isotope composition of diatoms as a paleoenvironmental proxy in Lake Huguangyan, South China. J. Asian Earth Sci. 45, 268–274.

Chu, G.Q., Liu, J.Q., Sun, Q., Lu, H.Y., Gu, Z.Y., Wang, W.Y., Liu, T.S., 2002. The 'Mediaeval Warm Period' drought recorded in Lake Huguangyan, tropical South China. Holocene 12, 511–516.

Farmer, J.G., Anderson, P., Cloy, J.M., Graham, M.C., MacKenzie, A.B., Cook, G.T., 2009. Historical accumulation rates of mercury in four Scottish ombrotrophic peat bogs over the past 2000 years. Sci. Total Environ. 407, 5578–5588.

Feng, X.B., Bai, W.Y., Shang, L.H., He, T.R., Qiu, G.L., Yan, H.Y., 2011. Mercury speciation and distribution in Aha Reservoir which was contaminated by coal mining activities in Guiyang, Guizhou, China. Appl. Geochem. 26, 213–221.

Fitzgerald, W.F., Engstrom, D.R., Lamborg, C.H., Tseng, C.M., Balcom, P.H., Hammerschmidt, C.R., 2005. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. Environ. Sci. Technol. 39, 557–568.

Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. Environ. Sci. Technol. 32, 1–7.

Fuhrmann, A., Mingram, J., Lucke, A., Lu, H.Y., Horsfield, B., Liu, J.Q., Negendank, J.F.W., Schleser, G.H., Wilkes, H., 2003. Variations in organic matter composition in sediments from Lake Huguang Maar (Huguangyan), South China during the last 68 ka: implications for environmental and climatic change. Org. Geochem. 34, 1497–1515.

Hao, L., Sun, L., Zhao, Y., Lu, J., 2013. Sedimentary records of evolution of heavy metals in Songhua Lake, Northeast China. Clean-Soil Air Water 41, 1010–1017.

Hermanns, Y.M., Biester, H., 2013. Anthropogenic mercury signals in lake sediments from southernmost Patagonia, Chile. Sci. Total Environ. 445, 126–135.

Hines, N.A., Brezonik, P.L., 2007. Mercury inputs and outputs at a small lake in northern Minnesota. Biogeochemistry 84, 265–284.

Hylander, L.D., Meili, M., 2005. The rise and fall of mercury: Converting a resource to refuse after 500 years of mining and pollution. Crit. Rev. Environ. Sci. Technol. 35, 1–36.

Jiang, G.B., Shi, J.B., Feng, X.B., 2006. Mercury pollution in China. An overview of the past and current sources of the toxic metal. Environ. Sci. Technol. 40, 3673–3678.

Kading, T.J., Mason, R.P., Leaner, J.J., 2009. Mercury contamination history of an estuarine floodplain reconstructed from a ^{210}Pb-dated sediment core (Berg River, South Africa). Mar. Pollut. Bull. 59, 116–122.

Kainz, M., Lucotte, M., 2006. Mercury concentrations in lake sediments - Revisiting the predictive power of catchment morphometry and organic matter composition. Water Air Soil Pollut. 170, 173–189.

Kainz, M., Lucotte, M., Parrish, C.C., 2003. Relationships between organic matter composition and methyl mercury content of offshore and carbon-rich littoral sediments in an oligotrophic lake. Can. J. Fish. Aquat. Sci. 60, 888–896.

Kirk, J.L., Muir, D.C.G., Antoniades, D., Douglas, M.S.V., Evans, M.S., Jackson, T.A., Kling, H., Lamoureux, S., Lim, D.S.S., Pienitz, R., Smol, J.P., Stewart, K., Wang, X., Yang, F., 2011. Response to comment on climate change and mercury accumulation in Canadian high and subarctic lakes. Environ. Sci. Technol. 45, 6705–6706.

Lamborg, C.H., Fitzgerald, W.F., Damman, A.W.H., Benoit, J.M., Balcom, P.H., Engstrom, D.R., 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. Global Biogeochemical Cycles 16, 51/1-51/11.

Li, H.B., Yu, S., Li, G.L., Deng, H., Xu, B., Ding, J., Gao, J.B., Hong, Y.W., Wong, M.H., 2013. Spatial distribution and historical records of mercury sedimentation in urban lakes under urbanization impacts. Sci. Total Environ. 445, 117–125.

Lindeberg, C., Bindler, R., Renberg, I., Emteryd, O., Karlsson, E., Anderson, N.J., 2006. Natural fluctuations of mercury and lead in Greenland Lake sediments. Environ. Sci. Technol. 40, 90–95.

Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Hakanson, L., Iverfeldt, A., Meili, M., Timm, B., 1991. Mercury in the Swedish environment-recent research on causes, consequences and corrective methods. Water Air Soil Pollut. 55, 1–261.

Liu, X.D., Xu, L.Q., Chen, Q.Q., Sun, L.G., Wang, Y.H., Yan, H., Liu, Y., Luo, Y.H., Huang, J., 2012. Historical change of mercury pollution in remote Yongle archipelago, South China Sea. Chemosphere 87, 549–556.

Lorey, P., Driscoll, C.T., 1999. Historical trends of mercury deposition in Adirondack lakes. Environ. Sci. Technol. 33, 718–722.

Maddison, A., 2001. The Word Economy: A Millennial Perspective. Organization for Economic Co-operation and Development (OECD), Paris, pp. 259.

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org. Geochem. 27, 213–250.

Mingram, J., Schettler, G., Nowaczyk, N., Luo, X.J., Lu, H.Y., Liu, J.Q., Negendank, J.F.W., 2004. The Huguang maar lake - a high-resolution record of palaeoenvironmental and palaeoclimatic changes over the last 78,000 years from South China. Quatern. Int. 122, 85–107.

Mirlean, N., Andrus, V.E., Baisch, P., 2003. Mercury pollution sources in sediments of Patos Lagoon Estuary, Southern Brazil. Mar. Pollut. Bull. 46, 331–334.

Outridge, P.M., Sanei, H., 2010. Does organic matter degradation affect the reconstruction of pre-industrial atmospheric mercury deposition rates from peat cores? – A test of the hypothesis using a permafrost peat deposit in northern Canada. Int. J. Coal Geol. 83, 73–81.

Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. Atmos. Environ. 40, 4048–4063.

Pacyna, J.M., Pacyna, E.G., Steenhuisen, F., Wilson, S., 2003. Mapping 1995 global

anthropogenic emissions of mercury. Atmos. Environ. 37, S109–S117.
Perry, E., Norton, S.A., Kamman, N.C., Lorey, P.M., Driscoll, C.T., 2005. Deconstruction of historic mercury accumulation in lake sediments, northeastern United States. Ecotoxicology 14, 85–99.
Phillips, V.J.A., St Louis, V.L., Cooke, C.A., Vinebrooke, R.D., Hobbs, W.O., 2011. Increased mercury loadings to western Canadian alpine lakes over the past 150 years. Environ. Sci. Technol. 45, 2042–2047.
Qiu, G.L., Feng, X.B., Wang, S.F., Xiao, T.F., 2006. Mercury contaminations from historic mining to water, soil and vegetation in Lanmuchang, Guizhou, southwestern China. Sci. Total Environ. 368, 56–68.
Rose, N.L., Yang, H., Turner, S.D., Simpson, G.L., 2012. An assessment of the mechanisms for the transfer of lead and mercury from atmospherically contaminated organic soils to lake sediments with particular reference to Scotland, UK. Geochim. Cosmochim. Acta 82, 113–135.
Rydberg, J., Klaminder, J., Rosen, P., Bindler, R., 2010. Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes. Sci. Total Environ. 408, 4778–4783.
Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury – an overview. Atmos. Environ. 32, 809–822.
Shi, J.B., Carman, C.M.Ip., Zhang, G., Jiang, G.B., Li, X.D., 2010. Mercury profiles in sediments of the Pearl River Estuary and the surrounding coastal area of South China. Environ. Pollut. 158 (5), 1974–1979.
Stern, G.A., Sanei, H., Roach, P., Dalaronde, J., Outridge, P.M., 2009. Historical interrelated variations of mercury and aquatic organic matter in lake sediment cores from a subarctic lake in Yukon, Canada: further evidence toward the algal-mercury scavenging hypothesis. Environ. Sci. Technol. 43, 7684–7690.
Streets, D.G., Devane, M.K., Lu, Z., Bond, T.C., Sunderland, E.M., Jacob, D.J., 2011. All-time releases of mercury to the atmosphere from human activities. Environ. Sci. Technol. 45, 10485–10491.
Streets, D.G., Hao, J.M., Wu, Y., Jiang, J.K., Chan, M., Tian, H.Z., Feng, X.B., 2005. Anthropogenic mercury emissions in China. Atmos. Environ. 39, 7789–7806.
Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A., Brezonik, P.L., 1992. Increasing rates of atmospheric mercury deposition in midcontinental north-America. Science 257, 784–787.
Teisserenc, R., Lucotte, M., Houel, S., 2011. Terrestrial organic matter biomarkers as tracers of Hg sources in lake sediments. Biogeochemistry 103, 235–244.
Wang, X., Bao, Z.D., Lin, C.J., Yuan, W., Feng, X.B., 2016. Assessment of global mercury deposition through litterfall. Environ. Sci. Technol. 50, 8548–8557.
Watras, C., Bloom, N., Hudson, R., Gherini, S., Munson, R., Claas, S., Morrison, K., Hurley, J., Wiener, J., Fitzgerald, W., Mason, R., Vandal, G., Powell, D., Rada, R., Rislov, L., Winfrey, M., Elder, J., Krabbenhoft, D., Andren, A., Babiarz, C., Porcella, D., Huckabee, J., 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes. In: Watras, C., Huckabee, J. (Eds.), Mercury Pollution: Integration and Synthesis. Lewis Publishers, Boca Raton, pp. 153–177.
Wu, L.L., Brucker, R.P., Beard, B.L., Roden, E.E., Johnson, C.M., 2013. Iron isotope characteristics of hot springs at Chocolate Pots, Yellowstone National Park. Astrobiology 13, 1091–1101.
Yang, H., Battarbee, R.W., Turner, S.D., Rose, N.L., Derwent, R.G., Wu, G., Yang, R., 2010. Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediments. Environ. Sci. Technol. 44, 2918–2924.
Yang, H., Smyntek, P., 2014. Use of the mercury record in Red Tarn sediments to reveal air pollution history and the implications of catchment erosion. Environ. Sci.: Process. Impacts 16, 2554–2563.
Yang, H.D., Rose, N.L., 2003. Distribution of mercury in six lake sediment cores across the UK. Sci. Total Environ. 304, 391–404.
Yang, H.D., Rose, N.L., Battarbee, R.W., Boyle, J.F., 2002. Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. Environ. Sci. Technol. 36, 1383–1388.
Zeng, H., Wu, J., Liu, W., 2014. Two-century sedimentary record of heavy metal pollution from Lake Sayram: a deep mountain lake in central Tianshan, China. Quatern. Int. 321, 125–131.
Zeng, Y., Chen, J.A., Zhu, Z.J., Li, J., Wang, J.F., Wan, G.J., 2012. The wet Little Ice Age recorded by sediments in Huguangyan Lake, tropical South China. Quatern. Int. 263, 55–62.
Zhang, H., Yin, R.S., Feng, X.B., Sommar, J., Anderson, C.W.N., Sapkota, A., Fu, X.W., Larssen, T., 2013. Atmospheric mercury inputs in montane soils increase with elevation: evidence from mercury isotope signatures. Sci. Rep. 3, 1–8.
Zhang, H., Zhang, N., Zhong, L., 2011. A 1955–2004 record of Hg contamination in Dianshan Lake sediments, Shanghai. Environ. Chem. Lett. 9 (4), 479–484.