



Contamination trends of trace metals and coupling with algal productivity in sediment cores in Pearl River Delta, South China



Dandan Duan^{a,b}, Yong Ran^{a,*}, Hefa Cheng^a, Jing'an Chen^c, Guojiang Wan^c

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong 510640, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550002, China

HIGHLIGHTS

- Sediment cores were collected from reservoir sediments of the Pearl River Delta.
- Cu, Zn, Ag, Cd, and As were significantly accumulated during last three decades.
- Heavy metals were strongly associated with algal organic matter in the sediments.
- Principal component analysis was used to assess the enrichment of heavy metals.
- Sedimentary process of heavy metals was affected by primary productivity.

ARTICLE INFO

Article history:

Received 18 July 2013

Received in revised form 31 October 2013

Accepted 6 November 2013

Available online 28 November 2013

Keywords:

Sedimentary history

Sediment core

Trace metals

Algal organic matter

Aquatic ecosystem

ABSTRACT

Several sediment cores from the Pearl River Delta were collected to investigate the relationship of trace metal contamination with algae-derived organic matter in the last 50 years. Trace metals were analyzed with ICP-MS, and algal organic matter (AOM) was measured with Rock-Eval pyrolysis. It was found that Cu, Zn, Ag, Cd, and As were elevated in the last three decades from three reservoirs, while all of the target metals showed no significant enrichment in estuarine sediment cores. Cu, Cr, Co, Cd, Zn, Ag, Ni, As, and Mn normalized to Ti were strongly associated with AOM in the sediments of eutrophic reservoirs, suggesting that AOM played an important role in controlling the accumulation of trace metals. Principal component analysis (PCA) and enrichment factor (EF) were also used to assess the enrichment of trace metals. The above result indicated that the sedimentary process of As, Cd, Cu, Zn, Ni, Cr, Co, Ag, and Mn was significantly affected or/and controlled by primary productivity in eutrophic, non-point polluted reservoirs.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Heavy metals in fast industrialization areas are one of the environmental problems. When they enter the aquatic system, they are mainly bound to particulate matter and eventually settled into sediments. Numerous investigators have investigated the contamination of heavy metals in the aquatic ecosystem (Fernandes, 1997; Vicente-Martorell et al., 2009).

During the recent years, significant impacts of natural organic matter (NOM) on distribution of mercury in sediments have been observed (Kainz et al., 2003; Kainz and Lucotte, 2006). Algal organic matter (AOM) as a biological pump effect in Arctic and sub-Arctic lakes may significantly affect the concentrations of mercury in sediments during the past decades (Sanei and Goodarzi, 2006; Outridge et al., 2007; Carrie et al., 2009; Stern et al., 2009).

Although one investigation (Kirk et al., 2011) on fourteen Canadian Arctic and sub Arctic lakes suggested that phytoplankton was not an important factor in controlling mercury concentrations of sediments, recent studies on some Chinese lakes indicated important impacts of AOM not only on activity of ²¹⁰Pb but also on contents of polycyclic aromatic hydrocarbons in sediments (Xu et al., 2011; Wu et al., 2012). Therefore, the accumulation mechanism of contaminants by AOM in sediments and its affecting factors need further investigations.

Pearl River Delta (PRD) covers an area of 461,000 km² with subtropical monsoon climate and has become one of the most developed regions in China in recent years (Wong et al., 2003). Nonpoint source pollution of heavy metals in the PRD has not been well investigated, especially in suburb and rural aquatic environments. Reservoirs in these areas, which are mainly fed by the precipitation, are suitable to the investigation on non-point source pollution of heavy metals. Atmospheric deposition is the major pathway of heavy metals in this aquatic system. Moreover, the

* Corresponding author. Tel.: +86 20 85290263; fax: +86 20 85290706.

E-mail address: yrans@gig.ac.cn (Y. Ran).

accumulation and deposition of heavy metals in different trophic aquatic systems may experience different processes (Sanei and Goodarzi, 2006). Therefore, it is essential to assess their contamination levels and biogeochemical cycling.

This study investigated the accumulation of heavy metals during sedimentary process in a period of 50 years in subtropical reservoirs far from industrial centers. Deposition history of heavy metals was analyzed by using ^{210}Pb and ^{137}Cs radiometric dating. The relationship between heavy metals and algae-derived organic matter was also studied. Other processes such as physical and biological disturbance, sedimentation mechanism, hydrologic effect, diagenesis and remobilization were also taken into consideration. This study would help to assess the actual anthropogenic impacts and to improve the environmental management and abatement policy in the PRD.

2. Methodology

2.1. Study areas

Three reservoirs (Zengtang, Lian'an, and Xingfengjiang) in the PRD were chosen to collect the sediment cores. Some basic properties of these three reservoirs are shown in Table S1 in Supporting data.

Zengtang reservoir (ZT) (23.22°N, 113.76°W) is a shallow, meso-eutrophic lake located in the east of Zengcheng city, and covers a surface area of 2.53 km² with a catchment area of 34.4 km². It has a mean depth of 2.5 m and maximum depth of 5 m. It is about 35 km away from the southern industrial center in Guangzhou. It is mainly fed by rainfall and heavily influenced by the atmospheric input. ZT reservoir had been an oligo-mesotrophic lake before 2003, and then has been becoming an eutrophication lake due to increasing nitrogen and phosphorus by fry misuse (Liu et al., 2011).

Lian'an reservoir (LA) (23.4°N, 113.66°W) covers a catchment area of 43 km² and is the largest drinking-water reservoir in Zengcheng city. It is situated in the northwest of ZT reservoir and is

far away from the southern industrial center in Guangzhou. A dam was constructed in 1960, which raised the water level to its maximum depth of 60 m. According to the aquatic data we collected, this reservoir can be classified as a mesotrophic lake and is mainly fed by precipitation.

Xingfengjiang reservoir (XFJ) (23.77°N, 114.57°W) is the largest reservoir in Guangdong province, which covers a surface area of 370 km² and a catchment area of 5730 km². It has supplied drinkable water to several cities since the construction in 1958. The average depth of XFJ is 28.7 m and the maximum depth is more than 93 m. In order to prevent the water pollution, industry activity is prohibited. Especially after 1990, a lot of efforts were taken for the management and protection of this valuable reservoir. Therefore, the reservoir maintains low nutrient level and low aquatic biomass, and has been classified as an oligotrophic lake by many investigators (Lin et al., 2003). XFJ reservoir is 200 km away from the southern industrial center. PRE and its upstream river network form the largest river system in South China. This river network covers a watershed area of more than 8000 km². Pearl River Estuary (PRE) is a bell-shaped area, with the distance from north to south averaging about 49 km, and from east to west varying from 4 km to 58 km. The southern part of PRE is far away from the southern industrial center and is not affected by point source contaminants. Two sediment cores in PRE were collected. All the five sampling sites were shown in Fig. 1.

2.2. Sample collection

In 2010 and 2011, undisturbed sediment cores were collected from three reservoirs and the southern PRE using a 6 cm diameter gravity corer with a Plexiglass liner. The water depths for the sampling sites at ZT, LA and XFJ reservoir are 1 m, 17 m, and 36 m, and those at estuarine No. 1 and No. 2 are 17 and 20 m, respectively. The core liners were cleaned before each sampling with native water. The sediments were collected in the center of the three reservoirs. The sediment cores were sliced at 2 cm thick intervals with

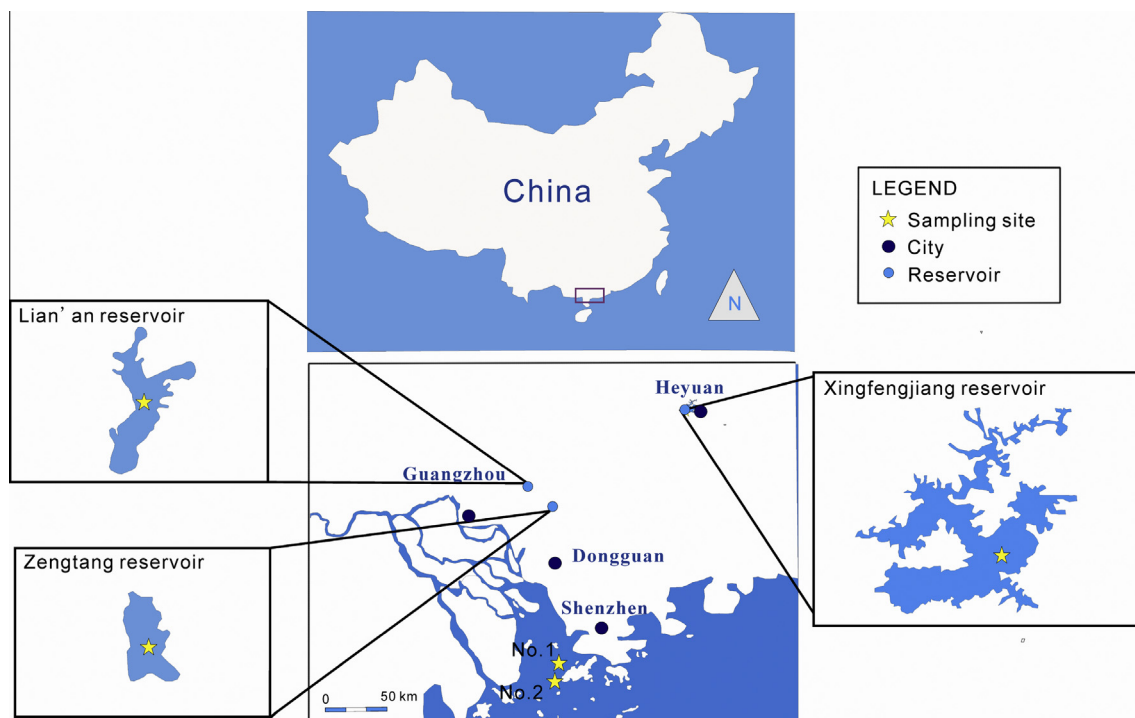


Fig. 1. The location of sampling sites in Pearl River Delta and Estuary.

slicing equipment. These subsamples were immediately placed into plastic bags, sealed, and stored at low temperature (0–10 °C), and then were transported to the laboratory, where they were freeze-dried and stored until further analysis.

2.3. Analysis

All freeze-dried samples for heavy metal analysis were ground and passed an 80 mesh sieve. A given quantity of each sample was completely digested using a mixture of nitric and hydrofluoric acids (BV-III grade) according to US EPA method 3052. 9 mL of nitric acid and 1 mL of hydrofluoric acid were added to each sample (0.20 g) and then heated with a temperature-programmed microwave in a digester (CEM, USA). After the digestion, the residue was dissolved in 1 mL of nitric acid, diluted to 100 mL with deionized water, and then analyzed by inductively coupled plasma/mass spectrometry (ICP/MS, Agilent 7700X, USA).

All the sediments were analyzed by Rock-Eval-6 (Vinci Technologies, France). This method can qualitatively and quantitatively determine the organic matter in the sediments, based on the pyrolysis degree and evolution of various organic compounds. Each bulk sediment was first heated in an inert, O₂-free oven at temperature increasing from 100 °C to 650 °C, followed by combustion in an oxidation oven at temperature increasing from 400 °C to 850 °C. The pyrolysis steps released two specific classes of hydrocarbons (HC), defined as S1 and S2, which were detected by flame ionization detector (FID). S1 mostly composes of small volatile molecules, which are generated during pyrolysis under 300 °C and are highly susceptible to the degradation. S2, released by the thermal cracking of organic matter (OM) under 650 °C, represents higher molecular weight, krogen-derived aliphatic hydrocarbons, and is resistant to the degradation. Simultaneously, CO and CO₂ (milligrams of CO and CO₂ per gram) detected by infrared (IR), representing oxygen-bearing OM, was defined as S3. After the pyrolysis, the combustion process continued and removed the remaining OM, yielding the residual carbon (RC, weight percent) peak. Total organic carbon (TOC, weight percent) is the sum of OM fractions released from the above steps.

2.4. Sediment age dating

The sediment samples from three reservoirs were dated by ²¹⁰Pb radiometric dating and ¹³⁷Cs radiometric dating. The activity of ²¹⁰Pb and ¹³⁷Cs were measured by S-100 Multi Channel Spectrometer (Canberra, USA) with a PIPS Si detector and GCW3022 H-P Ge coaxial detector (efficiency 50%), respectively. ¹³⁷Cs activity was determined using its gamma emission at 661 keV. Excess ²¹⁰Pb was measured by subtracting the average ²¹⁰Pb activities of deeper layers. ²¹⁰Pb activity data were used for chronological calculation based on a constant rate of supply dating model (CRS) (Appleby and Oldfield, 1978; Appleby et al., 1986). ¹³⁷Cs activities in sediment cores showed two peaks, one derived from the nuclear weapon test period in the middle of 1960s, and one derived from the Chernobyl nuclear accident in 1986 (Ritchie and McHenry, 1990). Thus ¹³⁷Cs dating method usually is coupled with ²¹⁰Pb technique to support each other. In this study, the deviation of dating is within the range of 0.01–1.95 years.

2.5. Quality control and quality assurance

For Rock-Eval analyzes, accuracy and precision were checked by using a geological survey standard sample as internal standard (CFP160000). Accuracy and precision were within 3% and better than 3% of the established values, respectively.

For heavy metals analyzes, the quality assurance was provided by analyzing one of the certified reference materials (CRMs) (1646a, Estuarine Sediment, NIST), a replicate sample, and a blank

sample along with each batch of 10 samples. The recovery ratios for heavy metals in the certified reference material were around 80–105%. Accuracy and precision were within 5% and better than 5% of the established values, respectively.

3. Results and discussion

3.1. Dating of sediment cores

The vertical profiles of ¹³⁷Cs and ²¹⁰Pb activities at three reservoirs are shown in Fig. S1 in Supporting data. For the ZT reservoir, an apparent peak of ¹³⁷Cs activity is identified at 22 cm with a value of 6.9 Bq kg⁻¹, which is in accordance with significant ¹³⁷Cs event in 1963 nuclear weapon testing (Ritchie and McHenry, 1990). Thus a mean sedimentation rate of 0.47 cm a⁻¹ with an average flux of 0.26 g cm⁻² a⁻¹ is obtained. The sediment core covers a time scale of about 60 years. The LA sediment core shows a maximum value of 23.3 Bq kg⁻¹ for the ¹³⁷Cs profile at 20 cm depth and gives a mean sedimentation rate of 0.43 cm a⁻¹, while the XFJ sediment core shows a maximum value of 30.3 Bq kg⁻¹ for the ¹³⁷Cs profile at 24 cm depth and gives a mean sedimentation rate of 0.51 cm a⁻¹. The average sedimentation flux of LA and XFJ are 0.17 g cm⁻² a⁻¹ and 0.30 g cm⁻² a⁻¹, respectively. The ¹³⁷Cs profiles from the LA and XFJ reservoirs do not show apparent tailing effect, suggesting that the mobilization of ¹³⁷Cs is negligible. These results are similar to the results of ²¹⁰Pb dating calculation, which was estimated by using a CRS model.

3.2. Heavy metal concentrations in the sediment cores

The vertical distribution of heavy metals in the sediment cores from three reservoirs is shown in Fig. S2. The profiles of Al, Ti, and Fe are shown in Fig. S4. The concentrations for most of heavy metals are elevated in the top layers of the sediment cores. Ni, Cu, Zn, Ag, Cd, and As contents at ZT significantly increase from the bottom to the top layer (Fig. S2a). As contents increase from the bottom layers to the 11 cm depth and then slightly decrease to the surface sediments. On the contrary, the concentrations of Cr, Co, and Pb slightly decrease from the bottom to the surface layer. Moreover, all of heavy metals are enriched in the upper layer of the sediment core at LA, showing an increasing trend from the bottom to the top layer (Fig. S2b). Almost all of the metals increase abruptly when the dam was built in 1960, which is related to its enlarged catchment area, increasing runoff and soil erosion, and deep water column (about 60 m). Furthermore, the As and Cd concentrations in the surface layer at the XFJ sediment core are 16.64-fold and 4.4-fold higher than in the bottom layer (Fig. S2c). The other metals vary slightly from the bottom to the top layer. It is noted that the distribution of heavy metals at XFJ may suggest a different accumulation pattern from that at ZT and LA during deposition process. The ZT reservoir, which is the shallowest one with similar catchment area to LA reservoir, is supposed to receive the highest amount of anthropogenic metals because of the closest distance to the southern industrial center. But the concentrations of trace metals are quite similar at ZT and at LA. This observation implies that there must be other important factors in controlling metal accumulation in the three reservoirs.

The vertical profiles of heavy metals in the estuarine No. 1 and No. 2 (Fig. 1) sediment cores display a pattern of uniform distribution, which agrees with the previous studies on heavy metals in the PRE sediments (Li et al., 2000; Liu et al., 2003). These sites are located in the high tidal current area with high salinity water and are subject to strong mixing from ocean currents, and thus are not appropriate to the purpose in this study.

In order to understand the contamination levels of heavy metals in the selected sampling sites, their mean concentrations in each of

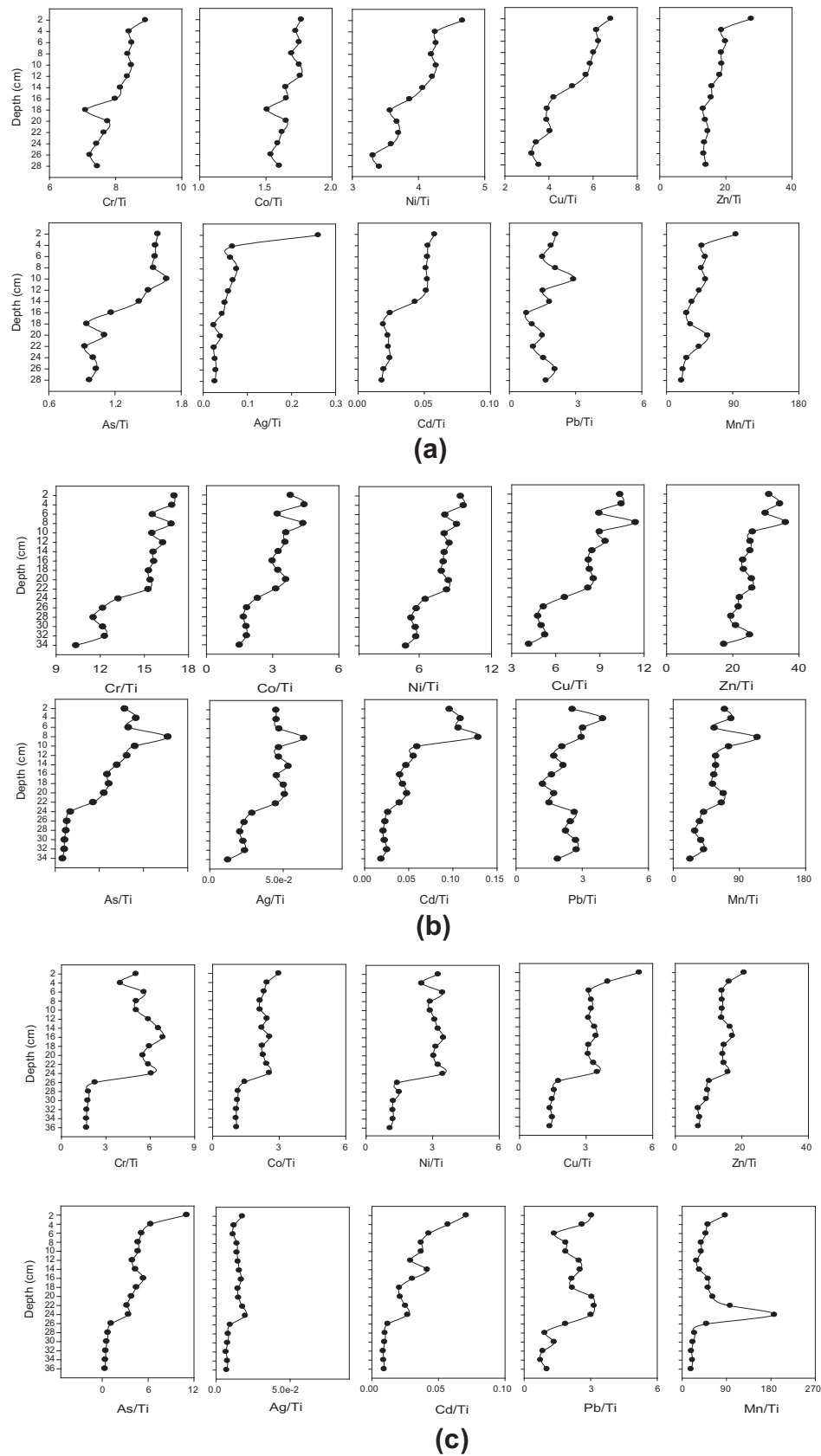


Fig. 2. Vertical profiles of Ti-normalized trace metals for ZT reservoir (a), LA reservoir (b) and XFJ reservoir (c).

the sediment core in this study and in previous studies, and regional background values are compared (Table 1). It is found that the concentrations of heavy metals in this study are significantly high-

er than the background values for soils of Guangdong province, indicating obvious accumulation of heavy metals (Table 1). Moreover, the concentrations of heavy metals at LA and ZT are similar.

Table 1

Comparison of mean concentrations of trace metals in sediment cores of Pearl River Delta from different studies and related quality standards.

Region	Mean concentration (mg kg ⁻¹)										References
	Cr	Co	Ni	Cu	Zn	As	Ag	Cd	Pb	Mn	
ZT reservoir	49.87	10.40	24.52	30.07	104.45	7.96	0.33	0.23	10.53	265.84	This study
LA reservoir	65.16	13.28	33.69	34.96	112.94	29.22	0.18	0.24	10.02	252.13	This study
XFJ reservoir	29.60	14.01	17.49	19.90	93.95	23.47	0.09	0.19	14.08	358.73	This study
South of Estuary No. 1	55.21	11.28	28.13	41.70	107.54	17.60	0.24	0.22	15.04	592.36	This study
South of Estuary No. 2	57.93	11.74	29.18	30.44	99.71	16.21	0.18	0.18	14.28	621.13	This study
Daya Bay	32.9	4.1		10.6	74.9	18.6		0.035	38.1	543	Du et al. (2008)
West of Pearl River Estuary	102.3	19.9	49.8	70.8	146.6			0.56	47.3		Liu et al. (2011)
BK ^a	36.1	3.5	10.98	8	21	5.4		0.034	23.4	162	
BK ^b	15	na	11	8	51			0.06	21		

^a Background values of soils in Guangdong Province (Guangdong Environmental Monitoring Central Station, 1990).

^b Background values of marine sediments in Hong Kong (EPD, 1992).

However, they are lower at XFJ than at ZT and LA, except for As, but still higher than the Guangdong soil background values (Table 1). Furthermore, heavy metals in the No. 1 and No. 2 estuarine sediments are lower than the mean concentrations in the whole estuary and West of PRE, but are higher than the average concentrations in the sediments from the Daya Bay (Du et al., 2008). The above results indicate that heavy metals are significantly enriched in comparison with their background values.

3.3. Normalization of heavy metals

Heavy metals normalized with reference elements can be used to remove the influences of geological and hydrodynamic processes and to estimate the anthropogenic impact (Soto-Jiménez and Páez-Osuna, 2001). As Ti is stable in aquatic environment (Din, 1992; Rubio et al., 2000; Aloupi and Angelidis, 2001), it was used to normalize heavy metals in this investigation, which are shown in Fig. 2. Most of normalized heavy metals show significant increases in each of the sediment profiles. Especially at ZT, normalized Cr, Co, and Ni are significantly elevated in the upper layers after 1978, which is the same as normalized Mn, Fe and Al. Therefore, the vertical fluctuation of Cr, Co, and Ni may be ascribed to biological mixing and physical disturbance due to its low water level, and to the redox processes coupled with that of Mn and Fe (Fig. 2a). Compared with its original heavy metals, the Ti-normalization data of LA show a continuous increasing trend (Fig. 2b). These patterns are very different from those of the original heavy metals, which show an abrupt change at the depth of 22–23 cm. These observations may indicate that the construction of the dam at 1960 might not be the only reason affecting the elevation of heavy metals. Other factors such as the effect of AOM need to be taken into consideration.

At XFJ, the elevations for most of normalized heavy metals are significant from the bottom layer at the depth of 23–24 cm (1958–1960) to the top layer (Fig. 2c). In addition, the Cd or As profiles are not similar to any of others, implying some special pollution source for them. Moreover, the profiles of Mn or Fe show a peak at 23–24 cm, which is usually regarded as important oxidation and reduction boundary in oligotrophic lakes. The oxidation of Mn²⁺ and Fe²⁺ occurred in the oxidation and reduction boundary and led to the accumulation of Mn and Fe oxides (Granina et al., 2004). Therefore, the Mn and Fe profiles, which are different from those of other metals, can be used to understand the process of remobilization after their deposition.

Positive correlation between activities of ²¹⁰Pb and total contents of Pb were observed in the XFJ core (Fig. S3, Supporting data). The two lower concentrations of Pb at 15–16 cm and 27–28 cm depth were in accordance with the two lowest water levels recorded in 1964 and 1980, respectively, which was obtained from

the Water Resources Department of Guangdong Province. In addition, the water runoff at XFJ had been reduced since 1970s due to the other reservoir construction in the upstream and/or the global change, as the flood discharge gate had not been used any more since then. The above observations further indicate that the variation of Pb in this oligotrophic reservoir is associated with geological process and hydrological process, consistent with other investigations in other aquatic environments (Lockhart et al., 1998; Outridge et al., 2007).

3.4. Relationship between heavy metal concentrations and algae-derived organic matter

NOM was characterized by the Rock-Eval pyrolysis in the three reservoirs. The analytical results of S1, S2, RC, TOC, and hydrogen index (HI) in the three reservoirs are shown in Table 2. S1 and S2 have been used as indicators of the AOM during the recent years (Sanei and Goodarzi, 2006; Outridge et al., 2007, 2011; Stern et al., 2009). Although S1 and S2 as AOM indicators have been questioned in a few studies (Disnar et al., 2003; Stern et al., 2009; Carrie et al., 2012; Wu et al., 2013), S2 represents the hydrogen-rich aliphatic biomacromolecules of AOM, which is resistant to decomposition and can be used in the reservoirs in this study (see the below discussion).

The variations of S1 and S2 were highly correlated with RC in the three reservoirs (for ZT, S1:RC $R^2 = 0.91$, S2:RC $R^2 = 0.95$; for LA, S1:RC $R^2 = 0.90$, S2:RC $R^2 = 0.93$; for XFJ, S1:RC $R^2 = 0.98$, S2:RC $R^2 = 0.97$), suggesting that terrestrial sources of organic matter were negligible (Outridge et al., 2007). The vertical profile of S2 in the sediment core of ZT or LA is similar and shows an increase by more than 7.41-fold and 5.2-fold, respectively (Table 2). These results indicate that ZT and LA may have similar historical primary productivity, and accumulate nearly the similar AOM even though the size and water capacity of ZT are smaller than those of LA. In addition, hydrogen index can usually be used to determine the relative richness of H-rich NOM. The HI values at ZT and LA reservoirs also reflect their similar productivity (Table 2).

However, the decreasing trends for S1, S2, and TOC at XFJ are presented, suggesting that NOM in this oligotrophic reservoir, where primary productivity is low and dissolved oxygen concentrations are high, might experience higher degree of degradation and oxidation than at ZT and LA (Table 2). Moreover, the TOC concentrations in XFJ are highest prior to construction of the reservoir, which is related to the fact that this site was a much smaller body of water, and hence more like ZT. Nutrient concentrations and light penetration would presumably be much larger in such a system, thus providing for a greater algal biomass. After the dam construction, it is likely that decreasing OM was brought upon by a variety of OM-diluting ecological processes (e.g., lower light penetration

Table 2
Concentrations of S1 and S2 carbon, residual carbon, total organic carbon and hydrogen index in the sediment cores of three reservoirs.

Depth (cm)	LA reservoir					ZT reservoir					XFJ reservoir				
	[S1] (HC mg g ⁻¹ dw)	[S2] (HC mg g ⁻¹ dw)	RC (wt%)	TOC (wt%)	HI (mg HC g ⁻¹ POC ⁻¹)	[S1] (HC mg g ⁻¹ dw)	[S2] (HC mg g ⁻¹ dw)	RC (wt%)	TOC (wt%)	HI (mg HC g ⁻¹ POC ⁻¹)	[S1] (HC mg g ⁻¹ dw)	[S2] (HC mg g ⁻¹ dw)	RC (wt%)	TOC (wt%)	HI (mg HC g ⁻¹ POC ⁻¹)
2	1.18	7.77	2.27	3.40	219	1.31	8.38	2.27	3.38	248	0.17	1.24	0.36	0.64	194
4	0.85	5.61	1.87	2.78	173	0.74	5.50	1.82	2.58	213	0.14	1.04	0.29	0.53	196
6	1.00	6.77	2.17	3.20	168	0.82	6.09	1.93	2.76	221	0.13	0.95	0.29	0.53	179
8	1.32	9.45	2.94	4.31	159	0.67	5.14	1.79	2.52	204	0.11	0.87	0.26	0.50	174
10	0.69	5.10	2.06	2.94	151	0.58	4.29	1.68	2.32	193	0.10	0.80	0.24	0.49	164
12	0.62	4.50	1.87	2.68	164	0.47	3.69	1.36	1.92	192	0.10	0.73	0.23	0.47	155
14	0.51	3.51	1.53	2.21	162	0.40	3.05	1.4	1.89	161	0.11	0.86	0.31	0.57	151
16	0.46	3.17	1.48	2.10	155	0.24	1.47	0.76	1.05	140	0.13	0.97	0.35	0.62	156
18	0.56	3.91	1.67	2.38	154	0.16	1.31	0.52	0.78	168	0.15	1.11	0.43	0.75	148
20	0.50	3.65	1.59	2.26	173	0.16	1.11	0.68	0.97	114	0.19	1.42	0.61	0.99	143
22	0.44	3.23	1.49	2.08	175	0.16	1.23	0.69	0.97	127	0.28	2.18	0.99	1.50	145
24	0.31	2.17	1.04	1.41	166	0.13	1.14	0.64	0.88	130	0.31	2.49	1.13	1.76	141
26	0.26	1.87	0.78	1.08	176	0.15	1.10	0.6	0.82	134	0.33	2.66	1.22	1.76	151
28	0.24	1.80	0.75	1.03	167	0.15	1.13	0.59	0.81	140	0.29	2.45	1.07	1.54	159
30	0.23	1.63	0.71	0.98	219						0.29	2.47	1.07	1.53	161
32	0.22	1.64	0.67	0.93	173						0.28	2.37	1.06	1.52	156
34	0.21	1.47	0.64	0.88	168						0.32	2.78	1.14	1.64	170
36											0.33	2.89	1.11	1.63	177

from deeper water yielding lower photosynthesis, and lower concentration of nutrients) in the large XFJ reservoir, while at the same time observing an increase in the metal influx due to anthropogenic activity. Furthermore, the colors of the sediment cores are very different. They are brown-black at ZT and LA, but are yellow at XFJ, suggesting that the former sediments are in an anoxic condition and the latter one is in an oxic condition. Therefore, the decreasing NOM at XFJ can be attributed to low primary productivity and/or bacterially mediated oxidation of NOM.

The Pearson correlation analysis among trace elements, major elements, S1, S2, and TOC were performed. All of the organic matter fractions in each of the three reservoirs were found to be highly correlated (For ZT, S1 vs. S2, $R^2 = 0.983$, S2 vs. TOC, $R^2 = 0.977$, $p < 0.01$; For LA, S1 vs. S2 $R^2 = 0.993$, S2 vs. TOC $R^2 = 0.944$, $p < 0.01$; For XFJ, S1 vs. S2 $R^2 = 0.99$, S2 vs. TOC $R^2 = 0.965$, $p < 0.01$), indicating that the algal production is closely associated with the increase in sedimentary organic matter. Moreover, chlorophyll a (Chl a) concentration is a critical parameter in determining lake productivity. The Chl a concentration in the investigated reservoirs can be arranged in the sequence: ZT > LA > XFJ, which is similar to the sequence of S2 and TOC (Tables 2 and S1). The above observations demonstrate that S2 in the sediments is a good indicator of the aquatic productivity in the investigated reservoirs.

As shown in Table S2 in Supporting data, strong positive correlations among Cu, Zn, As, Ag, Cd, Mn, S1, S2, and TOC were observed at ZT, indicating that Cu, Zn, As, Ag, Cd, and Mn are significantly controlled by algae-derived organic matter, except for Cr, Co and Pb. They are not significantly correlated with Fe and Al, suggesting that their deposition process may not be affected by Fe/Al oxide. Moreover, the positive correlations among Cr, Co, Ni, and other trace metals after the Ti-normalization were observed (Table S2). Most of the normalized trace metals are significantly correlated with S1 and S2 except for Pb, Al, and Fe, further indicating that Cr, Co, Cu, Zn, As, Ag, Cd, and Mn are strongly controlled by AOM. Phytoplanktons can adsorb and assimilate heavy metals from aqueous environment. Simultaneously, they can release extracellular organic ligands capable of complexing trace metals. After phytoplanktons die, their AOM together with heavy metals eventually settles down into the sediments (Davis et al., 2003; Xu et al., 2011; Wu et al., 2012).

Al is extremely immobile and is a typical lithogenic element (Price et al., 1999). And Ti-normalized Al is positively correlated with Ti-normalized Fe, suggesting that Fe and Al are mainly originated from the erosion of soils in the reservoir watershed. Moreover, the trace metals and major metals at LA are strongly correlated with each other or with S1 and S2, but not with Al and Ti (Table S3). Pb is not correlated with any elements and organic fractions. However, Al after normalization with Ti was found to be positively correlated with most of trace metals except for Ni, Cd, Pb, and Ti. The above results indicate that the accumulation of heavy metals at ZT and LA is largely controlled by local algae-derived organic matter.

Strong positive correlations are only observed among Cr, Cd, Co, Ni, Cu, Zn, As, and Ag at XFJ (Table S4). However, these heavy metals are not related to S1, S2 and TOC, and to Fe and Al either even after the Ti normalization. These observations are attributed to its oligotrophic condition, and to the oxidation of NOM (see the above discussion). Besides, the concentrations of trace metals at XFJ show no obvious change after 1965 (Fig. S2), are lower than at ZT or LA, and are close to the background values in the soils of Guangdong province, further suggesting that most of the trace metals may be mainly originated from weathered soils.

To further assess the extent of trace metal contamination and investigate the accumulation of trace metals associated with AOM and Fe/Mn oxides, the principal component analysis (PCA) was performed by SPSS statistics 20 (Table S5).

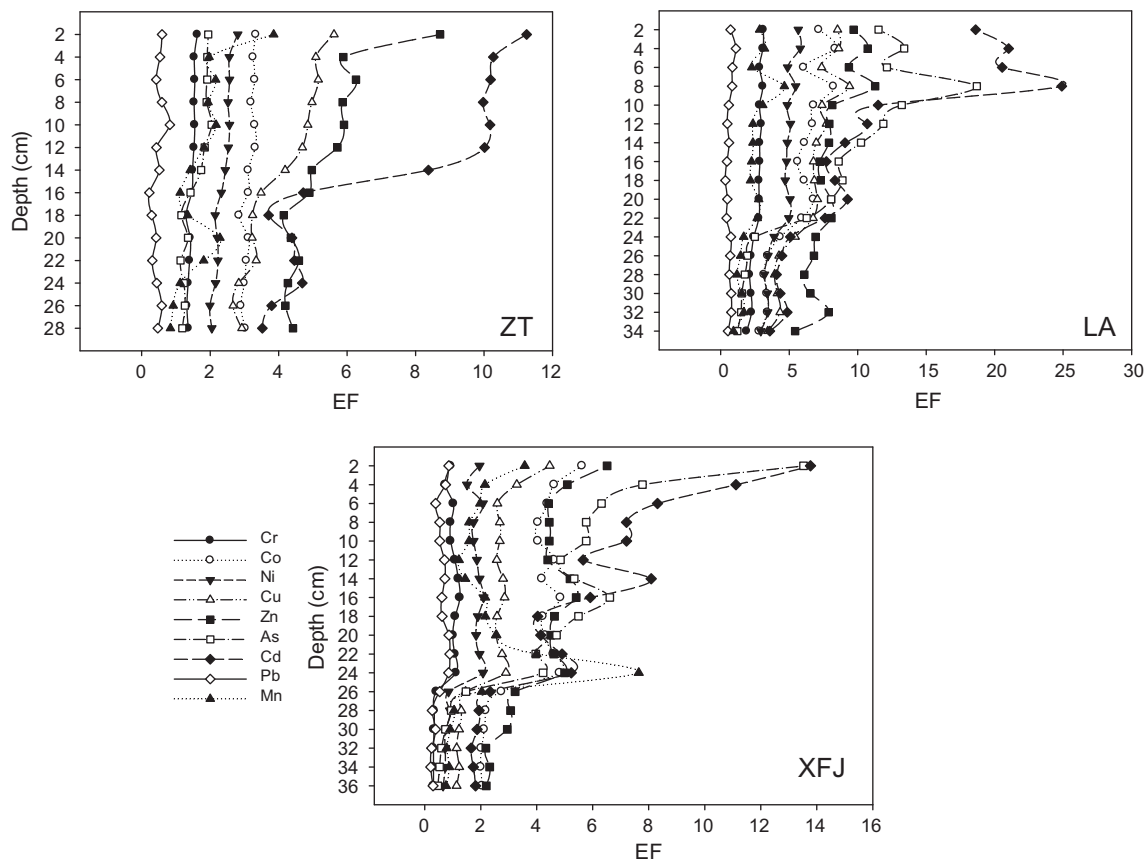


Fig. 4. Enrichment factor (EF) for selected trace metals in sediment cores of three reservoirs.

primary productivity, providing another important evidence to support the influences of AOM. Furthermore, the EF values in most of the sediments at XFJ are low for Cr, Ni, Pb, Cu, and Mn, moderately high to high for Co, Zn, and high for Cd and As. In addition, most of other trace metals also show their increased EF values at the upper layers of the sediment cores in these three reservoirs.

More attention should be paid to As due to its strongly enriched levels in the upmost layer of the sediment cores at LA and XFJ, which might be resulted from illegal usage of trypanamide in aquaculture and/or mine tailings from some illegal activities nearby in recent years (Li et al., 1999). The relatively high EF values of Cd were also found in the three reservoirs, but the primary source is not identified in this investigation. These metals (Cd and As) will cause serious environmental problems when they are released from the sediments to the water with changing environmental conditions.

4. Conclusion

Five sediment cores in PRD were investigated for the pollution records of heavy metals and their relationship with algae-derived organic matter. Most of heavy metals increased in the last 30 years at the three reservoirs. The Pearson correlation analysis and principal component analysis demonstrated that the accumulation of trace metals is strongly associated with algae-derived organic matter. This accumulation process is closely related to the primary productivity as biological pump in the aquatic ecosystem can accumulate heavy metals from atmospheric source. Moreover, the EF values indicate that most of heavy metals at these sites are at moderately enriched levels, leading to a potential impact

on the local aquatic system. The investigation suggests that most of the investigated metals could be accumulated in the sediments during their biogeochemical cycling in the reservoirs.

Acknowledgments

This study was supported by a key project of NNSFC-Guangdong (U1201235), a "Team Project" and a general project of National Natural Science Foundation of China (41121063 and 41073082), and a Key Field Project, Chinese Academy of Sciences (Y234081A07). This is contribution No. IS-1767 from GIGCAS.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.11.011>.

References

- Aloupi, M., Angelidis, M.O., 2001. Normalization to lithium for the assessment of metal contamination in coastal sediment cores from the Aegean Sea, Greece. *Mar. Environ. Res.* 52, 1–12.
- Appleby, P.G., Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena* 5, 1–8.
- Appleby, P.G., Nolan, P.J., Gifford, D.W., Godfrey, M.J., Oldfield, F., Anderson, N.J., Battarbee, R.W., 1986. Pb-210 dating by low background gamma-counting. *Hydrobiologia* 143, 21–27.
- Birth, G., 2003. A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Woodcoffe, C.D., Furness, R.A. (Eds.), *Coastal GIS 2003*. Wollongong University Papers in Center for Maritime Policy, 14, Australia.

- Carrie, J., Wang, F., Sanei, H., Macdonald, R.W., Outridge, P.M., Stern, G.A., 2009. Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate. *Environ. Sci. Technol.* 44, 316–322.
- Carrie, J., Sanei, H., Stern, G., 2012. Standardisation of Rock-Eval pyrolysis for the analysis of recent sediments and soils. *Org. Geochem.* 46, 38–53.
- Davis, T.A., Volesky, B., Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* 37, 4311–4330.
- Din, Z.B., 1992. Use of aluminium to normalize heavy-metal data from estuarine and coastal sediments of Straits of Melaka. *Mar. Pollut. Bull.* 24, 484–491.
- Disnar, J.R., Guillet, B., Kéravis, D., Di-Giovanni, C., Sebag, D., 2003. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations. *Org. Geochem.* 34, 327–343.
- Du, J.Z., Mu, H.D., Song, H.Q., Yan, S.P., Gu, Y.J., Zhang, J., 2008. 100 Years of sediment history of heavy metals in Daya Bay, China. *Water, Air, and Soil Poll.* 190, 343–351.
- EPD, 1992. Marine Water Quality in Hong Kong. Environmental Protection Department. Hong Kong Government Printer, Hong Kong.
- Fernandes, H.M., 1997. Heavy metal distribution in sediments and ecological risk assessment: the role of diagenetic processes in reducing metal toxicity in bottom sediments. *Environ. Pollut.* 97, 317–325.
- Förstner, U., Wittmann, G.T.W., Prosi, F., Van Lierde, J., 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, New York.
- Granina, L., Müller, B., Wehrli, B., 2004. Origin and dynamics of Fe and Mn sedimentary layers in Lake Baikal. *Chem. Geol.* 205, 55–72.
- Guangdong Environmental Monitoring Central Station, 1990. Soil Background Values of Guangdong.
- Hübner, A., De Lange, G.J., Dittmer, J., Halbach, P., 2003. Geochemistry of an exotic sediment layer above sapropel S-1: mud expulsion from the Urania Basin, eastern Mediterranean? *Mar. Geol.* 197, 49–61.
- 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.M., Antoniadis, 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.W., Yang, F., 2011. Climate change and mercury accumulation in Canadian high and subarctic lakes. *Environ. Sci. Technol.* 45, 964–970.
- Li, F.B., Wan, H.F., Li, D.Q., He, J.H., Ma, B.Y., 1999. The current eutrophication status of Xinfengjiang reservoir and its comprehensive control countermeasure. *Soil Environ. Sci.* 8, 26–30.
- Li, X.D., Wai, O.W.H., Li, Y.S., Coles, B.J., Ramsey, M.H., Thornton, I., 2000. Heavy metal distribution in sediment profiles of the Pearl River Estuary, South China. *Appl. Geochem.* 15, 567–581.
- Lin, Q.Q., Hu, R., Duan, S.S., Han, B.P., 2003. Reservoir trophic states and the response of plankton in Guangdong Province. *Acta Ecol. Sin.* 6, 9.
- Liu, W.X., Li, X.D., Shen, Z.G., Wang, D.C., Wai, O.W.H., Li, Y.S., 2003. Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environ. Pollut.* 121, 377–388.
- Liu, Y.F., Qin, J.Q., Liang, Y.S., 2011. Analysis of aquatic ecosystem of Zeng Tang reservoir from virtuous cycle to eutrophication. *Guangdong Chem. Ind.* 7, 53.
- Lockhart, W.L., Wilkinson, P., Billeck, B.N., Danell, R.A., Hunt, R.V., Brunskill, G.J., Delaronde, J., Louis, V.S., 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry* 40, 163–173.
- Lopez, P., Navarro, E., Marce, R., Ordoñez, J., Caputo, L., Armengol, J., 2006. Elemental ratios in sediments as indicators of ecological processes in Spanish reservoirs. *Limnetica* 25, 499–512.
- Outridge, P.M., Sanei, H., Stern, G.A., Hamilton, P.B., Goodarzi, F., 2007. Evidence for control of mercury accumulation rates in Canadian High Arctic lake sediments by variations of aquatic primary productivity. *Environ. Sci. Technol.* 41, 5259–5265.
- Outridge, P.M., Sanei, H., Stern, G.A., Goodsite, M., Hamilton, P.B., Carrie, J., Goodarzi, F., Macdonald, R.W., 2011. Comment on climate change and mercury accumulation in Canadian high and subarctic lakes. *Environ. Sci. Technol.* 45, 6703–6704.
- Price, N.B., Brand, T., Pates, J.M., Mowbray, S., Theocharis, A., Civitarese, G., Miserochchi, S., Heussner, S., Lindsay, F., 1999. Horizontal distributions of biogenic and lithogenic elements of suspended particulate matter in the Mediterranean Sea. *Prog. Oceanogr.* 44, 191–218.
- Ran, Y., Fu, J.M., Sheng, G.Y., Beckett, R., Hart, B.T., 2000. Fractionation and composition of colloidal and suspended particulate materials in rivers. *Chemosphere* 41, 33–43.
- Ritchie, J.C., McHenry, J.R., 1990. Application of radioactive fallout cesium-137 for measuring soil erosion and sediment accumulation rates and patterns: a review. *J. Environ. Qual.* 19, 215–233.
- Rubio, B., Nombela, M.A., Vilas, F., 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. *Mar. Pollut. Bull.* 40, 968–980.
- Sanei, H., Goodarzi, F., 2006. Relationship between organic matter and mercury in recent lake sediment: the physical-geochemical aspects. *Appl. Geochem.* 21, 1900–1912.
- Sinex, S.A., Helz, G.R., 1981. Regional geochemistry of trace elements in Chesapeake Bay sediments. *Environ. Geol.* 3, 315–323.
- Soto-Jiménez, M.F., Páez-Osuna, F., 2001. Distribution and normalization of heavy metal concentrations in mangrove and lagoonal sediments from Mazatlán Harbor (SE Gulf of California). *Estuar. Coast. Shelf Sci.* 53, 259–274.
- 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.
- Trefry, J.H., Presley, B.J., 1976. Heavy metals in sediments from San Antonio Bay and the northwest Gulf of Mexico. *Environ. Geol.* 1, 283–294.
- Vicente-Martorell, J.J., Galindo-Riaño, M.D., García-Vargas, M., Granado-Castro, M.D., 2009. Bioavailability of heavy metals in monitoring water, sediments and fish species from a polluted estuary. *J. Hazard. Mater.* 162, 823–836.
- Wong, C.S.C., Li, X.D., Zhang, G., Qi, S.H., Peng, X.Z., 2003. Atmospheric deposition of heavy metals in the Pearl River Delta, China. *Atmos. Environ.* 37, 767–776.
- Wu, F.C., Xu, L.B., Sun, Y.G., Liao, H.Q., Zhao, X.L., Guo, J.Y., 2012. Exploring the relationship between polycyclic aromatic hydrocarbons and sedimentary organic carbon in three Chinese lakes. *J. Soils Sediments* 12, 774–783.
- Wu, F.C., Xu, L.B., Liao, H.Q., Guo, F., Zhao, X.L., Giesy, J.P., 2013. Relationship between mercury and organic carbon in sediment cores from Lakes Qinghai and Chenghai, China. *J. Soils Sediments*, 1–9.
- Xu, L.B., Wu, F.C., Wan, G.J., Liao, H.Q., Zhao, X.L., Xing, B.S., 2011. Relationship between Pb-210(ex) activity and sedimentary organic carbon in sediments of 3 Chinese lakes. *Environ. Pollut.* 159, 3462–3467.