Applied Geochemistry 66 (2016) 140-148

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Polycyclic aromatic hydrocarbons (PAHs) and Pb isotopic ratios in a sediment core from Shilianghe Reservoir, eastern China: Implying pollution sources

Fan Zhang ^{a, b}, Rui Zhang ^{c, d, e, *}, Minglei Guan ^d, Yujie Shu ^d, Liya Shen ^d, Xixi Chen ^d, Tiegang Li ^{c, **}

^a Jiangsu Marine Resources Development Research Institute, Lianyungang 222001, Jiangsu Province, China

^b Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, Jiangsu Province, China

^c Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

^d School of Geodesy and Geomatics Engineering, Huaihai Institute of Technology, Lianyungang 222005, Jiangsu Province, China

^e State Key Laboratory of Pollution Control and Resources Reuse, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history: Received 1 July 2015 Received in revised form 30 November 2015 Accepted 9 December 2015 Available online 12 December 2015

Keywords: Anthropogenic input PAHs Lead isotopes Reservoir sediments Sediment accumulation rates Source identification

ABSTRACT

The history records of polycyclic aromatic hydrocarbons (PAHs), lead and its stable isotope ratios were determined in a sediment core to receive anthropogenic impacts on the Shilianghe Reservoir in eastern China. The historical changes of PAHs concentrations, PAHs fluxes, Pb/Al and Pb isotope ratios showed a synchronous trend throughout the core, suggesting changes in energy usage and correlating closely with the experience of a rapid economic and industrial development of the catchment, Linyi City in eastern China. PAHs isomer ratios results reveal PAHs in sediments are dominantly anthropogenic pyrogenic source, dominated by the combustion of coal and biomass. Furthermore, the Pb isotopic composition also clearly indicates that coal combustion dust mainly contributed to the Pb burden in the reservoir sediments. Based on mix end member model of Pb isotope ratios, coal combustion dust dominated anthropogenic Pb sources over fifty years contributing from 31% to 62% of total Pb in sediment. And the contribution of leaded gasoline was low than average 25%. In addition, a stable increase of coal combustion source was found in sediment core, while the contribution of leaded gasoline had declined in recent decades, with the phase-out of leaded gasoline in China.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are toxic and carcinogenic and are ubiquitous in the environment (Christensen and Arora, 2007; Tsang et al., 2011). They are mainly released from the incomplete combustion of fossil fuels, municipal wastes, and biomass (Yunker et al., 2002), the spills of petroleum-derived products, and the diagenesis of organic matter in the anoxic environment (Lima et al., 2005; Berrojalbiz et al., 2011). In aquatic environments, PAHs and heavy metals such as Pb tend to associate with particulate matter due to their hydrophobic nature and are finally deposited to the underlying sediments of lakes (Gerritse,

1998; Tolosa et al., 2004). PAH isomer ratios can be used to differentiate the sources apportionment of these compounds (Yunker et al., 1999, 2002). Moreover PAH isomer ratios can also be used to indicate the 'fuels' combusted (e.g., coal versus oil-derivate products) (Yunker et al., 1999, 2002; Vane et al., 2011). Given their fingerprinting properties, stable Pb isotopes can be used to discriminate among several sources and to identify environmental pathways of this metal (Ault et al., 1970; Chow and Earl, 1972; Sturges and Barrie, 1987, 1989; Carignan and Gariepy, 1995; Gallon et al., 2004; Zheng et al., 2004; Cheng and Hu, 2010). Thus, PAHs (and their isomer ratios) and Pb stable isotopes in the core sediments can be used as effective proxies to trace information about contaminant sources and distribution pathways, which were closely related to the differences in energy structure and socioeconomic development in catchment areas (Guo et al., 2007; Guo et al., 2010, 2011; Louchouarn et al., 2012; Leorri et al., 2014). In China, the majority of studies on lake sediments involve mainly







^{*} Corresponding author. No.7, Nanhai Road, Qingdao, Shandong Province, China.

^{**} Corresponding author. No.7, Nanhai Road, Qingdao, Shandong Province, China. E-mail addresses: rzhang_838@163.com (R. Zhang), tgli@qdio.ac.cn (T. Li).

reconstructions of anthropogenic activities based on PAHs or trace metals (Zhi et al., 2015; Guo et al., 2011), but far less attention has been given to the environmental record provided by stable Pb isotopes (Chen et al., 2000; Li et al., 2012; Liu et al., 2013; Zhang et al., 2012; Zhang et al., 2008; Yao et al., 2013). Moreover, the few studies have examined ratios of stable Pb isotopes in conjunction with PAHs in sediments to identify the anthropogenic sources that contributed combustion-derived contaminants to the sediment.

In this study, we report on the distribution of lead, stable Pb isotope ratios, and PAH in a dated sediment core from Shilianghe Reservoir, an artificial lake in eastern China. A few environmental studies have determined trace metal concentrations, accumulating rates, pollution history, and the extent of contamination in Shilianghe Reservoir (Meng et al., 2008; Meng and Zhang, 2008; Tian et al., 2008). Here, we use the concentrations of PAHs and their isomer ratios composition, in combination with stable Pb isotopes in a sediment core, to: 1) delineate the temporal trends of concentrations and fluxes of PAHs in Shilianghe Reservoir recorded by a sedimentary core based on ²¹⁰Pb, ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu dating; 2) elucidate anthropogenic impacts on the aquatic environment of Shilianghe Reservoir in the recent decades; and 3) determine anthropogenic sources of PAHs and Pb.

2. Materials and methods

2.1. Sample collection

This reservoir is at the margin of south Shandong hills, and belongs to Huai River drainage basin. Shilianghe Reservoir, built in 1962, is also named as Hailing Lake, and plays an important role in regional socio-economic development for water supply, for agricultural and industrial water use, for tourism as well as for protection against floods. It covers a mean total area of 85 km² within a catchment of 15,365 km², and an average water depth of 4 m. Its drainage basin locates in Linyi City of Shandong Province, and flows across extensive agricultural and industrial regions. In addition, Shilianghe Reservoir is a major fishery base, and aquaculture industries are the main drivers of economic growth in local government. A sediment core (SLH01) (118°51.81'E, 34°46.72'N) with depth 200 cm were collected from the Shilianghe Reservoir in October 2014 using a gravity corer with a 75-mm internal diameter polycarbonate tube insert, and the water depth is 3.1 m. Location of sediment core is shown in Fig. 1. In the laboratory, the core was subsampled at 1 cm intervals. All the samples were immediately transferred to the laboratory and kept at -20 °C. The homogenized core samples were freeze-dried, and then dried sediments were then grounded, passed through a nylon sieve of 100 mesh to remove vegetable root, wood debris and dead organisms. All the equipment used for sample collection, transportation, and preparation were thoroughly washed and rinsed with acetone and hexane to minimize the likelihood of cross contamination.

2.2. PAHs analysis

The PAH analysis procedure followed the procedure described by Grimalt et al. (2004). Approximately 3-5 g of the sample was spiked with a mixture of recovery standards of two deuterated PAHs (phenanthrene-d₁₀ and perylene-d₁₂). The samples were sonic extracted with dichloromethane methanol (20 ml, 2:1) for 20 min; this procedure was repeated three times. The extract was vacuum evaporated to approximately 10 ml and hydrolyzed overnight with 20 ml of 6% KOH in methanol. The neutral fractions were recovered with 30 ml of n-hexane and fractionated with 2 g of an alumina: silica (1:1) gel column. The PAHs were eluted with 30 ml of hexane/dichloromethane (1:1). The PAHs fraction was concentrated to 0.5 ml in isooctane prior to GC-MS analysis. PAHs in all samples and procedure blanks were analyzed using a gas chromatograph (GC) with an ion-trap mass spectrometer (MS) (Finnigan Trace GC/PolarisQ). A 30 m \times 250 mm i.d. HP-5MS capillary column was used for separation. High-purity helium was used as a carrier gas at a constant flow rate of 1.0 ml min⁻¹. Each sample was analyzed using splitless injection and 70-eV electron impact (EI) ionization. The temperature of the injector was 250 °C, and the temperature of the transfer line was 280 °C. The oven-temperature program for PAHs was adjusted to the following parameters: the column was held at 50 °C for 2 min before the temperature was increased to 180 °C at a rate of 20 °C min⁻¹; the temperature was then increased at 4 °C min⁻¹ up to 250 °C, then increased to 280 °C at a rate of 2 °C min⁻¹ and held for 2 min. Finally, the temperature was brought to 300 °C at a rate of 10 °C min⁻¹ and then held for 5 min. Sixteen United States Environmental Protection Agency (US EPA) priority PAHs were measured: naphthalene (Nap), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benz[a]anthracene (BaA), chrysene(Chr), benzo[b]fluoranthene (BbF), benzo[k]fluor-anthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3-cd]pyrene (Inp), dibenz[a,h]anthracene (DBA), and benzo [ghi]perylene (BghiP). Procedural blanks, standard-spiked blanks, and standard-spiked matrices were analyzed for quality assurance and control, and showed no noticeable interference. Recovery for field samples was 99 \pm 11% for phenanthrene-d₁₀ and 85 \pm 10% for pervlene-d₁₂. Ouantification was performed by the internal calibration method based on five point calibration curves. The quantification limit for individual PAH species was set at three times the detected amount in the procedural blank. In addition, 30% of field samples were analyzed in duplicate, and the relative standard deviation for individual PAHs was less than 14%. PAH concentrations were not recovery corrected.

2.3. Pb concentrations and stable Pb isotope ratios

About 0.25 g sample was digested with a mixture of concentrated HF-HClO₄-HNO₃ for the determination of total metal concentrations. The Pb concentrations were analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Thermo Electro Co., ICAP 6300, USA). The accuracy of the analytical method was established with the standard reference material aquatic sediments GBW07312 (GSD-12). The recovery for Pb was 85%-106%. Three replicates of each sample were run, and the coefficient of variation was 2.85%. The analysis method of stable Pb isotopes was described by Jiang et al. (2006). The stable Pb isotopic compositions of samples were measured by the Finnigan Triton Thermal Ionization Mass Spectrometer (TIMS). Measurements of the reference material SRM-981 from the National Institute of Standards and Technology (NIST), were certified for stable Pb isotope ratios to correct for instrumental drift. The measured values for NIST SRM-981 were ${}^{206}Pb/{}^{204}Pb = 16.8872 \pm 0.0043$, ${}^{207}Pb/{}^{204}Pb = 15.4463 \pm 0.0071$, ${}^{208}Pb/{}^{204}Pb = 36.4589 \pm 0.0185$, ²⁰⁷Pb/²⁰⁶Pb = 0.913925 0.0173, and ± $^{208}\text{Pb}/^{206}\text{Pb} = 2.16211 \pm 0.0102$ (2 σ , external standard deviation, n = 5). The standard accepted values are: ${}^{206}Pb/{}^{204}Pb = 16.9322$, ²⁰⁸Pb/²⁰⁴Pb 207 Pb/204 Pb ${}^{207}\text{Pb}/{}^{204}\text{Pb}=15.4855,$ ${}^{208}\text{Pb}/{}^{204}\text{Pb}=36.6856,$ ${}^{207}\text{Pb}/{}^{206}\text{Pb}=0.914559,$ and ${}^{208}\text{Pb}/{}^{206}\text{Pb}=2.166617.$ Pb isotopic ratios reported in this work were corrected according to the accepted value for the SRM 981.



Fig. 1. Location of sampling site.

2.4. Measurement of 210 Pb, 137 Cs and $^{239+240}$ Pu and sediment dating

²¹⁰Pb was determined by alpha counting of the ²¹⁰Po deposited onto Ag discs (Flynn, 1968) by using ²⁰⁹Po as a yield tracer. The sediment was dissolved by adding a mixture of HNO3:HCI:HF (1:1:0.5 v/v/v) to 2 g of sediment and heating to 200 °C overnight in closed Teflon containers. Counting was conducted by computerized multichannel α -spectrometry with gold-silicon surface barrier detectors (Model Otetc PLUS, ORTEC Co., USA). The 30–50 g of the sub-sample thus obtained was subjected to ¹³⁷Cs analysis, using the method described by Pan et al. (1997). In brief ¹³⁷Cs was measured by γ -spectrometry using the 661.62 keV photo peak that results from the decay. The counting system is equipped with a 40% efficiency HPGe detector (GMX30P-A, ORTEC) interfaced to a digital γ ray spectrometer (ORTEC DSPEC Plus™). IAEA-327 and a sediment standard supplied by Bedford Institute of Oceanography were used to calibrate the detector. Following 137 Cs activity determination approximately 2-3 g of the counted material was taken for Pu isotopic analysis. Details of sample pretreatment, chemical separation and purification for Pu isotopes determination have been described in previous studies (Zheng and Yamada, 2006; Zheng et al., 2012). Pu analysis was conducted by SF-ICP-MS (Finnigan Element 2, Bremen, Germany) using the method described by Zheng and Yamada (2006). The detection limits for Pu isotopes are 0.0006 mBq/g for ²³⁹Pu and 0.003 mBq/g for ²⁴⁰Pu, calculated for 1 g of sediment sample. Reference materials of IAEA-368 and NIST-4357 are used for analytical method validation.

2.5. Sediment dating based on ²¹⁰Pb and PAHs flux

The CRS model has proved to be reliable in most cases (Appleby, 2008; Kirchner, 2011). In addition, ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu can been used to identify the 1963 nuclear weapons peak. Thus, we employed the CRS model to date the sediment core. The age of each layer is obtained by CRS model as:

$$t = \frac{1}{\lambda} \ln\left(\frac{A(0)}{A_x}\right) \tag{1}$$

where A(0) is the total inventory along the core (Bq cm⁻²), λ is the decay constant (0.03114 yr⁻¹) and A_x is the cumulative inventory of ²¹⁰Pb_{ex} concentrations below depth x (cm or g cm⁻²).

The PAHs flux was estimated from the following equation:

$$F = S \times C_i \tag{2}$$

where *F* is the PAHs flux (ng cm⁻²yr⁻¹), *C_i* is the PAHs concentration at *i* depth (ng g⁻¹), *S* is the sediment accumulation rate (g cm⁻² yr⁻¹).

3. Results and discussions

3.1. Sediment chronology

Sedimentation accumulate rates (SAR) were derived from the CRS method (Appleby, 2008), which were calibrated based on ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu time markers. The down-core profile of ¹³⁷Cs shows a clear subsurface maximum activity at 155 cm depth (Supplementary Material Fig. S1). The peak of ²³⁹⁺²⁴⁰Pu activities appears at the depth of 155 cm in agreement with the peak of ¹³⁷Cs in core SLH01 (Fig. S1). Distinctly, the maximum peaks for Pu and ¹³⁷Cs in core SLH01 at the depth of 155 cm were attributed to the maximum deposition in 1963 (UNSCEAR, 2000). SAR and sediments age are shown in Fig. 2.

3.2. Down-core flux and concentration variation of 16 PAHs

The sedimentary flux and concentration profiles of the 16 PAHs in the sediment core are shown in Fig. 3. The total concentrations of PAHs ranged from 17.37 to 839.55 ng g^{-1} dry weight (dw), with the mean value of 213.51 ng g^{-1} (dw). The PAH concentrations in the core were higher than those reported in lakes in western China (29.1–475 ng g^{-1} dw) (Guo et al., 2010), central continental shelf of the East China Sea (27–132 ng g^{-1} dw) (Guo et al., 2006), but were lower than those in Donghu Lake in Wuhan City (33.32–937.24 ng g^{-1} dw), Lake Baiyangdian in northern China (97.2–2402 ng g^{-1} dw) (Guo et al., 2006; Liu et al., 2009) and Yalujiang River (68–1500 ng g^{-1} dw) (Wu et al., 2003). In addition, the levels were significant lower than those reported in urbanized



Fig. 2. Sediment accumulation rates (SAR) and age of core SLH01.



Fig. 3. Down-core concentrations and fluxes of the 16 USEPA priority PAHs in core SLH01.

and industrialized areas, such as Pearl River (1434-10,811 ng g^{-1} dw) (Mai et al., 2002), the Macao Harbor (294-12,714 ng g^{-1} dw) (Mai et al., 2003).

The concentration profiles of the 16 PAHs showed small fluctuations from the 1950s to the 1960s (Fig. 3). After the establishment of the People's Republic of China in 1949, China's economy went through rapid development. The presence of a small peak associated with PAH concentrations in the sediment core in 1968 might be associated with the short-term economic development in China. An increase of total PAH concentrations from 17.4 to 110.24 ng g⁻¹ was recorded by sediment (Fig. 3), which is similar with to the results of East China Sea and Lake Baiyangdian (Guo et al., 2006, 2007; Guo et al., 2011).

The Cultural Revolution period in China was from 1966 to 1976. During this period, China's economy stagnated, many of manufacturing plants either closed or greatly reduced production. Consequently, a decrease in total PAHs concentration and flux in the early 1970s was observed, respectively (Fig. 3). However, the total PAHs concentration and flux gradually increased beginning in 1975, which corresponded to the increasing consumption of oil and coal production (Guo et al., 2007; Guo et al., 2011). A similar increase was also detected in the late 1970s in the sediment cores from the Changjiang River Estuary and the Yellow Sea (Guo et al., 2007; Liu et al., 2012).

The profiles of the total PAHs concentration and flux basically coincided with economic development trends during this period (Guo et al., 2006). A significant increase in total PAHs concentrations occurred in the late 1970s (Fig. 3). After the "Reform and Open" policy in 1978, the resuscitation of China's economy, accompanied by urbanization and industrialization, resulted in rising energy consumption and consequently increased PAHs emissions (Liu et al., 2005), which is consistent with the rapid increase in PAHs concentrations from the late 1970s until 2000. From 1980 to 2000, economic growth has been rising in Linvin City (Supplementary Material Fig. S2). The total PAHs concentrations rose until they reached the subsurface maximum, from 428.56 ng g^{-1} in 1980 to 807.81 ng g^{-1} in 2000, reflecting the increase in demand for energy from fossil fuels and coal. Although, economic development during this period remained rapid, the management of Shilianghe Reservoir catchment took measures to mitigate the adverse effects on the environment. For example, improve industrial wastewater treatment rate and cyclic utilization rate, and as well as closed and integrated some heavy contaminated factories including paper mills, chemical plants and printing and

dyeing mills were implemented since 2000 (Gao and Huang, 2009). The total PAHs concentrations and flux have decreased from 2000 to the present. This decrease may have reflected the pollution control of overall volume as a consequence of legal restrictions and improvements in waste processing technology, which is similar with to the result of other lakes in China (Liu et al., 2009; Guo et al., 2011).

The trends of PAHs concentration profiles in this study were also found in Lake Baiyangdian of northern China (Guo et al., 2011) and Donghu Lake of central China (Yang et al., 2011), but not similar to previously reported sediment cores from Taihu Lake in eastern China (Liu et al., 2009), the lakes in western China (Xu et al., 2014), East China Sea (Guo et al., 2006) and the Pearl River Delta (Peng et al., 2008), in which the PAHs concentrations show a sustained increase since 1978. The difference in the vertical PAHs profile patterns between Shilianghe Reservoir and other regions may reflect different levels of economic development in China.

As shown in Fig. 3, the variations of sedimentary flux were similar to the profiles of the total PAHs concentrations in this sediment core. To further assess the impact of rapid economic development on the local environment, the relationship between the time-dependent fluxes of total PAHs and gross domestic product (GDP) in Linyi was examined during the period of 1978–2013 (Fig. S2). The total PAH fluxes and the regional GDP development exhibited strong exponential correlations ($R^2 = 0.83$, n = 14, p < 0.01). (Supplementary Material Fig. S2), which reflect the level of PAHs emissions from the combustion of domestic coal and biomass (Liu et al., 2012).

3.3. Profiles of Al, Pb and their ratios

Al and Pb are shown in Supplementary Material (Fig. S3). Variations were observed for SLH01 core elements in vertical profiles. No significant variation in Al in the sediment profiles was found, which suggested that the increase in heavy metals in sediments of Shilianghe Reservoir from the decades may mainly come from anthropogenic sources in catchment. Differing from the profiles of Al contents, the Pb concentrations increased from the bottom to the top, and the maximum values were observed at depth of 25 cm. Interestingly, the minimum values of Al and Pb were observed at depth of 80 cm.

Conservative elements such as Al are derived mainly from aluminum silicate of parent material of soil or bedrock (Soto-Jimenez et al., 2003; Roach, 2005; Franco-Uria et al., 2009). These elements in the sediments are less affected by human activities and have notable relationships with mineral composition. The variations of these elements in lake sediments are dependent on differences in natural mineral sources. Therefore, natural and anthropogenic contribution of selected metals can be distinguished based on the correlation between metals and suitable conservative elements (Yao et al., 2013). Fig. S3 also shows the vertical distributions of the ratios between Pb and Al in the core. The ratios of Pb/ Al tended to increase from the bottom to the depth of 93 cm, corresponding to 1973, due to the establishment of the People's Republic of China. During this period, the peak was found at the depth of 175 cm (1960). Then its ratio decreased upward up to the depth of 75 cm (1975), which resulted from the Cultural Revolution in China. Whereas, the Pb/Al increased moving from the bottom to the top, beginning the Reform and Open in China, and the maximum was found at the surface. In recent decades, the heavy metal discharges in the reservoir sediment has decreased due to legal measures and the introduction of new technology.



Fig. 4. Vertical variations of relative abundance of PAHs in the sediment from Shilianghe Reservoir.

3.4. PAHs compositions

Fig. 4 describes the variation in PAHs categories in the studied sediment core. Since 1950s, the percentage of low molecular weight PAHs (2+3 rings) gradually decreased. In contrast, the percentage of high molecular weight (5+6 ring) PAHs to total PAHs increased from an average of 39% in 1960s-mid 1970s to the mean of 52%. Apart from petrogenic sources, low molecular weight PAHs with a 2+3 ring typically originate from low to moderate temperature combustion processes, including biomass and coal burning in homes and small factories (Mai et al., 2003; Guo et al., 2006, 2007; Wang et al., 2009). High molecular weight (5+6 rings) PAHs are generated mainly through high-temperature combustion processes, involving coal and petroleum, such as combustion processes in power plants, factories, automotive engines, and gas-fired cooking appliances (Khalili et al., 1995; Harrison et al., 1996; Yunker et al., 2002; Guo et al., 2007). Consequently, the change in PAHs compositions from low molecular weight to high molecular weight PAHs reflects the transformation of catchment from an agricultural economy to an industrial economy, which is more evident after the late 1970s.

The PAHs species Flu, Phe, Ant, Fluo, Pyr, BaA, Chr, BbF, BkF, DBA, InP, BghiP, and BaP are important tracers for PAH source identification because of their stability and abundance in the environment (Guo et al., 2006). The profiles of the selected PAHs concentrations in the sediment core from Shilianghe Reservoir are shown in Supplementary Material (Fig. S4). Flu, Phe and Ant are mainly from low and moderate temperature combustion processes, such as biomass burning and domestic coal burning (Khalili et al., 1995; Harrison et al., 1996; Wang et al., 2009; Guo et al., 2006). The concentrations of Flu and Phe in sediment core increased rapidly after the late 1970s (Fig. S4), due to biomass burning and domestic coal combustion, which might be related to the growth of the population in catchment of Shilianghe Reservoir, Linyi City. Similar trends of Flu and Phe were also observed in Donghu Lake of central China (Wang et al., 2009). A correlation was found between the population of Linyi City and total PAHs with $R^2 = 0.87$, n = 7 and p < 0.01 from 1978 to 2013.

Fluo, Pyr, BaA, Chr, InP and BghiP usually act as tracers for coal and petroleum combustion and its combustion process, such as vehicular exhaust (Harrison et al., 1996; Guo et al., 2006; Mai et al., 2003; Wang et al., 2010). Since the late 1970s, their concentrations gradually increased (Fig. S4), which correlates with the increasing energy demand for coal and petroleum after the initiation of "Reform and Open" in China. In addition, an exponential correlations was found between gross industrial and agricultural products (GIAP) and total PAHs with $R^2 = 0.84$, n = 14 and p < 0.01 (Fig. S2). These results also demonstrated that the increase of the high molecular weight PAHs corresponds with regional economic development.

3.5. Pb isotopic compositions

 $^{207}\text{Pb}/^{206}\text{Pb}$ ratio is commonly used in environmental studies tracking lead pollution (Cheng and Hu, 2010). Down-core profile of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios is shown in Fig. 5. $^{207}\text{Pb}/^{206}\text{Pb}$ ratios ranged from 0.8395 \pm 0.002 to 0.8922 \pm 0.001, with average of 0.8576 \pm 0.002. Significant increases of $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in core were characterized from the bottom sediments (0.8395 \pm 0.001, corresponding to 1958) to near-surface sediments (0.8922 \pm 0.002, corresponding to 2004). While, a correlations was observed between GDP and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios with R2 = 0.80, n = 14 and p < 0.01 (Fig. S2), reflecting the increase of anthropogenic Pb load to Shilianghe Reservoir from the 1950s, with high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios.

3.6. Anthropogenic impact on the reservoir

Anthropogenic PAHs can be mainly divided into petrogenic and pyrogenic sources based on spills and incomplete combustion of fossil fuels, respectively (Yunker et al., 1999, 2002). The ratios of individual PAHs with similar molecular weights can have been used as indexes to determine their origins (Khalili et al., 1995; Yunker et al., 1999, 2002; Mandalakis et al., 2005; Zhang et al., 2005). In the present study, we calculated the ratios of BaA/(BaA + Chr), Fluo/ (Fluo + Pry) and InP/(InP + BghiP) and used the results to identify the PAH sources (Fig. 6). BaA/(BaA + Chr) ratio between 0.2 and 0.35 is attributed to the combustion of liquid fossil fuels (gasoline for vehicles, crude oil), whereas a ratio <0.2 corresponds to petrogenic sources and a ratio >0.35 corresponds to combustion of coal, grass or wood (Martins et al., 2010). Fluo/(Fluo + Pry) ratios <0.4 indicate petrogenic sources, and those between 0.4 and 0.5 indicate liquid fossil fuel combustion, while ratios >0.5 are characteristics of coal or biomass combustion (Yunker et al., 1999, 2002). InP/(InP + BghiP) ratios <0.2 indicate possible petrogenic sources, those between 0.2 and 0.5 indicate liquid fossil fuel combustion, and ratios >0.5 are presumed to mean that a pyrogenic source was dominant (Yunker et al., 1999, 2002). These results suggest that the dominant source of PAHs in Shilianghe Reservoir



Fig. 5. ²⁰⁷Pb/²⁰⁶Pb profile of the core SLH01.

was incomplete combustion inputs, which mainly derived from coal, grass, and wood combustion. Fluo/(Fluo + Pry) showed a clear decreasing trend since the late 1970s, resulting from an increase in the introduction of PAHs into Shilianghe Reservoir through petroleum combustion from the catchment, Linyi City. It was similar with the depositional records in the East China Sea and the Changjiang Estuary as well as Donghu Lake in central China (Guo et al., 2006, 2007; Yang et al., 2011). The ratios of InP/(InP + BghiP) and BaA/ (BaA + Chr) also emphasized this characteristic energy consumption, indicating that coal combustion was the dominant pyrolytic source of PAHs in this area.

Several possible anthropogenic Pb sources in sediments include atmospheric deposition, soil erosion, vehicle exhaust, the emission of coal and industrial discharges, and so on. The background Pb in sediments originated from the natural weathering of surrounding crystalline and sedimentary rocks, which had similar isotopic characteristics (Jeong et al., 2012). The natural Pb isotopic ratios in background sediments of East China have narrow variations with ²⁰⁷Pb/²⁰⁶Pb ratio of 0.8367-0.8420, and ²⁰⁸Pb/²⁰⁶Pb ratio of 2.0793-2.0910 (Zhu et al., 1995; Choi et al., 2007; Wang et al., 2014; Hao et al., 2008). The ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratio of the exhaust of leaded gasoline vehicles in China are 0.896-0.911 and 2.1840-2.2039, whereas, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratio of unleaded vehicle exhaust are 0.8634-0.8788 and 2.1174-2.1373, respectively (Chen et al., 2005, 2008; Tan et al., 2006; Zheng et al., 2004). The Pb isotope ratios of Chinese coal showed a large variation of ²⁰⁷Pb/²⁰⁶Pb ratio, ranging from 0.828 to 0.877, with an average of 0.860, and the 208 Pb/ 206 Pb ratio ranged from 2.0890 to 2.111 (Mukai et al., 1993: Bollhofer and Rosman, 2001: Chen et al., 2005). The ²⁰⁷Pb/²⁰⁶Pb ratio of coal combustion dust in China varied from 0.8456 to 0.8649, ²⁰⁸Pb/²⁰⁶Pb ratio of 2.17-2.20 (Zheng et al., 2004; Chen et al., 2005 Tan et al., 2006). These ratios for the atmospheric aerosols (TSP, PM2.5 and PM10) are 0.8565-0.8650 for ²⁰⁷Pb/²⁰⁶Pb, and 2.1020-2.180 for ²⁰⁸Pb/²⁰⁶Pb (Mukai et al., 2001; Zheng et al., 2004; Chen et al., 2005, 2008; Hu et al., 2014). The correlations between ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb of natural background and potential Pb pollution sources are shown in Fig. 7. The ²⁰⁷Pb/²⁰⁶Pb ratio of the core bottom samples deposited before 1960s was similar to that of natural background; however, the ²⁰⁷Pb/²⁰⁶Pb of the upper layer samples after 1960s fell on that of various anthropogenic sources in sediment core SLH01. Most measured sediment layers of core were distinct to the isotope ratios of vehicle exhaust particles (leaded), while, sediment located in the coal, coal combustion dust and vehicle exhaust particles (unleaded) Pb signature block (Fig. 7). Additionally, some sediment had Pb isotopic signature close to industry waste discharge and atmospheric aerosols.

Given that the natural Pb source, leaded gasoline, and coal/coal combustion dust were considered as three major contributors for Pb in these sediment cores. Applying the three end-member model of Pb source apportionment (Li et al., 2013) to the sediment cores, coal/coal combustion dust contributed averagely 31-62% of Pb in the sediment core SLH01 (Supplementary Material Fig. S5). The contributions of leaded gasoline and natural background were an average of 18% and 38% for the core, respectively (Fig. S5). Previous studies of some areas in Shanghai City of eastern China show that the contributions of coal/coal combustion are estimated to range from 52% to 69%, and ones of leaded gasoline range from 10 to 26% to Pb pollution (Tan et al., 2006; Li et al., 2012). In addition, the contribution from leaded gasoline to airborne anthropogenic Pb in Shanghai was lower than 30% before the phase-out of leaded gasoline (Chen et al., 2005). Our findings from Shilianghe Reservoir were in a good agreement with these previous reports, which receive Pb from atmospheric deposition in a majority. These results also indicated that anthropogenic Pb that accumulated after about



Fig. 6. Source identification using PAH ratios; Fluo/(Fluo + Pyr) < 0.4 = petrogenic source (I), 0.4-0.5 = liquid fossil fuel combustion (II), >0.5 = coal, grass or wood combustion (III); InP/(InP + BghiP) < 0.2 = petrogenic (I), 0.2-0.5 = liquid fossil fuel combustion (II), >0.5 = coal, grass and wood combustion (III); BaA/(BaA + Chr) < 0.2 = petrogenic source, 0.2-0.35 = liquid fossil fuel combustion (II), >0.35 = coal, grass or wood combustion (III) (Yunker et al., 2002; Mai et al., 2003; Guo et al., 2006).



Fig. 7. Correlations between ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb of the core SLH01 (this work). Natural background data are from Choi et al. (2007), Hao et al. (2008) and Zhu (1995), vehicle exhausts of leaded and unleaded gasoline are from Chen et al. (2005, 2008), Tan et al. (2006) and Zheng et al. (2004), coal date are from Mukai et al. (1993), Bollhofer and Rosman (2001), Chen et al. (2005) and Hu et al. (2013), coal combustion dust are from Zheng et al. (2004), and Tan et al. (2006), atmospheric aerosols are from Zheng et al. (2004), Tan et al. (2006), Mukai et al. (2001), Hu et al. (2014), industry waste discharges from Hu et al. (2013).

the 1950s in the Shilianghe Reservoir mainly originated from coal, coal combustion dust and vehicle exhaust particles. Interestingly, some sediment had Pb isotopic signature close to industry waste discharge, implying that anthropogenic Pb also originated from this source.

History records of three Pb source contributions in the studied sediment cores were shown from 1958 to 2014 (Fig. S5). Contributions of coal combustion slightly increased over time while the natural Pb contributions declined. In contrast, the leaded gasoline Pb contribution rate generally increased from 1950s to early 2000s, whereas, this contribution decreased since mid-2000s. This also illustrates that Pb from alkyl lead additives was effectively removed after the final phase-out of leaded gasoline in China.

4. Conclusions

Reconstructing the history of PAHs pollution from a sedimentary record was an important in the study to understand the socioeconomic development impact on the catchment of Shilianghe Reservoir. The results indicated that human activities had a great contribution to PAHs input. The significant increase in 16 PAH concentrations and fluxes after the 1980s closely correlated with the intensifying in human activities and rapid economic development. The sources of PAHs had transferred from pyrolytic origin and were dominated by the combustion of coal and biomass. Based on well constrained Pb isotopic signatures, we reconstructed the chronologies of the Pb deposition in Shilianghe Reservoir sediments. These chronologies are consistent with historical records of PAHs predominantly sourced from coal combustion and with fossil fuel uses in the catchment. With the end-member model of Pb isotopes, coal combustion derived Pb emission dominated a contribution of 31-69%, in contrast, leaded gasoline related Pb emission contributed less than average 25% of Pb since the late 1950s. In sediment core SLH01, Pb contribution from coal/coal combustion showed an increasing trend upward, and this from leaded gasoline also increased from 1950s to early 2000s. However, the decline of leaded gasoline Pb contribution in mid-2000s was mainly due to forbidding the use of leaded gasoline.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 41406055), Open Fund of State Key Laboratory of Pollution Control and Resources Reuse (No. PCRRF11024), the Project of Innovation for Undergraduate in Jiangsu Province (No. SY201511641107001), Natural Science Foundation of Jiangsu Provincial Department of Education (No. 14KJB170001), China Postdoctoral Science Foundation (No. 2014M561973), Postdoctoral Science Foundation of Qingdao City, and Natural Science Foundation of Huaihai Institute of Technology (No. Z2014017).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.12.010.

References

- Appleby, P.G., 2008. Three decades of dating recent sediments by fallout radionuclides: a review. Holocene 18, 83–93.
- Ault, W.A., Senechal, R.G., Erlebach, W.E., 1970. Isotopic composition as a natural tracer of lead in the environment. Environ. Sci. Technol. 4, 305–313.
- Berrojalbiz, N., Dashes, J., Ojeda, M.J., Valle, M.C., Castro-Jimenez, J., Wollgast, J., Ghiani, M., Hanke, G., Zaldivar, J.M., 2011. Biogeochemical and physical controls on concentrations of polycyclic aromatic hydrocarbons in water and plankton of the Mediterranean and Black seas. Glob. Biogeochem. Cycles 25, GB4003. http:// dx.doi.org/10.1029/2010GB003775.
- Bollhofer, A., Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the northern hemisphere. Geochim. Cosmochim. Acta 65, 1727–1740.
- Carignan, J., Gariepy, C., 1995. Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric lead emissions in southern Québec, Canada. Geochim. Cosmochim. Acta 59, 4427–4433.
- Chen, J.A., Wan, G.J., Tang, D.G., Huang, R.G., 2000. Recent climatic changes recorded by sediment grain sizes and isotopes in Erhai Lake. Prog. Nat. Sci. 10, 54–61.
- Chen, J.M., Tan, M.G., Li, Y.L., Zhang, Y.M., Lu, W.W., Tong, Y.P., Zhang, G.L., 2005. A lead isotope record of Shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline. Atmos. Environ. 39, 1245–1253.
- Chen, J.M., Tan, M.G., Li, Y.L., Zheng, J., Zhang, Y.M., Shan, Z., Zhang, G.L., Li, Y., 2008. Characteristics of trace elements and lead isotope ratios in PM2.5 from four sites in Shanghai, J. Hazard. Mater 156, 36–43.
- Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. Environ. Pollut. 158, 1134–1146.
- Choi, M.S., Yi, H.-I., Yang, S.Y., Lee, C.-B., Cha, H.-J., 2007. Identification of Pb sources in Yellow sea sediments using stable Pb isotope ratios. Mar. Chem. 107 (2), 255–274.
- Chow, T.J., Earl, J.L., 1972. Lead isotopes in North American coals. Science 176, 510-511.
- Christensen, E.R., Arora, S., 2007. Source apportionment of PAHs in sediments using factor analysis by time records: application to Lake Michigan, USA. Water Res. 41 (1), 168–176.
- Flynn, W.W., 1968. The determination of low level of polonium-210 in environmental materials. Anal. Chim. 43, 221–226.
- Franco-Uría, A., López-Mateo, C., Roca, E., Fernández-Marcos, M.L., 2009. Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. J. Hazard. Mater 165, 1008–1015.
- Gallon, C., Tessier, A., Gobeil, C., Alfaro-De la Torre, M.C., 2004. Modeling diagenesis of lead in sediments of a Canadian Shield lake. Geochim. Cosmochim. Acta 68, 3531–3545.
- Gao, Q.B., Huang, L.H., 2009. The present situation of rural environmental pollution and comprehensive improvement in Linyi City. Agro. Environ. Develop. 51, 1–6 (in Chinese).
- Gerritse, R.G., Wallbrink, P.J., Murria, A.S., 1998. Accumulation of phosphorus and heavy metals in the Swan-Canning Estuary, Western Australia. Est. Coast. S. 47, 165–170.
- Grimalt, J.O., Van Drooge, B.L., Ribes, A., Fernandez, P., Appleby, P., 2004. Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes. Environ. Pollut. 131, 13–24.
- Guo, Z.G., Lin, T., Zhang, G., Zheng, M., Zhang, Z.Y., Hao, Y.C., Fang, M., 2007. The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River Estuary coastal sea for the past century. Sci. Total Environ. 386, 33–41.
- Guo, Z.G., Lin, T., Zhang, G., Yang, Z.S., Fang, M., 2006. High-resolution depositional records of polycyclic aromatic hydrocarbons in the Central Continental shelf Mud of the East China sea. Environ. Sci. Technol. 40, 5304–5311.
- Guo, J.Y., Wu, F.C., Luo, X.J., Liang, Z., Liao, H.Q., Zhang, R.Y., Li, W., Zhao, X.L., Chen, S.J., Mai, B.X., 2010. Anthropogenic input of polycyclic aromatic hydrocarbons into five lakes in Western China. Environ. Pollut. 158 (6), 2175–2180. Guo, J.Y., Wu, F.C., Zhang, L., Liao, H.Q., Li, W., 2011a. Screening level of PAH in
- Guo, J.Y., Wu, F.C., Zhang, L., Liao, H.Q., Li, W., 2011a. Screening level of PAH in sediment core from lake Hongfeng, Southwest China. Arch. Environ. Contam. Toxicol. 60, 590–596.
- Guo, W., Pei, Y., Yang, Z., Chen, H., 2011b. Historical changes in polycyclic aromatic hydrocarbons (PAHs) input in Lake Baiyangdian related to regional socio-economic development. J. Hazard. Mater 187, 441–449.
 Hao, Y., Guo, Z., Yang, Z., Fan, D., Fang, M., Li, X., 2008. Tracking historical lead
- Hao, Y., Guo, Z., Yang, Z., Fan, D., Fang, M., Li, X., 2008. Tracking historical lead pollution in the coastal area adjacent to the Yangtze River Estuary using lead isotopic compositions. Environ. Pollut. 156, 1325–1331.
- Harrison, R.M., Smith, D.J.T., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. Environ. Sci. Technol. 30, 825–832.
- Hu, G.R., Yu, R.L., Zheng, Z.M., 2013. Application of stable lead isotopes in tracing heavy-metal pollution sources in the sediments. Act. Sci. Circum. 33 (5), 1326–1331 (in Chinese).
- Hu, X., Sun, Y.Y., Ding, Z.H., Zhang, Y., Wu, J.C., Lian, H.Z., Wang, T.J., 2014. Lead contamination and transfer in urban environmental compartments analyzed by

lead levels and isotopic compositions. Environ. Pollut. 187, 42-48.

- Jeong, Y.J., Cheong, C.S., Shin, D., Lee, K.S., Jo, H.J., Gautam, M.K., Lee, I., 2012. Regional variations in the lead isotopic composition of galena from southern Korea with implications for the discrimination of lead provenance. J. Asian Earth Sci. 61, 116–127.
- Jiang, Y.H., Jiang, S.Y., Ling, H.F., Dai, B.Z., 2006. Low-degree melting of a metasomatized lithospheric mantle for the origin of Cenozoic Yulong monzograniteporphyry, east Tibet: geochemical and Sr–Nd–Pb–Hf isotopic constraints. Earth Plan. 241, 617–633.Kirchner, G., 2011. ²¹⁰Pb as a tool for establishing sediment chronologies: examples
- Kirchner, G., 2011. ²¹⁰Pb as a tool for establishing sediment chronologies: examples of potentials and limitations of conventional dating models. J. Env. Rad. 102, 490–494.
- Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atmos. Environ. 29, 533–542.
- Leorri, E., Mitra, S., Irabien, M.J., Zimmerman, A.R., Blake, W.H., Cearret, A., 2014. A 700 year record of combustion-derived pollution in northern Spain: tools to identify the Holocene/Anthropocene transition in coastal environments. Sci. Total Environ. 470–471, 240–247.
- Li, H.B., Yuan, S., Li, G.L., Deng, H., 2012. Lead contamination and source in Shanghai in the past century using dated sediment cores from urban park lakes. Chemosphere 88, 1161–1169.
- Liu, E.F., Zhang, E.L., Li, K., Nath, B., Li, Y.L., Shen, J., 2013. Historical reconstruction of atmospheric lead pollution in central Yunnan province, southwest China: an analysis based on lacustrine sedimentary records. Environ. Sci. Pollut. Res. 20, 8739–8750.
- Liu, G.Q., Zhang, G., Li, X.D., Li, J., Peng, X.Z., Qi, S.H., 2005. Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River Estuary, South China. Mar. Pollut. Bull. 51, 912–921.
- Liu, G.Q., Zhang, G., Jin, Z.D., Li, J., 2009. Sedimentary record of hydrophobic organic compounds in relation to regional economic development: a study of Taihu Lake, East China. Environ. Pollut. 157, 2994–3000.
- Liu, L.Y., Wang, J.Z., Wei, G.L., Guan, Y.F., Wong, C.S., Zeng, E.Y., 2012. Sediment records of polycyclic aromatic hydrocarbons (PAHs) in the continental shelf of China: implications for evolving anthropogenic impacts. Environ. Sci. Technol. 46, 6497–6504.
- Louchouarn, P., Kuo, L.J., Brandenberger, J.M., Marcantonio, F., Garland, C., Gill, G.A., 2012. Pyrogenic inputs of anthropogenic Pb and Hg to sediments of the Hood Canal, Washington, in the 20th century: source evidence from stable Pb isotopes and PAH signatures. Environ. Sci. Technol. 46, 5772–5781.
- Lima, A.L., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment-a review. Environ. Forens. 6, 109–131.
- Mai, B.X., Fu, J.M., Sheng, G.Y., Kang, Y.H., Lin, Z., Zhang, G., 2002. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. Environ. Pollut. 117, 457–474.
- Mai, B.X., Qi, S.H., Zeng, E.Y., Yang, Q.S., Zhang, G., Fu, J.M., 2003. Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. Environ. Sci. Technol. 37, 4855–4863.
- Mandalakis, M., Gustafsson, O., Alsberg, T., Egeback, A.L., Reddy, C.M., Xu, L., 2005. Contribution of biomass burning to atmospheric polycyclic aromatic hydrocarbons at three European background sites. Environ. Sci. Technol. 39, 2976–2982.
- Martins, C.C., Bicego, M.C., Rose, N.L., Taniguchi, S., Lourenco, R.A., Figueira, R.C.L., Mahiques, M.M., Montone, R.C., 2010. Historical record of polycyclic aromatic hydrocarbons (PAHs) and spheroidal carbonaceous particles (SCPs) in marine sediment cores from Admiralty Bay, King George Island, Antarctica. Environ. Pollut. 158, 192–200.
- Meng, H.M., Zhang, Z.K., Tian, H.T., 2008. Contents and contamination of heavy metals in the surface sediments of shilianghe reservoir. J. Agro. Environ. Sci. 27 (2), 721–725 (in Chinese).
- Meng, H.M., Zhang, Z.K., 2008. Accumulation on heavy metals of sediments in shilianghe reservoir. Res. Environ. Sci. 21, 44–50 (in Chinese).
- Mukai, H., Furuta, N., Fujii, T., Ambe, Y., Sakamoto, K., Hashimoto, Y., 1993. Characterization of sources of lead in the urban air of Asia using ratios of stable lead isotopes. Environ. Sci. Technol. 27, 1347–1356.
- Mukai, H., Tanaka, A., Fujii, T., Zeng, Y., Hong, Y., Tang, J., Guo, S., Xue, H., Sun, Z., Zhou, J., Xue, D., Zhao, J., Zhai, G., Gu, J., Zhai, P., 2001. Regional characteristics of sulphur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environ. Sci. Technol. 35, 1064–1071.Pan, S.M., Zhu, D.K., Li, Y., 1997. ¹³⁷Cs profile in the sediments in estuaries and its
- Pan, S.M., Zhu, D.K., Li, Y., 1997. ¹³⁷Cs profile in the sediments in estuaries and its application in sedimentology. Act. Sediment. S. 15, 67–71 (in Chinese).
- Peng, X.Z., Wang, Z.D., Yu, Y.T., Tang, C.M., Lu, H., Xu, S.P., 2008. Temporal trends of hydrocarbons in sediment cores from the Pearl River Estuary and the northern South China Sea. Environ. Pollut. 156, 442–448.
- Qiao, M., Wang, C.X., Huang, S.B., Wan, D.H., Wan, Z.J., 2006. Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. Environ. Int. 32, 28–33.
- Roach, A.C., 2005. Assessment of metals in sediments from Lake Macquarie. New South Wales, Australia, using normalisation models and sediment quality guidelines. Mar. Environ. Res. 59, 453–472.
- Soto-Jimenez, M., Paez-Osuna, F., Ruiz-Fernandez, A.C., 2003. Geochemical evidences of the anthropogenic alteration of trace metal composition of the sediments of Chiricahueto marsh (SE Gulf of California). Environ. Pollut. 125, 423–432.

- Sturges, W.T., Barrie, L.A., 1987. Lead 206/207 isotope ratios in the atmosphere of North America as tracers of U.S. and Canadian emissions. Nature 329, 144–146.
- Sturges, W.T., Barrie, L.A., 1989. Stable lead isotope ratios in arctic aerosols; evidence for the origin of arctic air pollution. Atmos. Environ. 23, 2513–2519.
- Tan, M.G., Zhang, G.L., Li, X.L., Zhang, Y.X., Yue, W.S., Chen, J.M., Wang, Y.S., Li, A.G., Li, Y., Zhang, Y.M., Shan, Z.C., 2006. Comprehensive study of lead pollution in Shanghai by multiple techniques. Anal. Chem. 78 (23), 8044–8050.
- Tian, H.T., Zhang, Z.K., Ding, H.Y., Li, Y.M., Meng, H.M., 2008. Recent 40-year sedimentary record of heavy metal pollution in the Shilianghe Reservoir, Jiangsu Province, J. Lake Sci. 20 (5), 600–604 (in Chinese).
- Tolosa, I., Mora, S.D., Sheikholeslami, M.R., Villeneuve, J.P., Bartocci, J., Cattini, C., 2004. Aliphatic and aromatic hydrocarbons in coastal Caspian sea sediments. Mar. Pollut. Bull. 48, 44–50.
- Tsang, H.L., Wu, S.C., Leung, C.K., Tao, S., Wong, M.H., 2011. Body burden of POPs of Hong Kong residents, based on human milk, maternal and cord serum. Environ. Int. 37 (1), 142–151.
- UNSCEAR, 2000. Sources and Effects of Ionizing Radiation, vol. 1. United Nations, New York, p. 213.
- Vane, C.H., Chenery, S.R., Harrison, I., Kim, A.W., Moss-Hayes, V., Jones, D.G., 2011. Chemical signatures of the Anthropocene in the Clyde estuary, UK: sedimenthosted Pb, Pb-207/206, total petroleum hydrocarbon, polyaromatic hydrocarbon and polychlorinated biphenyl pollution records. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 369, 1085–1111.
- Wang, X.P., Yang, H.D., Gong, P., Zhao, X., Wu, G.J., Turner, S., 2010. One century sedimentary records of polycyclic aromatic hydrocarbons, mercury and trace elements in the Qinghai Lake, Tibetan Plateau. Environ. Pollut. 158, 3065–3070.
- Wang, Z., Chen, J.W., Yang, P., Tian, F.L., Qiao, X.L., Bian, H.T., 2009. Distribution of PAHs in pine (Pinus thunbergii) needles and soils correlates with their gasparticle partitioning. Environ. Sci. Technol. 43, 1336–1341.
- Wang, H., Wang, C., Wu, W., Wang, Z., 2002. Persistent organic pollutants (POPs) in surface sediments of Donghu Lake, Wuhan, Hubei, China. J. Environ. Sci. Health. Part A Toxic Hazard. Subst. Environ. Eng. 37, 499–507.
- Wang, D.L., Zhao, Z.Q., Dai, M.H., 2014. Tracing the recently increasing anthropogenic Pb inputs into the East China Sea shelf sediments using Pb isotopic analysis. Mar. Pollut. Bull. 79, 333–337.
- Wu, Y., Zhang, J., Zhu, Z.J., 2003. Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China. Mar. Pollut. Bull. 46, 619–625.

- Yao, S.C., Xue, B., Tao, Y.Q., 2013. Sedimentary lead pollution history: Lead isotope ratios and conservative elements at East Taihu Lake, Yangtze Delta, China. Quat. Int. 304, 5–12.
- Yang, Z.F., Tang, Z.W., Shen, Z.Y., Niu, J.F., Wang, H.Y., 2011. One-hundred-Year sedimentary record of polycyclic aromatic hydrocarbons in urban Lake sediments from wuhan, Central China. Water Air Soil Pollut. 217, 577–587.
- Yunker, M.B., Macdonald, R.W., Goyette, D., Paton, D.W., Fowler, B.R., Sullivan, D., 1999. Natural and anthropogenic inputs of hydrocarbons to the Strait of Georgia. Sci. Total Environ. 225, 181–189.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem 33, 489–495.
- Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ. Sci. Technol. 39, 9109–9114.
- Zhang, W., Feng, H., Chang, J., Qu, J., Yu, L., 2008. Lead (Pb) isotopes as a tracer of Pb origin in Yangtze River intertidal zone. Chem. Geol. 257, 257–263. Zhang, E.L., Liu, E.F., Shen, J., Cao, Y.M., Li, Y.L., 2012. One century sedimentary record
- Zhang, E.L., Liu, E.F., Shen, J., Cao, Y.M., Li, Y.L., 2012. One century sedimentary record of lead and zinc pollution in Yangzong Lake, a highland lake in southwestern China. J. Environ. Sci. 24 (7), 1189–1196.
- Zheng, J., Yamada, M., 2006. Inductively coupled plasmasector field mass spectrometry with a high-efficiency sample introduction system for the determination of Pu isotopes in settling particles at femtogramlevels. Talanta 69, 1246–1253.
- Zheng, J., Tagami, K., Watanabe, Y., Uchida, S., Aono, T., Ishii, N., Yoshida, S., Kubota, Y., Fuma, S., Ihara, S., 2012. Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident. Sci. Rep. 2, 304. http:// dx.doi.org/10.1038/srep00304.
- Zheng, J., Tan, M.G., Yasuyuki, S., Atsushi, T., Li, Y., Zhang, G., Zhang, Y., Shan, Z., 2004. Characteristics of lead isotope ratios and elemental concentrations in PM10 fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. Atmos. Environ. 38, 1191–1200.
- Zhi, H., Zhao, Z.H., Zhang, Lu, 2015. The fate of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water from Poyang Lake, the largest freshwater lake in China. Chemosphere 119, 1134–1140.
- Zhu, B.Q., 1995. The mapping of geochemical provinces in China based on Pb isotopes. J. Geochem. Explor. 55, 171–181.