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Lead Concentration Distribution and Source Tracing of Urban/Suburban Aquatic Sediments in Two Typical Famous Tourist Cities: Haikou and Sanya, China

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Abstract The content and spatial distribution of lead in the aquatic systems in two Chinese tropical cities in Hainan province (Haikou and Sanyan) show an unequal distribution of lead between the urban and the suburban areas. The lead content is significantly higher (72.3 mg/kg) in the urban area than the suburbs (15.0 mg/kg) in Haikou, but quite equal in Sanya (41.6 and 43.9 mg/kg). The frequency distribution histograms suggest that the lead in Haikou and in Sanya derives from different natural and/or anthropogenic sources. The isotopic compositions indicate that urban sediment lead in Haikou originates mainly from anthropogenic sources (automobile exhaust, atmospheric deposition, etc.) which contribute much more than the natural sources, while natural lead (basalt and sea sands) is still dominant in the suburban areas in Haikou. In Sanya, the primary source is natural (soils and sea sands).

Keywords Lead · Lead isotope · Source · Aquatic sediments

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Urbanization and industrialization cause continuous anthropogenic release of heavy metals from point and diffuse pollution sources (for instance, industrial discharges, fossil fuel combustion, etc.), and result in their accumulation in aquatic ecosystems. These pollutants are usually considered to accumulate in sediments and released when aquatic environmental conditions (such as pH, redox potential or the presence of organic chelators) change (Förstner and Wittman 1981). Lead, as a toxic heavy metal, is harmful to human health since it is bioaccumulative but non-biodegradable (e.g., Duzgoren-Aydin et al. 2004). It can damage the kidneys, nervous system, and reproductive system and can cause high blood pressure (Joseph and Shawn 2010). It is therefore the importance of understanding the source, content and distribution of lead in sediments (e.g., Arakel and Hongjun 1992).

The isotopic compositions of lead are not affected to a large extent by physical and/or chemical fractionation processes (Duzgoren-Aydin et al. 2004), and are distinct in different environmental matrices (automobile exhaust, lichens, sediments, soils, etc.) (Komárek et al. 2008). Thus, based on similarities or differences, the isotopic ratios of lead, $^{206}Pb/^{207}Pb$ in particular, are useful indicators in environmental studies to trace and distinguish different lead sources in the past few decades (e.g., Abi-Ghanem et al. 2009). However, lead isotopic researches on lead source tracing in aquatic sediments started relatively late and focused mainly on lake sediments (e.g., Renberg et al. 2002). Few studies have investigated the various lead sources of urban and/or suburban aquatic sediments in China (Shang et al. 2005; Lu et al. 2006). Thus, using $^{208}Pb/^{207}Pb$ and $^{207}Pb/^{206}Pb$ as indicators to distinguish urban and suburban aquatic sediment lead from the various natural sources (rock, etc.) and the anthropogenic (automobile exhaust, coal and fly ashes, etc.) sources has a great significance when based on the differentiation of lead contents and distribution.

Both Haikou and Sanya, with tropical maritime monsoon climate, are very typical and relatively clean tourist cities in China. However, they have different population density, leading industries, geologic setting, etc. Haikou city, the capital of Hainan province, located at the northmost of Hainan Islands, is a political, economic, cultural, financial, educational, and transportation center (Fig. 1). It has an area of 2,304.84 km^2 and a population of 1.6 million. Its industry involves car factories, petrochemical processing, rubber industry, electronic industry, etc. Basic volcanic rock or basalt is the main rock type outcropped in the region and latosols prevail. Its biggest aquatic system is the Nandu River. Sanya, located at the south of the same province (Fig. 1), is the second largest city which is considered as one of the least polluted cities in China. It has an area of 1,919.58 km^2 and a population of 0.524 million. Compared to Haikou, there are less industries. The rock outcrop and soils are mainly granites and sandy/silt loams. The primary aquatic systems are the Sanya River and Linchun River. Very few studies have examined lead of the urban/suburban aquatic systems, particularly in the sediments, in these two cities. In this paper, we present the result of our investigation of the sources of lead by the analysis of the content and spatial distribution of lead in the urban/suburban aquatic sediments of the two cities, the lead isotopic ratios of the sediment samples and various natural and anthropogenic source materials.

Materials and Methods

89 sediment samples (see Fig. 1) were collected by shovel in the urban/suburban areas of the two cities during the dry season of 2008, immediately placed in acid-cleaned ziplocked polyethylene bags and transported to laboratory to be air-dried at room temperature. Then, the samples were homogenized, sieved into 2 mm grain size, grinded by mortar and pestle, and quartered. A fraction of less than 0.074 mm grain size were chosen and stored in a refrigerator at 4°C for laboratory analysis.

For lead analysis, an aliquot of approximately 200 mg of dry sediment was digested for 2.5 h at 120°C with 250 μL HNO_3 (65%), 750 μL HCl (30%) and 6 mL HF (48%) in Teflon bombs according to Loring and Rantala (1990). The digested samples were then transferred into polypropylene tubes where 2.7 g of boric acid were added. The

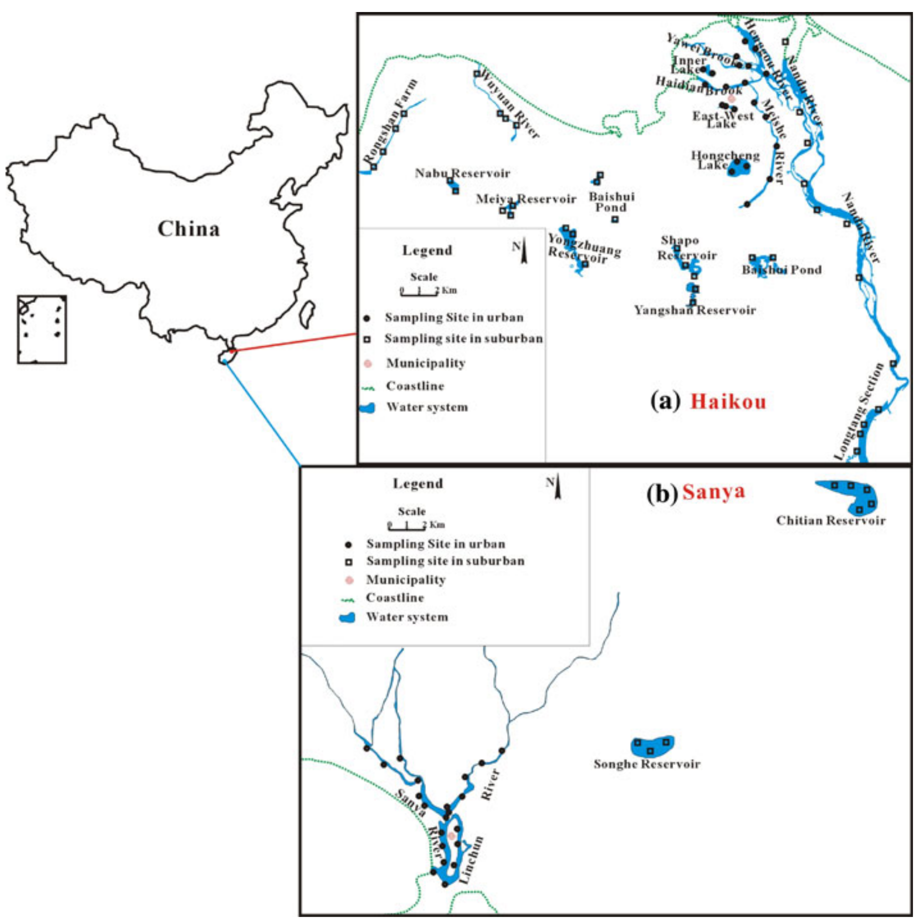

Fig. 1 Sampling sites of aquatic sediments in Haikou (**a**) and Sanya (**b**)

solution was then diluted to a final volume of 50 mL with deionized distilled water. Lead concentrations were determined using an inductive coupled plasma mass spectrometer (ICP-MS, Thermo Electron Corporation, Element X Series). Sediment samples with certified concentration of metals (GSD-8, China National Center for Standard Materials) were used for quality assurance. The recovery of this fortified sample was 96%. The limit of detection for lead is 0.01 mg/L.

Lead isotopic ratios were measured by solid-source thermal ionization mass spectrometry (TIMS) using a multi-collector Finnigan MAT 261. The aliquot was loaded onto a single Re filament with 4 μL silica gel, 1 μL H_3PO_4 and 1 μL (30%) HNO_3, at State Key Laboratory of Geological Processes and Mineral Resources in China University of Geosciences (Wuhan).

All the statistical analyses were performed by using STATISTICA 6.0 for windows. And CorelDraw 9.0 was used to draw the sample map.

Results and Discussion

The lead content of the sediment samples are presented in the table and figure below (Table 1 and Fig. 1). These data to be more significant were compared to data from different environments in China and around the world.

As shown in Table 1, the lead contents of the aquatic sediments in Haikou show a wide range of variation, from 0.3 to 419.8 mg/kg, than in Sanya (22.2–157.7 mg/kg). The average lead concentrations in the two cities are higher than the background values of the stream sediments in China and Europe, and the sediments of the Yellow River, Yangtze River, Pearl River, the China Shelf Sea, etc., showing a degree of anthropogenic effect in the two cities. These values are obviously lower than those of the sediments of the Mississippi, Danube, Rhine, and Yangtze River reaches near the major cities, indicating that, on an average level, the anthropogenic effect is still minor. It is very important to note that in contrast to our assumption that Sanya has a cleaner environment than Haikou, the average lead concentration in aquatic sediments in Sanya is higher than that in Haikou. A reasonable explanation to this fact should be found in the difference in the geological setting of the two cities. According to Turekian and Wedepohl (1961), the aboundance of lead in magmatic rocks increases orderly from ultrabasic rock to granite. As mentioned above, the main rock outcrops are basalt in Haikou, while extensive granite in Sanya. Therefore, the majority of the lead had most possibly been brought into the aquatic systems by

Table 1 Lead concentrations in aquatic sediments (mg/kg)

District	N		Mean	Range	Reference
Haikou					
Urban	22		72.3	10.3–419.8	This study
		36.0			
Suburban	38		15.0	0.3–80.3	
Sanya					
Urban	21		41.6	22.2–157.7	
		42.2			
Suburban	8		43.9	23.2–96.2	
China					
Yangtze River near cities	–		53.4	–	Zhu and Zang (2001)
Stream sediments in China	869		27	–	Chi et al. (2007)
China Shelf Sea	286		20	–	
Yellow River	–		15	–	
Yangtse Rive	–		27	–	
Pearl River	–		30	–	
The world					
The upper continental crust	–		17	–	
Shale	–		20	–	Turekian and Wedepohl (1961)
Stream sediments in Europe	802		38.6	–	Chi et al. (2007)
Danube	–		46.3	–	Woitke et al. (2003)
Mississippi	–		50.5	–	Li et al. (1989)
Rhine	–		30	–	

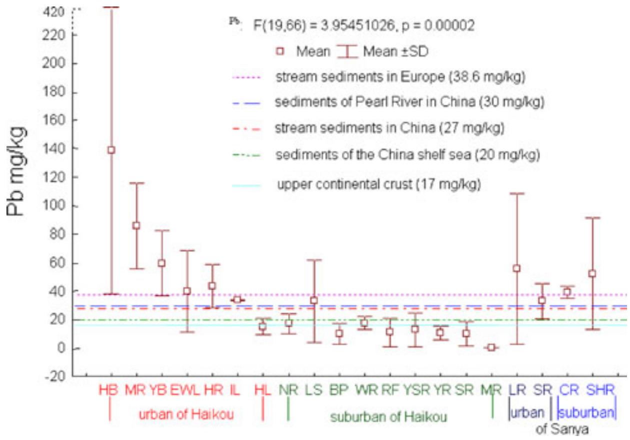

Fig. 2 Lead content and distribution in different types of aquatic sediments in Haikou and Sanya cities *HB* Haidian Brook, *MR* Meishe River, *YB* Yawei Brook, *EWL* East–West Lake, *HR* Henggou River, *IL* Inner Lake of Hainan University, *HL* Hongcheng Lake, *NR* Nandu River, *LS* Longtang Section of Nandu River, *BP* Baishui Pond, *WR* Wuyuan River, *RF* Rongshan Farm, *YSR* Yangshan Reservoir, *YR* Yongzhuang Reservoir, *SR* Shapo Reservoir, *MR* Meiya Reservoir, *LR* Linchun River, *SR* Sanya River, *CR* Chitian Reservoir, *SHR* Songhe Reservoir

natural weathering of rocks in both cities, indicating the minor impact of human activities.

Figure 2 presents the spatial variation of lead between the urban and the suburban areas in the two cities. It appears that the average lead contents of the urban aquatic sediments in Haikou, showing a wider variation, are four times higher than their suburban counterparts. However, the differences of lead contents and distributions between urban and suburban aquatic sediments in Sanya are not as obvious as in Haikou. As mentioned, Haikou is a political, economic, cultural, financial, educational, and transportation center of Hainan province. With the development of industry, tourism and transportation, more stress brought by the human activities results in the content variation and the spatial differentiation of lead between urban and suburban aquatic sediments. Sanya as a typical tourist city experience less environment stress from human activities so that the content changes and the spatial differentiation of lead are not obvious. The spatial distribution of lead is also related to the position in the drainage basin of the principal rivers. The sediment lead concentration in Nandu River's upper reaches (Longtang Section) is higher than in its lower reaches, indicating a likely downstream dilution of lead-bearing sediment particles (Lottermoser 1997). Besides, the maximum lead concentration in Haikou (419.82 mg/kg) is found at the Haidian Brook, and in Sanya, at Linchun River (157.67 mg/kg). These high lead concentrations relates to the concentration and intensity of human activities (commerce, industry, marine transportation, etc.) there.

In sum, the lead content and its spatial distribution in aquatic sediments are obviously different in these two cities, and differences exist between urban and suburban areas in Haikou. These differentiations of content changes and distribution imply that sediment lead originates from different sources. Based on the data presented, the lead content and distribution differentiations are related to both natural background and anthropogenic activities in the study area.

The statistical distribution of element contents is revealed most clearly by histograms and can usually be used to delineate different sources of the elements. Thus, the frequency distribution histograms of sediment lead concentrations in Haikou and Sanya are represented in Fig. 3. The lead concentration distribution of sediments in Haikou is characterized by a multimodal distribution with an isolated extremely high value. They show a noticeable peak with a value range of 13.0–26.1, and two small peaks of 64.2–76.9 and 89.6–102.3. These three peaks may imply that the lead in the aquatic sediments in Haikou can be attributed to different sources. The lowest one probably represents natural lead from the weathering of parent rocks, which has a similar concentration as the upper continental crust, while the higher ones represent lead from anthropogenic sources

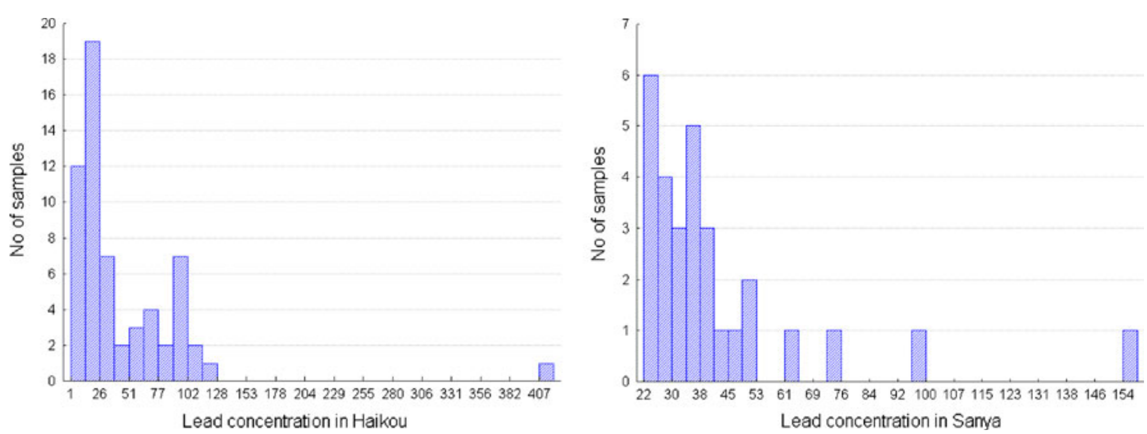

Fig. 3 Frequency distribution histogram of lead concentrations of aquatic sediments in Haikou and Sanya

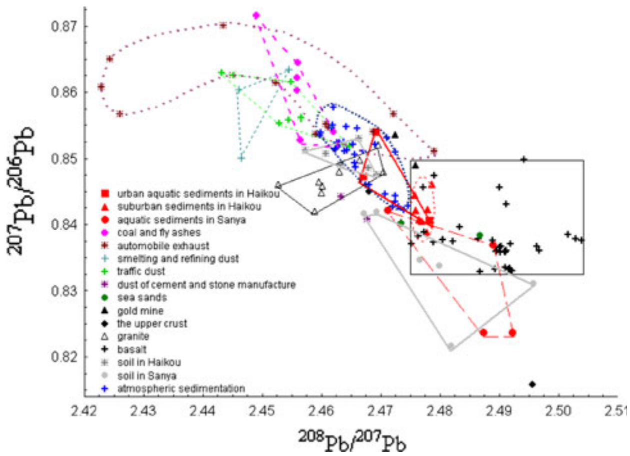

Fig. 4 Plot of $^{208}Pb/^{207}Pb$ vs. $^{207}Pb/^{206}Pb$ for aquatic sediments in Haikou and Sanya and samples of known sources. The isotopic compositions of smelting and refining dust, traffic dust, automobile exhaust, dust of cement and stone manufacture, sea sands, urban soil and atmospheric deposition are from the unpublished data in the two cities. Other data sources: coal and fly ashes (Chen et al. 1998; Shang et al. 2005), other automobile exhaust (Chen et al. 1998; Zhu et al. 2001; Shang et al. 2005), gold mine (Zhu et al. 2001), the upper crust (Chang et al. 2002), granite (Xu et al. 2001), basalt (Fan et al. 2004; Zhang et al. 1992)

in regard to their high values. The isolated extremely high value attest a strong anthropogenic point source(s) of lead. Thus, the concentration distribution histogram indicates that the lead of aquatic sediments in Haikou derives mainly from multiple anthropogenic and/or natural sources and an isolated strong anthropogenic point source(s). In contrast to Haikou, the lead concentration distribution in Sanya shows at some extent a uni-modal distribution with a long tail consisted of dispersed high values. The lower lead concentration values are similar to those of Haikou, presumably implying natural lead, while the dispersed high values indicate some dispersed anthropogenic point sources. In total, this fact confirms the natural and anthropogenic sources of the lead.

To trace the sediment lead sources and to assess the relative contributions of these sources, the isotopic compositions of 14 sediment samples were measured and their isotopic characterization are demonstrated on a plot of $^{208}Pb/^{207}Pb$ vs. $^{207}Pb/^{206}Pb$ (Fig. 4). The figure also shows the isotopic compositions of the possible sources. Some researchers state that the urban lead in China is mainly derived from leaded gasoline, industrial discharge, coal and fly ash, and atmospheric deposits of mining and smelting dust, etc. (Mukai et al. 2001).

As illustrated on Fig. 4, anthropogenic lead sources (e.g. smelting and refining dust, coal combustion, automobile exhaust, traffic dust, etc.), on the upper left portion of the diagram, are characterized by higher $^{207}Pb/^{206}Pb$ ratios and lower $^{208}Pb/^{207}Pb$ ratios. Natural lead sources (such as basalt, sea sands, etc.) on the lower right part, are represented by higher $^{208}Pb/^{207}Pb$ ratios and/or lower $^{207}Pb/^{206}Pb$ ratios. This is consistent with the results of Oskierski et al. (2009). The evolution of lead from natural to anthropogenic is represented by the changes of isotopic ratios from the lower right to the upper left of the diagram.

Similar to the lead concentrations and spatial distributions, the lead isotopic composition differs between the urban and suburban aquatic sediments in Haikou, but not in Sanya. In the urban aquatic sediments in Haikou, the $^{208}Pb/^{207}Pb$ ratio and $^{207}Pb/^{206}Pb$ ratio show a wide range from 2.467 to 2.478 with a mean of 2.471 and from 0.841 to 0.854 (mean: 0.847). These sediment lead isotopic compositions are similar to automobile exhaust, atmospheric deposition, soils, basalt, and sea sands, to some exten indicating that the sediment lead mainly generate from these natural (basalt and sea sands) and anthropogenic sources (e.g. automobile exhaust, atmospheric deposition, soils in Haikou). Other anthropogenic effects, such as smelting and refining, coal combustion, traffic, etc., contribute more or less to lead origin as found by other researchers (for example, Gobeil et al. 1995). Moreover, the sediment lead isotopic compositions are changing from natural (characterized as higher $^{208}Pb/^{207}Pb$ ratio but lower $^{207}Pb/^{206}Pb$ ratio) to anthropogenic (marked with higher $^{207}Pb/^{206}Pb$ ratio but lower $^{208}Pb/^{207}Pb$ ratio). Therefore, this confirms that the lead content of the urban aquatic sediments in Haikou is mainly controlled by anthropogenic effects, which contributes more than the natural sources.

However, the $^{208}Pb/^{207}Pb$ ratio (range: 2.476–2.479, mean: 2.477) and $^{207}Pb/^{206}Pb$ ratio (range: 0.840–0.846, mean: 0.842) of the suburban aquatic sediments in Haikou does not vary much. The lead isotopic compositions fall exactly in the region of basalt and sea sands. It indicates that sediment lead seems to be mainly originating from natural sources (basalt, sea sands, etc.), though the global biogeochemical cycle of lead is vastly dominated by human activities at present (e.g. Pacyna and Pacyna 2001). The natural geochemical cycles can be influenced by the addition of hydrologic elements or compounds originating from anthropogenic activities (Lottermoser 1997). Result shows that the lead isotopic compositions of suburban aquatic sediments in Haikou have an evolutive trend towards the anthropogenic (marked with higher $^{207}Pb/^{206}Pb$ ratio but lower $^{208}Pb/^{207}Pb$ ratio). However, natural lead sources still contribute more.

In Sanya, the isotopic composition differences are not obvious between the urban and suburban aquatic sediments. The sediment lead isotopic compositions, plotted on the lower right of the diagram, are similar to some extent to those of some natural sources such as the soils and the sea sands, indicating that the sediment lead in Sanya generates to a greater extent from natural sources. Although no changing trend of the lead isotopic compositions towards the anthropogenic sources is discovered in Fig. 4, some anthropogenic lead resultant from human activities (such as traffic, etc.) may exist. Thus, anthropogenic effects contribute extremely little to the sediment lead in Sanya. In addition, it should be shown that the aquatic sediments in Sanya have a higher $^{208}Pb/^{207}Pb$ ratio and lower $^{207}Pb/^{206}Pb$ ratio than granite, but still remain within the variation of the upper crust. Unfortunately, the specific reason(s) is still unknown.

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References

Abi-Ghanem C, Chiffoleau JF, Bermond A, Nakhlé K, Khalaf G, Borschneck D, Cossa D (2009) Lead and its isotopes in the sediment of three sites on the Lebanese coast: identification of contamination sources and mobility. Appl Geochem 24:1990–1999

Arakel AV, Hongjun T (1992) Heavy metal geochemistry and dispersion pattern in coastal sediments, soil, and water of Hedron Brook floodplain area, Brisbane, Australia. Environ Geol Wat Sci 20:219–231

Chang XY, Zhu BQ, Chen YW, Chen YH (2002) Application of element—isotope tracing to environmental science. J Guangzhou U (Nat Sci Ed) 1:67–70 (In Chinese with English abstract)

Chen HS, Pei HD, Zhang XY, Wang LS (1998) Isotope tracing of major sources of lead pollution in the atmosphere of Hangzhou City. Bull Mineral Petrol Geochem 17:146–149 (In Chinese)

Chi QH, Yan MC (2007) Handbook of elemental abundance for applied geochemistry. Geological Publishing House, Beijing (In Chinese)

Duzgoren-Aydin NS, Li XD, Wong SC (2004) Lead contamination and isotope signatures in the urban environment of Hong Kong. Environ Int 30:209–217

Fan QC, Sun Q, Li N, Sui JL (2004) Periods of vocanic activity and magma evolution of Holocene in North Hainan Island. Acta Petrologica Sinia 20:533–544

Förstner U, Wittman GTW (1981) Metal pollution in the aquatic environment, vol 2. Springer, Berlin, Heidelberg, p 486

Gobeil C, Johnson WK, MacDonald RW, Wong CS (1995) Sources and burden of lead in St. Lawrence estuary sediments: isotopic evidence. Environ Sci Technol 29:193–201

Joseph AG, Shawn G (2010) An evaluation of lead contamination in plastic toys collected from day care centers in the Las Vegas Valley, Nevada, USA. Bull Environ Contam Toxicol 85: 363–366

Komárek M, Ettler V, Chrastný V, Mihaljevic M (2008) Lead isotopes in environmental sciences: a review. Environ Int 34: 562–577

Li J, Zheng CJ, Guo XL (1989) Manual data of environmental background value. China Environ Science Press, Beijing (In Chinese)

Loring DH, Rantala RTT (1990) Sediments and suspended particulate matter: total and partial methods of digestion. Tech Mar Environ Sci ICES 9:1–14

Lottermoser BG (1997) Heavy metal pollution of coastal river sediments, north-eastern New South Wales, Australia: lead isotope and chemical evidence. Environ Geol 36:118–126

Lu YF, Chen HS, Chen ZD, Yang HM, Gu MG, Ma LY, Mei YP (2006) Lead isotopic composition of sediments from West Lake and the Grand Canal in Hangzhou and its significance for lead source tracing. Geochinica 35:443–452 (In Chinese)

Mukai H, Tanaka A, Fujii T, Zeng YQ, Hong YT, Tang J, Guo S, Xue HS, Sun ZL, Zhou JT, Xue DM, Zhao J, Zhai GH, Gu JL, Zhai PY (2001) Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environ Sci Technol 35:1064–1071

Oskierski HC, Sindern S, Lima RFS, Petta RA (2009) Geogenic and anthropogenic lead isotope signatures in the urban environment of Natal (NE-Brazil). Environ Geol 58:1811–1817

Pacyna JM, Pacyna EG (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ Rev 9:269–298

Renberg I, Brannvall ML, Bindler R, Emteryd O (2002) Stable lead isotopes and lake sediments—Useful combination for the study of atmospheric lead pollution history. Sci Total Environ 292: 45–54

Shang YN, Yin G, Yan QS, Ni SJ, Zhang CJ (2005) Lead pollution character of urban river sediments in Chengdu City. Urban Environ Urban Ecol 18:40–42 (In Chinese)

Turekian K, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geol Soc Am Bull 72:175–192

Woitke P, Wellmitz J, Helm D, Kube P, Lepom P, Litheraty P (2003) Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. Chemosphere 51:633–642

Xu DR, Fan WM, Liang XQ, Tang HF (2001) Characteristics of Proterozoic metamorphic basement in Hainan Island and its implications for crustal growth: Nd and Pb isotope constraints. Geol J China U 7:146–157 (In Chinese)

Zhang M, Tu K, Xie GH, Martin FJF, Richard WC (1992) The trace element and isotopic geochemistry of Cenozoic basalt in Hainan Island. In: Liu RX (ed) The age and geochemistry of Cenozoic volcanic rocks in China. Seismology Press, Beijing (In Chinese)

Zhu SQ, Zang XP (2001) On heavy metal pollution along Yangtze River stretches of urban areas in major cities. Yangtze River 32:23–25 (In Chinese)

Zhu BQ, Chen YW, Peng JH (2001) Lead isotope geochemistry of the urban environment in the Pearl River Delta. Appl Geochem 16:409–417