Arch Environ Contam Toxicol (2009) 57:230–238
DOI 10.1007/s00244-008-9268-5

Sequential Extractions and Isotope Analysis for Discriminating the Chemical Forms and Origins of Pb in Sediment from Liaodong Bay, China

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Received: 18 August 2008 / Accepted: 20 November 2008 / Published online: 5 December 2008

Abstract Sequential extraction integrated with isotope analysis was carried out on a sediment core from Liaodong Bay, northeast China, for characterizing Pb in various extraction phases and its possible sources. Results show that in all extracted fractions Pb concentrations increased abruptly in the top part of the sediments that deposited after 1980, but remained lower and rather constant before 1980. Consistent with the variation pattern of Pb concentration, the $^{206}Pb/^{207}Pb$ ratio displays a dramatic decrease around 1980. These findings strongly suggest serious Pb pollution since then. The Pb concentration and the isotopic ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the residual fraction show rather small changes through the entire core, and are similar to those of uncontaminated Chinese loess, possibly representing the characteristics of the regional geogenic background. The isotopic ratios of the sediments before 1980 varied in different extracted fractions with a linear pattern, from the residual at the highest toward the average signature of automobile exhausts and Pb-Zn deposits, implying a prominent two-end member mixing style of the Pb origin; one is the regional geologic background and the other is anthropogenic sources. The difference in isotopic ratios between the extractions might be indicative of varied proportions of the two sources. For sediments after 1980, however, the isotope ratios in nonresidual fractions are all relatively low and show little differentiation, which may suggest that polluted Pb dominates all the extracted fractions for the top part of the core.

The accumulation of anthropogenic Pb in sediments is a serious and widespread environmental problem because the sediments may reactivate as sources of the contaminant in aquatic systems (Adams et al. 1992; Mucha et al. 2003). The deposited lead can have different chemical forms, which differ in mobility, reactivity, and toxicity (Rauret et al. 1989; Land et al. 1999; Romas et al. 1999). The Pb in sediments can be derived from anthropogenic and/or lithogenic origins, and the latter is usually considered to be harmless to the ecosystem. Thus a high concentration of metals in sediments does not necessarily imply a great threat to the ecosystem. A comprehensive understanding of Pb speciation and its origins are necessary to accurately evaluate environmental contamination.

The sequential extraction method is often used to assess the availability and mobility of heavy metals in sediments (Rauret et al. 1989; Land et al. 1999; Romas et al. 1999; Li et al. 2001; Hlavay et al. 2004), sewage sludge (Sánchez-Martín et al. 2007; Torri and Lavado 2007), and water (Kersten et al. 1997). Although sequential extraction or fractionation of heavy metals in sediments cannot constrain specific speciation of metal in the sediment, it can provide valuable information on the relative trace-metal mobility in sediments with changing environmental conditions, such as pH and redox potential (Tessier et al. 1979; Romas et al. 1999; Al-Masri and Al-Bich 2002; Hlavay et al. 2004). In addition, lead isotopic ratios, particularly $^{206}Pb/^{207}Pb$, provide an effective tool and are widely used for

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identifying the sources of Pb in sediments and soils, because the isotopic ratios of anthropogenic Pb are usually different from that of natural background Pb (Komárek et al. 2007). Consequently, the combination of sequential extraction with isotope analysis has potential for providing insight into the mobilization and origins of lead in sediments. Up to now, there have been a few relevant studies (Li et al. 2001; Kober et al. 1999; Bacon et al. 2006), but various methods were used and the results are not consistent.

Liaodong Bay is located in the northwestern Bohai Sea. Most of the rivers which discharge into the bay were heavily polluted with industrial development around the drainage areas, because industrial wastes and urban sewage were discharged into the river without any treatment until the end of the last century. As a result, Liaodong Bay was a major source site and accounts for more than 55.7% of the total input of Pb in the Bohai Sea (Zhang 2001).

In this study, a sediment core from Liaodong Bay, which was dated by the combination of ^{210}Pb and ^{137}Cs, was analyzed using a sequential extraction procedure. Pb concentrations and the isotopic ratios of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb were measured on the sequentially extracted fractions. The objective of this study is to characterize the distribution of Pb in various phases and their origins.

Samples and Method

Sample

Samples for this study were collected from a sedimentary core drilled in Liaodong Bay, near the estuary of the Liaohe River (Fig. 1). The core was obtained using a piston corer fitted with a polycarbonate tube, sealed with plastic caps, and frozen for further analysis. In the laboratory, the sediment core was sliced into 2-cm-long cylinders with a plastic cutter. Samples were freeze-dried and then ground using an agate mortar.

Radionuclide Measurement

Activities of ^{137}Cs, ^{210}Pb, and ^{226}Ra were measured by counting γ-rays using a low-background, well-type, high-purity gernium detector (EGPC 100P-15R) supplied by Eurosystem. Each sample was packed in a 5-cm polyethylene tube for 3 weeks of storage in sealed containers to allow radioactive equilibration (Hamilton et al. 1994; Ruiz-Fernández et al. 2003). Each sample was counted for 48 h. Total activity of ^{210}Pb was determined by the gamma counter at 46.5 keV. Meanwhile, supported ^{210}Pb was determined by measuring the activities of the short-lived daughter nuclides of ^{226}Ra and ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV) for calculating excess ^{210}Pb (^{210}Pb$_{\text{excess}}$). ^{137}Cs was measured by the gamma counter at 662 keV. An activity standard having the same geometry and density as the sample was used. Details on energy and efficiency calibration methods, and on quality control, were given by Foster et al. (2005). The counting uncertainties are about 0.2 dpm/g for ^{210}Pb and 0.03 dpm/g for ^{137}Cs. Radiometric dates were calculated using the constant rate of supply (CRS) ^{210}Pb dating model (Goldberg 1963; Appleby and Oldfield 1978; Appleby et al. 1986) and corrected where appropriate using the 1963 depth determined from the ^{137}Cs stratigraphic record as a reference level (Appleby 2001; Jha et al. 2003). The result shows that the studied core was deposited during the interval from 1890 to 2000 (Fig. 2).

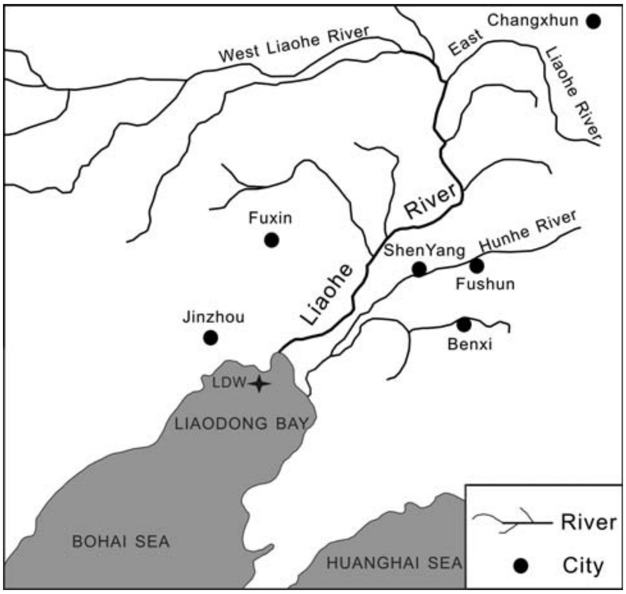


Fig. 1 The location of the studied core

Sequential Extraction

In principle, the sequential extraction technique is based on the selective extraction of heavy metals in different physicochemical fractions of a material using specific solvents (Bruder-Hubscher et al. 2002), and a large number of different methodological approaches have been developed (Tessier et al. 1979; Al-Masri and Al-Bich 2002; Hlavay et al. 2004). Among these, the five-step (Tessier et al. 1979) and six-step (Kersten and Förstner 1986) sequential extraction procedures are most widely used and have been modified (Rauret et al. 1989; Borovec et al. 1993; Campanella et al. 1995; Zdenek 1996; Land et al. 1999; Gomezariza et al. 2000; Cunong and Obbard 2006; Al-Masri et al. 2006) to optimize sequential extractions on sediments with different characteristics. In this study, the

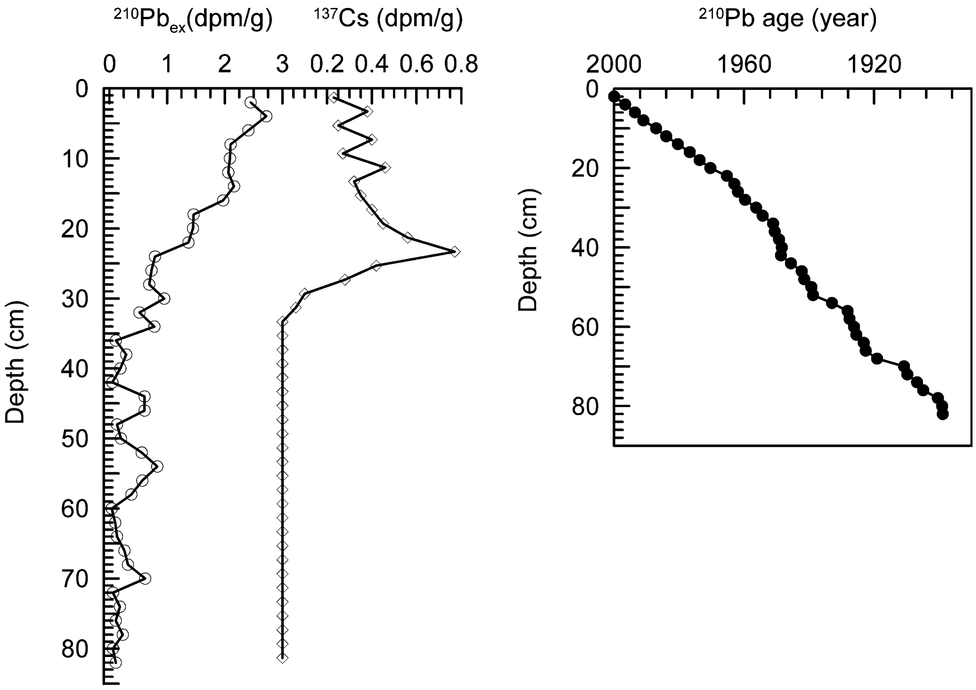


Fig. 2 ^{137}Cs and unsupported ^{210}Pb along the depth for the studied core and age-depth curve

six-step extraction procedure was used based on the methods of Al-Masri et al. (2006) and Land et al. (1999) with some modifications; it is described below.

Extraction 1

A 1-g sample in a centrifuge tube was mixed with a 10-ml $MgCl_2$ solution (1 mol/L, pH 7) and shaken for 8 h. Exchangeable species would be extracted (Rath et al. 2008).

Extraction 2

Ten milliliters of 1.0 M CHCOONa at pH 5 was added, and the mixture shaken for 16 h. During this step, heavy metals associated with the carbonate fraction were expected to be extracted (Land et al. 1999; Al-Masri et al. 2006; Lair et al. 2008).

Extraction 3

Twenty milliliters of 0.1 M $Na_4P_2O_7$ was added and the mixture shaken for 6 h. According to Land et al. (1999), metals involved with labile organics would be extracted.

Extraction 4

A 20-ml solution of 1.0 M $NH_4OH \cdot HCl$ in 25% CH_3COOH was added to the centrifuge tube, then the tube was placed in a water bath at 90°C for 8 h. During this step, metals with reducing forms, such as Fe-Mn oxides, would be extracted (Land et al. 1999; Al-Masri et al. 2006).

Extraction 5

Ten milliliters of 8.8 M H_2O_2 was added, the tube was kept at room temperature for 2 h, then the mixture was heated to 85°C for 4 h. Metals associated with refractory organic matter were expected to be extracted (Land et al. 1999; Al-Masri et al. 2006).

For extractions 1–5, separation was performed by centrifuging at 4,500 rpm for 20 min. The sediments were washed with 10 ml Milli-Q water and centrifuged twice. All supernatants were decanted into the volumetric flask and diluted to 50 ml with Milli-Q water.

Extraction 6

Solid residues after extractions 1–5 were transferred to a 50-ml Teflon beaker and digested with concentrated HNO_3 and HF at 90°C for 2h, then the temperature was increased to 150°C until the sample was completely digested. Afterward, the sample was dried, dissolved, and washed with 0.1 M HNO_3. The solution was transferred into a 50-ml flask and diluted to 50 ml with 0.1 M HNO_3. This step was used to determine the amount of trace metals mainly incorporated in aluminosilicate phases.

Analysis and Quality Control

The concentration of Pb was determined using an inductively coupled plasma-mass spectrometer (ICP-MS) with a detection limit of 0.1 ng/ml. Analytical blanks were also prepared and analyzed as samples to detect the possibility of contamination during digestion and analysis. To evaluate the reliability and reproducibility of the sequential extraction, a sample was analyzed using five replicates. The extracted fractions for each step are presented in Table 1. The relative standard deviation was better than 16% for all six extraction steps. In addition, the Pb concentrations of all bulk samples were directly digested and measured to check the recovery of sequential extractions. The recovery of sequential extractions fell within the range of 103%±10% (Table 2).

Table 1 Quality control of sequential extraction data by replicated analysis of sediment samples

	No. 1	No. 2	No. 3	No. 4	No. 5	STD (%)
Extraction 1	0.48	0.40	0.56	0.46	0.58	15
Extraction 2	1.27	1.40	1.11	1.01	1.43	14
Extraction 3	2.31	2.03	1.79	2.54	2.43	14
Extraction 4	7.84	6.44	8.59	6.68	7.61	12
Extraction 5	1.05	1.21	1.17	0.89	0.83	16
Extraction 6	10.80	12.51	9.65	12.24	11.92	10

For Pb isotopic analysis, the solutions were diluted to a Pb concentration of about 25 mg/L using 5% high-purity HNO_3 to optimize the analytical performance of the machine. An international standard reference (NIST SRM 981) and reagent blanks were used for quality control. The standard and blank samples were run between each of the five samples to ensure the accuracy and precision of isotope measurement. Measurement was repeated when differences between the measured and the certified values of the standard reference exceeded 0.5%. The precision (% RSD) of the Pb isotopic ratios of the 10 replicates was typically <0.5%. The average measured ratios of ^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/2^{07}Pb of SRM 981 were 0.06471±0.0004, 1.09319±0.0023, and 2.37108±0.0031, respectively—very close to the certified standard values (0.0646, 1.0933, and 2.3704, respectively).

Table 2 The concentration, isotopic ratio, and recovery of Pb in different extractions of sediments in Liaodong Bay

Sample code: Depth (cm):	BHW-01 0.0000	BHW-03 6	BHW-05 10	BHW-07 14	BHW-10 20	BHW-14 28	BHW-18 36	BHW-26 52	BHW-30 60	BHW-40 80
Extraction 1										
Pb (mg/kg)	0.74	0.57	0.44	0.55	0.47	0.46	0.38	0.48	0.44	0.58
^{206}Pb/^{207}Pb	1.1460	1.1486	1.1594	1.1797	1.1839	1.1953	1.1896	1.1918	1.1904	1.1931
^{208}Pb/^{207}Pb	2.3499	2.3532	2.3504	2.4322	2.4606	2.4532	2.4471	2.4537	2.4527	2.4442
Extraction 2										
Pb (mg/kg)	10.10	7.63	6.75	0.76	1.20	0.92	0.38	1.27	0.63	1.13
^{206}Pb/^{207}Pb	1.1590	1.1520	1.1489	1.1568	1.1633	1.1776	1.1684	1.1679	1.1672	1.1812
^{208}Pb/^{207}Pb	2.3519	2.3593	2.3551	2.3858	2.4021	2.4053	2.4104	2.4070	2.3966	2.4173
Extraction 3										
Pb (mg/kg)	4.81	5.10	4.28	3.21	3.30	2.40	3.35	2.31	2.30	1.72
^{206}Pb/^{207}Pb	1.1580	1.1455	1.1463	1.1589	1.1691	1.1705	1.1635	1.1594	1.1651	1.1700
^{208}Pb/^{207}Pb	2.3572	2.3620	2.3584	2.3987	2.4183	2.4388	2.4100	2.4289	2.4553	2.4422
Extraction 4										
Pb (mg/kg)	12.33	12.70	11.87	7.96	9.88	8.46	9.40	7.84	8.10	7.65
^{206}Pb/^{207}Pb	1.1632	1.1568	1.1485	1.1740	1.1735	1.1762	1.1711	1.1745	1.1760	1.1849
^{208}Pb/^{207}Pb	2.3566	2.3352	2.3453	2.4050	2.4387	2.4497	2.4362	2.4593	2.4206	2.4669
Extraction 5										
Pb (mg/kg)	1.73	1.73	1.88	0.91	1.18	1.27	1.30	1.05	1.44	1.17
^{206}Pb/^{207}Pb	1.1699	1.1434	1.1494	1.1614	1.1493	1.1508	1.1392	1.1527	1.1340	1.1452
^{208}Pb/^{207}Pb	2.3538	2.3584	2.3649	2.3714	2.3866	2.3785	2.3895	2.3911	2.3738	2.3977
Extraction 6										
Pb (mg/kg)	9.82	9.88	9.30	8.80	9.09	9.82	11.70	10.80	9.55	9.16
^{206}Pb/^{207}Pb	1.2042	1.2014	1.1971	1.2091	1.2055	1.2009	1.2042	1.2087	1.2087	1.2014
^{208}Pb/^{207}Pb	2.4761	2.4591	2.4932	2.5054	2.4844	2.4920	2.4773	2.4970	2.4868	2.4976
Total dissolved										
Pb (mg/kg)	44.88	38.86	35.83	22.02	21.98	24.48	24.02	22.99	19.02	19.99
Recovery[a]	88%	96%	96%	101%	114%	95%	110%	103%	118%	107%

[a] Recovery = ($\sum$extra$_i$/total concentration) × 100

Results and Discussion

Distributions of Pb in Different Fractions

The concentrations and relative percentages of Pb in different fractions are presented in Table 2 and in Fig. 3, respectively. The percentages of Pb extracted in individual extractions (P) are calculated from the ratio of $[\mathrm{Pb}]_i/\sum[\mathrm{Pb}]_i$.

Most lead in the sediments is released from Extractions 4 (Fe-Mn oxides) and 6 (residual fraction) in Liaodong Bay, accounting for 31.2–39.3% and 24.8–45.5%, respectively (Fig. 2), and suggesting that Fe-Mn oxides and residual are the main hosts for Pb. The percentages of Pb in Extractions 1 (exchangeable), 3 (labile organic), and 5 (refractory organic) are relatively low, averaging 1.92±0.4%, 11.6±2%, and 4.9±0.7%, respectively (Fig. 3). The percentage of Pb in Extraction 2, which is likely associated with carbonate (Land et al. 1999; Al-Masri et al. 2006), shows high-amplitude variations. In the down core, the percentage of this carbonate-related Pb is relative stable and low (~3%), but it increases abruptly in the top sediments and reaches the maximum (25.5%) in the top surface (Fig. 3). A high percentage of Pb in the carbonate fraction was also observed in the surficial sediments from Tee estuary, northeast England (Jones and Turki 1997), and sediments from the Mapocho River, Santiago, Chile (Segura et al. 2006).

Except for the residues, the Pb concentrations in all fractions show a similar pattern along the profile. It is characterized by rather small variation before 1980 and an abrupt increase afterward (Fig. 4). In contrast, the Pb concentration in the residue remains roughly constant through the entire profile (Fig. 4). Coinciding with the increase in Pb concentration of the nonresidue fractions, the first dominant host phase of Pb changes from the residue fraction to the Extraction 5 fraction, i.e., the Fe-Mn oxide held Pb (Fig. 3), due mainly to the great increase in carbonate-related Pb after 1980.

Pb Isotopic Ratios of the Extractions

In environmental studies, the ^{206}Pb/^{20}7Pb ratio is commonly used, because its measurement is more accurate due to the similar abundances of these two isotopes (Monna et al. 1998; Alfonso et al. 2001): ^{206}Pb and ^{207}Pb represent about 23.6% and 22.6% of the total lead, respectively. Moreover, anthropogenic Pb is often characterized by a low ^{206}Pb/^{207}Pb ratio (<1.2), while geochemical background Pb usually has a higher ^{206}Pb/^{207}Pb ratio (~1.2) (Hinrichs et al. 2002; Monna et al. 1995, 2000; Li et al. 2001). Compared with ^{206}Pb/^{207}Pb, the ^{208}Pb/^{207}Pb ratios of anthropogenic Pb display a wide range of variations. For example, the ^{208}Pb/^{207}Pb ratio of automobile exhausts ranges from 2.305 to 2.479 (Mukai et al. 2001; Zheng et al. 2004; Yang et al. 2008) and it varies from 2.357 to 2.543 for coal-burning derived materials in China (Mukai et al. 2001; Zheng et al. 2004; Yang et al. 2008). These could hardly be discriminated from those derived from lithogenic origins, such as Chinese loess, with ^{208}Pb/^{207}Pb ratios of ~2.487 (Biscaye et al. 1997).

The ^{207}Pb/^{206}Pb ratios display a similar pattern for all fractions except for Extractions 5 and 6 along the profile (Fig. 5). The ^{207}Pb/^{206}Pb ratio of the sediments shows relatively small changes before 1980 but an abrupt decrease

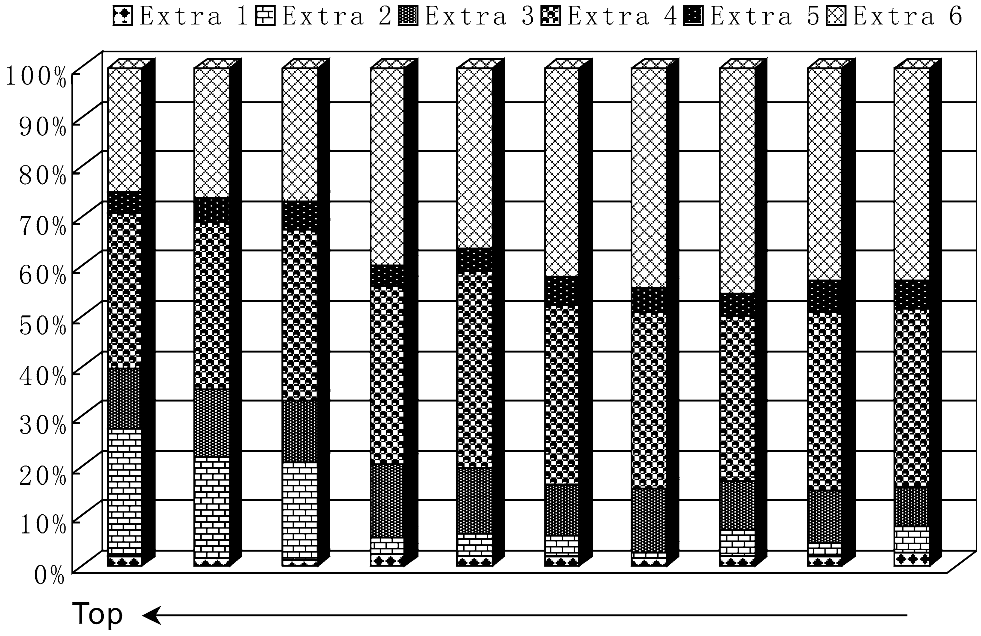
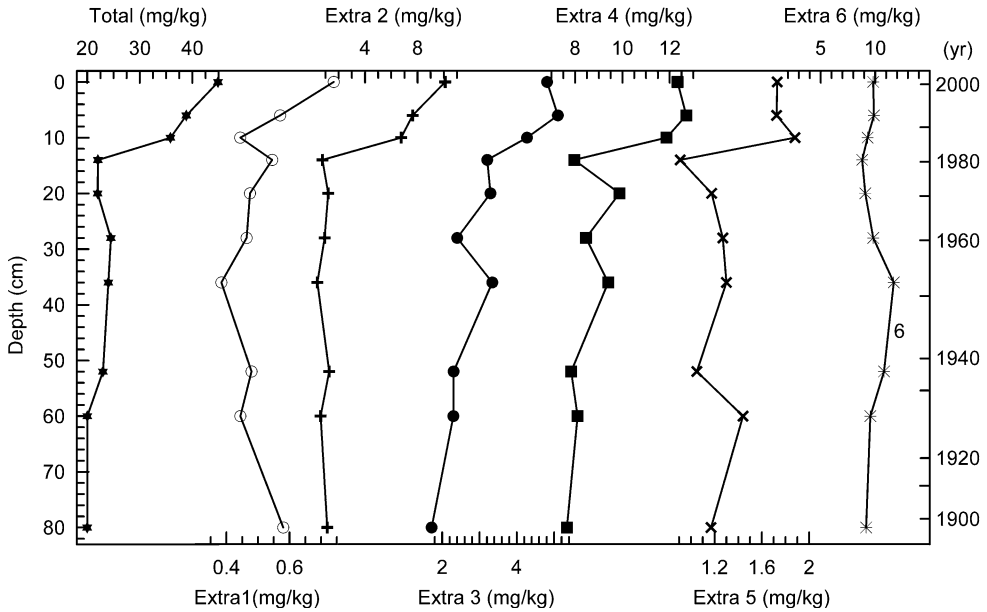


Fig. 3 Percentages of heavy metals associated with different fractions

Fig. 4 Distribution of Pb concentrations (mg/kg) in various fractions with depth in Liangdong Bay



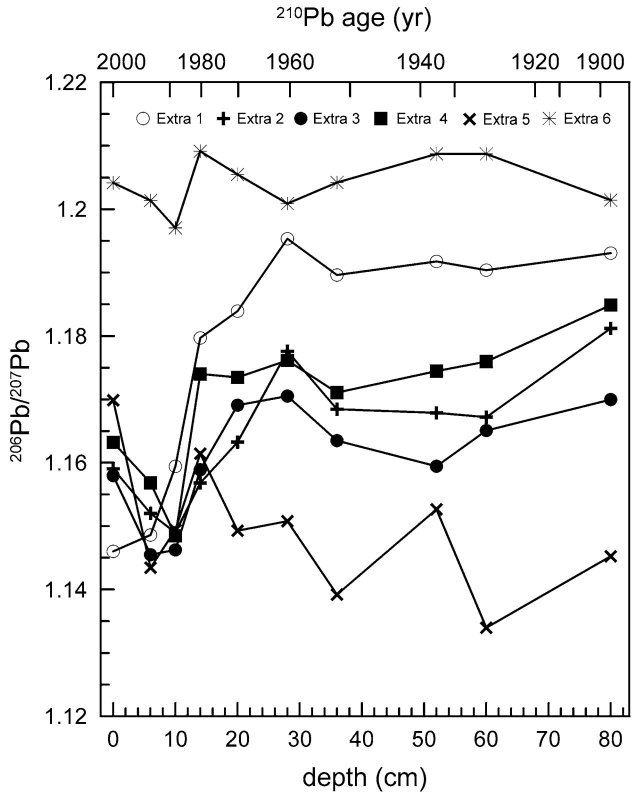


Fig. 5 Variations of $^{206}Pb/^{207}Pb$ ratios in different fractions along the sediment core of Liaodong Bay

since 1980s. It reaches the minimum value around 1990, then follows an increasing trend in surface sediments (Fig. 5), possibly attributable to the increased practice of waste treatment and prohibited use of leaded gas. In contrast, the isotopic ratios of the residual fraction are higher than those of the nonresidual fractions and display very little variation (1.1942–1.209) for all samples (Fig. 5), indicating that the Pb sources in the residual phase are rather constant. The obvious difference in Pb isotopic compositions between the residual and the nonresidue fractions suggests that these two fractions come from different sources.

Implications of Pb Isotopic Ratios of the Residues

To identify the potential sources of Pb for sediments in Liaodong Bay, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$ ratios of different fractions are plotted in Fig. 6, including the data for Pb-Zn deposits (Mao et al. 2001), automobile exhausts in northern China (Yang et al. 2008), and uncontaminated Chinese loess (Biscaye et al. 1997), which can be roughly representative of the upper crust for elemental composition. The Pb isotopic ratios of the residual fraction are high and similar to those of the loess (Fig. 6), suggesting that the Pb in the residual fraction might be derived mainly from the lithogenic material and represent the regional geogenic background level. Although direct comparison with other studies is difficult because of the different extraction methods used in various studies, they have demonstrated a higher $^{206}Pb/^{207}Pb$ ratio in residue than in nonresidual fractions, for example, the isotopic records in a sediment profile from the Pearl River estuary (Li et al. 2001) and sediment of Elefsis Bay in Greece (Kersten et al. 1997) and Lake Geneva in Switzerland-France (Monna et al. 1999).

Variations of the Pb Isotope Ratios Along the Profile

The $^{207}Pb/^{206}Pb$ ratios of nonresidual fractions display a different pattern between the top and the deeper sediments.

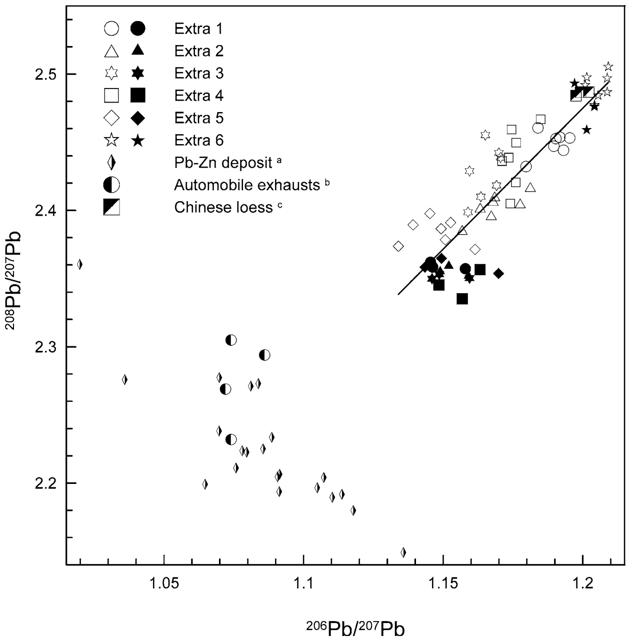


Fig. 6 The correlation between the ^{208}Pb/^{207}Pb and the ^{206}Pb/^{207}Pb ratios of different extracted fractions in Liaodong Bay. Filled symbols represent samples deposited after 1980s. References: [a]Mao et al. (2001); [b]Yang et al. (2008); [c]Biscaye et al. (1997)

In the top sediments (after 1980), the ^{206}Pb/^{207}Pb ratios decrease abruptly and there are no obvious differences among different fractions (Fig. 5). A similar pattern was also observed in sediments of the Pearl River Estuary (Li et al. 2001), though a different sequential procedure was applied. The abrupt decrease in ^{206}Pb/^{207}Pb ratios, together with the increased Pb concentrations, suggests that the input of anthropogenic Pb increased to be an important component in all nonresidual fractions in the top sediments. As shown in Fig. 6, the isotopic ratios of the nonresidual fractions of the top sediments fall in a region closer to those of anthropogenic Pb.

For deeper sediments (before 1980), the ^{206}Pb/^{207}Pb ratios are relative high and change little among various nonresidual fractions. The relatively high ^{206}Pb/^{207}Pb ratios could result from either a larger proportion of lithogenic lead at depth or an increasingly greater proportion of “old” anthropogenic Pb mixing with “younger” anthropogenic Pb through a longer migration from the top to the depths (Bacon et al. 2006). In this study, ^{210}Pb$_{\text{excess}}$ shows an approximately exponential decline with depth, and the ^{137}Cs depth profile does not show obvious tailing below the peak in our studied profile (Fig. 2), indicating no severe vertical Pb isotope exchange in the sediment column (Bollhöfer et al. 1994; Audry et al. 2004). In addition, the isotopic ratios of nonresidual fractions fall in the range between the residual and the anthropogenic Pb (Fig. 6) (e.g., Pb-Zn deposit and automobile exhausts), suggesting that the Pb in nonresidual fractions is a mixture of lithogenic and anthropogenic Pb (since1900s). Therefore, the relatively high Pb isotopic ratios in the deeper sediments of Liaodong Bay should be associated with a higher proportion of lithogenic, or less anthropogenic, lead.

Changes in Pb Isotopic Ratios Between Different Extracted Fractions

It is noteworthy that ^{206}Pb/^{207}Pb ratios in the deeper sediments are different among various fractions, particularly between Extraction 1 and Extraction 5 (Fig. 5). The ^{206}Pb/^{207}Pb ratio of Extraction 1 is higher than in other nonresidual extractions, while the isotopic ratio in the refractory organic fraction is the lowest in all nonresidual fractions (Fig. 5). Pb in Extraction 1 represents the soluble lead in the sediments. The relatively high ^{206}Pb/^{207}Pb ratio in Extraction 1 in this study is not consistent with the observation in soils (Bacon et al. 2006), which shows that the ^{206}Pb/^{207}Pb ratio in the soil solution was generally lower than those in any of the soil fractions in the deeper soils. Bacon et al. (2006) suggest that lead in the soil solution at a greater depth might be derived from soil components closer to the surface. As discussed above, there is no obvious vertical exchange in isotopic ratios in our studied core, possibly because there is lack of leaching processes under submarine conditions. Thus, the Pb of Extraction 1 at greater depths should be mainly derived from the sediments at the same depth, and the high ^{206}Pb/^{207}Pb ratio implies a greater proportion of lithogenic Pb. Extraction 5 is considered to be mainly associated with refractory organic matter (Land et al. 1999; Al-Masri et al. 2006), which is mainly composed of stable organic matter including materials derived from incompletely burning petroleum and coal; both could lead to a low ^{206}Pb/^{207}Pb ratio. Nevertheless, the introductions of leaded gasoline, which began in 1940s (Shiharata et al. 1980; Komárek et al. 2007), cannot explain the low ^{206}Pb/^{207}Pb ratios occurring in the 1900s in this study. Thus, Pb derived from coal-burning, which was a major pollutant source in the 18th and 19th centuries (Mukai et al. 1993, 2001; Nakano et al. 2006), might contribute to the low ^{206}Pb/^{207}Pb ratios in Extraction 5, at least for sediments deposited before 1940s. The available isotopic data on coal in northern China (^{206}Pb/^{207}Pb range, 1.085–1.181) (Yang et al. 2008) could lend support for this possibility. Based on the above discussion, we suggest that the difference in ^{206}Pb/^{207}Pb among nonresidual fractions might indicate variations in the proportion of the different sources. This may explain the observations in the deeper sediments. In Fig. 6, Extraction 1 is located close to the residues, while Extraction 5 falls toward the anthropogenic region, suggesting that the proportion of anthropogenic Pb in Extraction 5 is higher than that in Extraction 1.

Conclusion

This study provides insight into the Pb distribution and the characteristics of its isotope ratios in sequentially extracted fractions along a sediment profile from Liaodong Bay. The Pb concentrations in all nonresidual fractions display a remarkable increase since 1980. There is a distinct difference in Pb isotopic ratios between residual and nonresidual fractions. The $^{206}Pb/^{207}Pb$ ratio of the residual fraction shows little change along the studied core and is similar to those of uncontaminated Chinese loess, suggesting that the Pb in the residue is dominated by lithogenic lead and reflects a regional geological background. In contrast, the $^{206}Pb/^{207}Pb$ ratio of the nonresidual fractions displays an abrupt decrease and is closer to those of anthropogenic Pb after 1980. These observations, together with increased Pb concentrations, may suggest an intensified anthropogenic input of Pb (automobile exhaust, Pb-Zn deposit) since that time. The isotopic ratios of the nonresidual fraction of deeper sediments (before 1980) fall in the range between the residual fraction and the anthropogenic Pb, implying a notable input of anthropogenic Pb into Liaodong Bay as early as 1900. In addition, the $^{206}Pb/^{207}Pb$ ratio changed with different extracted fractions in deeper sediments, suggesting varied proportions of anthropogenic Pb in different phases. The isotopic ratios of all extractions of sediments before 1980 differed, with a linear trend between the residue and the anthropogenic input, seeming to suggest two possible end number sources for Pb, the regional geogenic background and anthropogenic input. For sediments after 1980, the isotope ratios in all nonresidual fractions were relatively low and showed little differentiation. This is possibly due to the greatly enhanced anthropogenic input of Pb, which dominates various extracted fractions.

Acknowledgments The authors thank Professor Zhaohui Wu for help with elemental and isotopic analysis. The critical review and constructive comments of Editor D. R. Doerge and two anonymous reviewers are greatly appreciated; they led to substantial improvement of the paper. This work was funded by the National Natural Science Foundation (40672118).

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