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The trend and extent of heavy metal accumulation over last one hundred years in the Liaodong Bay, China

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ABSTRACT

An integrated analysis has been carried out on two cores dated by combination of ^{210}Pb and ^{137}Cs in order to characterize the extent of heavy metal accumulation in the Liaodong Bay, Northern China. The concentrations and burial fluxes of Zn, Pb, Cd, and Hg increased abruptly after late 1970s. The enrichment factors of Cd, Hg, Zn and Pb are more than 30, 10, 7, and 3.5, respectively, in the surface sediments. Coincident to the increase of heavy metal contents, the decreasing trend of $^{206}Pb/^{207}Pb$ ratio indicated lead in the surface sediments mainly come from anthropogenic activities.

1. Introduction

The enrichment of heavy metal in the environment can result from both anthropogenic activities and natural processions (Forstner and Wittmann, 1979; Nriagu, 1989; Veena et al., 1997). High concentrations of heavy metals with geogenic origins in sediments, which are often enriched in refractory minerals, do not imply high potential toxicity to ecology. Consequently, a clear differentiation of the anthropogenic from the geogenic heavy metals is important in evaluating the extent of pollution, preventing further environmental damages, and planning remedial strategies. A thoroughly understanding of the source and sink will affect both short and long-term impact of human activities and natural processes on heavy metal accumulation.

Heavy metals are not removed from water by self-purification (Loska and Wiechula, 2003). The elevation of metal levels often results in a high concentration in the bottom sediment. As a result, sediments become "chemical archives" of heavy metal accumulations, which can provide valuable information in resolving the source and sink of heavy metal pollution (Cundy et al., 2003; Jha et al., 2003).

The Liaodong Bayis located in the northwest of the Bohai Sea. Several large heavily-polluted rivers including the Liaohe River, one of the most heavily polluted river in China, drain into the Liaodong Bay. As a result, Liaodong Bay becomes a major site from which pollutants are discharged into the Bohai Sea. The annual average flux of Pb from sewage along the coasts of Bohai Sea was about 613 t in the past, of which 55.7% were from the Liaodong Bay (Zhang, 2001). However, the extent of heavy metal accumulations in this area remains unknown, which limits properly evaluating and planning remedial strategies for a proper pollution cleanup strategy. This paper conducts a systematic analysis on two cores from the Liaodong Bay. The primary aim is to characterize the trend and extent of anthropogenic heavy metal accumulation in the Liaodong Bay.

2. Materials and methods

2.1. Area description

The semi-closed Liaodong Bay is near the Liaodong Penisula in Northeastern China. Liaohe, Dalinghe and Xiaolinghe rivers drain into the Liaodong Bay, a part of the Bohai Sea. Major pollution industries of Northeast China, such as mining, metal smelting, petroleum chemical industry, are situated inside the drainage areas of the Liaohe rivers. Most of the industrial wastes were directly discharged into the rivers and flowed into the Liaodong

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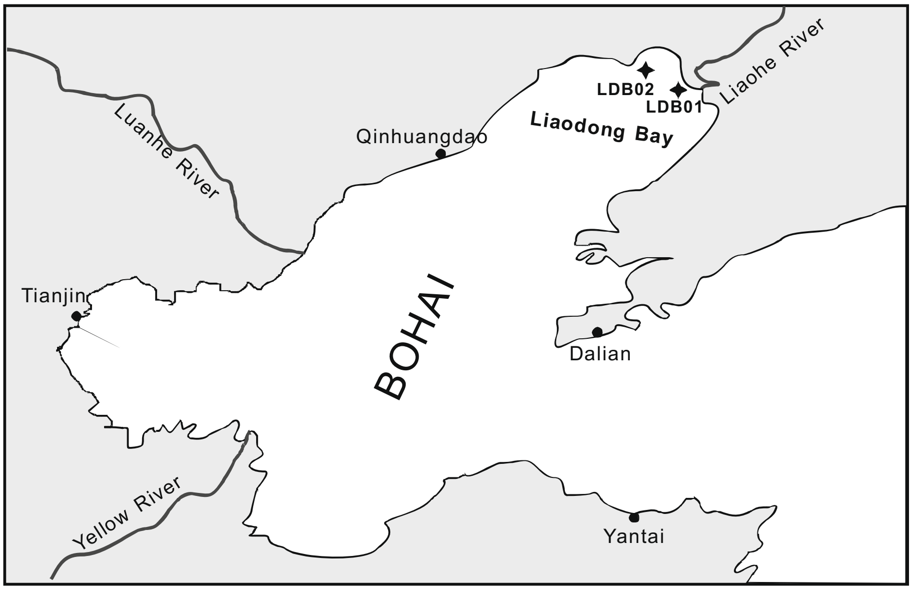

Fig. 1. Location of studied core sites (LDB01, LDB02).

Bay before the Chinese government started paying attention on the status of the Liaohe River in 1990s. The Liaohe River becomes the most heavily-polluted and biggest discharge channels of industrial and domestic waste draining into the Liaodong Bay. The studied cores are located in the estuary of Liaohe River (Fig. 1).

2.2. Sample and pretreatment

Two continuous sediments cores (LDB01, LDB02) were collected using a piston core fitted with a polycarbonate tube. Sediment cores were sealed with plastic caps and frozen for further analysis. In the laboratory, the sediments cores were sliced in thin horizontal section with a 2 cm space for LDB01 and 1 cm for LDB02 by a plastic cutter. Total 41 samples were collected from LDB01 and 29 samples from LDB02. Sediment samples are freeze-dried, lightly disaggregated using a pestle and mortar, and then sieved through <63 μm nylon sieve for later chemical analysis because most metals are often associated with small grains (Morillo et al., 2004).

2.3. Radionuclide measurement

The activity of ^{137}Cs, ^{210}Pb, and ^{226}Ra were measured by gamma spectrometry using a low-background well-type gernium detector (EGPC 100P-15R). Each sample was packed and stored in a 5 cm polyethylene tube for 3 weeks 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 gamma spectrometry via its energy at 46.5 keV. The short-lived ^{226}Ra daughter nuclides ^{214}Pb (241.9, 295.2, and 351.9 keV) and ^{214}Bi (609.3 keV) were measured to determine supported ^{210}Pb for the calculating excess ^{210}Pb (^{210}Pb$_{excess}$). ^{137}Cs was measured by its emissions at 662 keV. An activity standard, having essentially the same geometry and density was used. Details of energy and efficiency calibration methods, and quality control follow the method described in Foster et al. (2005). The counting errors were less than 5% and 3% for ^{210}Pb and ^{137}Cs, respectively. 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).

2.4. Elemental concentration

The metal concentrations were determined using 0.05 g freeze-dried sediment after totally digested by a 3-step acid attack (Aqua Regia, HF, $HClO_4$). Metal concentrations were determined using a Perkin–Elmer Sciex Elan 6000 inductively coupled plasma-mass spectrometer (ICP-MS). Detection limits are 0.0001 μg mL^{-1} for Zn, Pb, Cd, and between 0.0003 and 0.0005 μg mL^{-1} for Sc and Hg. The accuracy was checked by analysis of blank reagents, standard reference materials (GBW07314–offshore marine sediment from the Second Institute of Oceanography, SOA, a certificated reference standard material), and replicate samples. Analytical errors were less than 5% for trace elements.

2.5. ^{206}Pb/^{207}Pb ratios

^{206}Pb/^{207} Pb ratios of the selected samples were analyzed by ICP-MS. The analytical solution was diluted to bout 30 mg/kg Pb by 5% high-purity nitric acid. An international standard reference material (NIST SRM 981) and a reagent blank were used for bias correction and analytical control. Two standard deviations from the mean were better than 0.005% for ^{206}Pb/^{207}Pb ratios.

3. Result

^{210}Pb ($t_{1/2}$ = 22.3 a) is often used for sediment dating over a time scale of the past 100–150 years. The combination use of ^{210}Pb with ^{137}Cs can reduce the uncertainty in dating (Benninger et al., 1997). The 'Ideal' profiles are those in which the ^{210}Pb$_{excess}$ activity vs. depth distribution approximates to an exponential curve, which allows its solution by the simple model of ^{210}Pb dating, i.e. a constant influx of ^{210}Pb and a constant sediment accumulation rate. The ^{137}Cs activity vs. depth distribution usually shows distinct peaks in activity corresponding to periods of peak ^{137}Cs fallout from the bomb testing.

In the Liaodong Bay, ^{210}Pb$_{excess}$ shows an approximately exponential decline with depth in both cores, despite some fluctuations in the lower parts of the cores suggesting variations in sediment accretion over time, which may increase the dating uncertainty (Fig. 2). The plot of^{137}Cs activity against depth for the Liaodong Bay sediment cores is also displayed in Fig. 2. The peak of ^{137}Cs

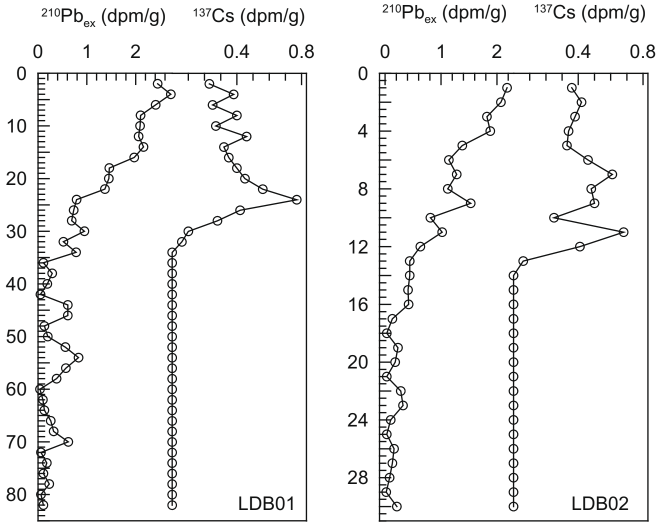

Fig. 2. ^{137}Cs and excess ^{210}Pb depth profiles.

activity is identified at 24 cm depth with corresponding activities of 0.77 dpm/g in LDB01 and at 11 cm depth with 0.68 dpm/g in LDB02. The peak of ^{137}Cs activity corresponds to a period of peak ^{137}Cs fallout in 1963. Chernobyl accident of 1986 is not identified in the studied cores being a less strong signal undistinguishable for low activities of ^{137}C in the Liaodong Bay. An uncertainty in interpretation of ^{137}Cs depth profile arises from possible post-depositional diagenesis mobility (Audry et al., 2004). In the studied cores, the ^{137}Cs depth profiles do not show obvious tailing effect, indicating that ^{137}Cs remobilization was negligible (Audry et al., 2004). The age calculated using the CRS (Goldberg, 1963) model of ^{210}Pb dating, which use the distinct peak of ^{137}Cs as a isochronal calibration point, indicates that the LDB01 was deposited during the interval from 1890 to 2000 and the LDB02 from 1930 to 2000.

In LDB01, the concentrations of Zn, Pb, Cd and Hg change little during the interval of 14–82 cm with average values of 20.648 mg/kg, 12.368 mg/kg, 0.074 mg/kg, and 0.024 mg/kg, respectively (Fig. 3a). At the top 14 cm, the concentrations of Zn, Cd, Pb, and Hg increase abruptly reaching values of 7-fold (Pb), 3.5-fold (Zn), 10-fold (Hg), 30-fold (Cd) higher than those at lower part of the core. The maximum values of Zn, Pb, Cd occur in surface sediments, while Hg reach its maximum value at interval of 8–10 cm (Fig. 3a). Similar distribution patterns of heavy metals also present in the LDB02 with abrupt increase occurring at interval of 0–7 cm (Fig. 3b).

4. Discussion

4.1. The sources of Pb

The ratio of ^{206}Pb/^{207}Pb, have been widely used to distinguish and quantify Pb inputs between natural and anthropogenic sources (Rabinowitz, 1995; Farmer et al., 1996; Munksgaard et al., 1998; Li et al., 2001) because the Pb isotopic composition in sediments usually depends on the parent materials and external inputs from the environment. According to previous studies (Monna et al., 1995, 2000; Hinrichs et al., 2002; Chen et al., 2005), ^{206}Pb/^{207}Pb ratios of geogenic Pb is around 1.2, while it is less than 1.2 in the human-affected sediments.

^{206}Pb/^{207}Pb ratios from the LDB01 and LDB02 cores show that the sediments deposited before 1970s have a stable ^{206}Pb/^{207}Pb ratio of ~1.2 (Fig. 3). In contrast, the ^{206}Pb/^{20}7Pb ratios present a decreasing pattern in the upper sediments and reach a minimum value in the surface sediments. These observations suggest that Pb in the surface sediments may have different sources from that in the lower part of the core. In order to gain a further understanding of potential Pb sources, the Pb isotopic ratios are plotted together with Pb contents (Fig. 3). The increase of Pb concentration coincides well with the decrease in Pb isotopic ratios in both cores (Fig. 3). This simultaneous variation between Pb contents and isotopic ratios is often considered as a reliable indicator of anthropogenic influences (Hamilton and Clifton, 1979; Shirahata et al., 1980; Petit et al., 1984; Hirao et al., 1986; Hamelin et al., 1990; Őhlander et al., 1993; Ritson et al., 1994; Croudace and Cundy, 1995; Graney et al., 1995; Monna et al., 2000). Thus, high concentration of Pb in the surface sediments is mainly associated with anthropogenic activities.

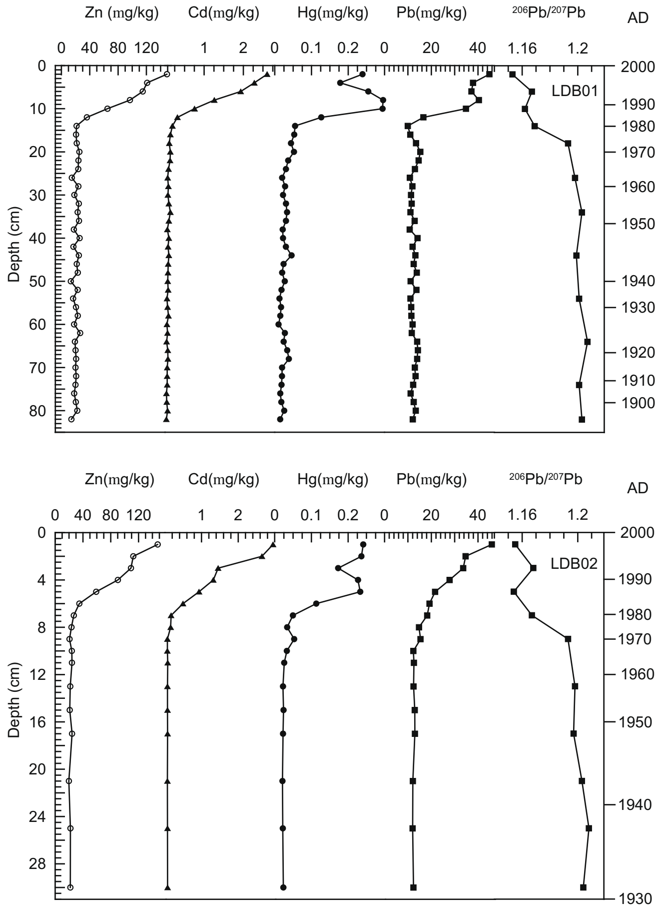

Fig. 3. Profiles of heavy metal concentrations and ^{206}Pb/^{207}Pb ratios in the sediments from Liaodong Bay.

4.2. Metal burial flux and extent of anthropogenic contamination

The burial flux of heavy metals in marine sediments is dependent on some environmental factors, such as sedimentation rate, sediment porosity, microbial activity, bioturbation rates and bottom water oxygen conditions (Schenau et al., 2005). On the whole, three pieces of information are required to calculate the burial flux in marine sediments: the elemental concentrations of sediments accumulating below a defined horizon, the sedimentation rate and the dry bulk density. The burial flux (BF) can be expressed as (Ingall and Jahnke, 1994):

$$BF_i = C_i \times \rho d \times S_i \qquad (1)$$

where BF [μg (y cm^2)$^{-1}$] is the burial flux of metals in sediments; C_i [μg g^{-1}] the concentration of metals in sediments; S (cm a^{-1}) and

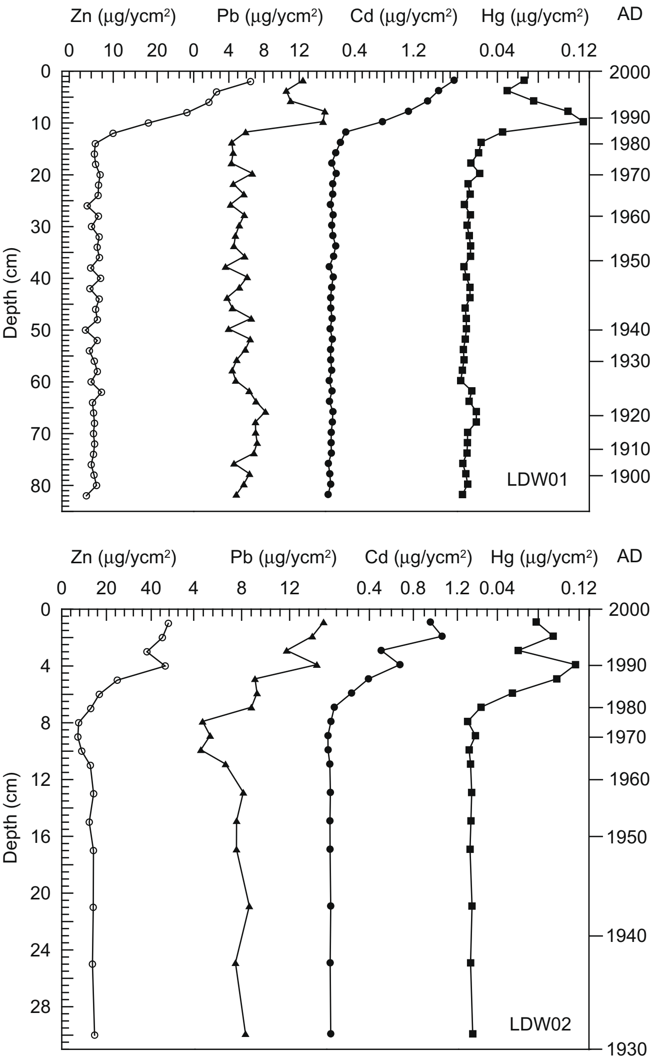

Fig. 4. Burial flux of heavy metals during the studied interval in the Liaodong Bay sediments.

ρd [g(cm^3)$^{-1}$] are the sedimentation rate and the sediment dry bulk density, respectively.

The burial fluxes of Zn, Pb, Cd and Hg calculated by formula (1) are presented in Fig. 4. The burial fluxes of all heavy metals display similar patterns with their concentrations characterized by little changes in the lower parts of the cores and abrupt increase in the surface sediments (Fig. 4). For the LDW01, the average values of burial fluxes are 5.8, 0.08, 0.01, and 5.5 μg (y cm^2)$^{-1}$ for Zn, Cd, Hg and Pb respectively in the sediments before the late 1970s, but increase to 33, 1.45, 0.075, and 12 μg (y cm^2)$^{-1}$ in the surface sediments (Fig. 4).

The high concentrations and burial fluxes of Zn, Pb, Cd, and Hg could be attribute to either the increased natural weathering of soil materials or inputs from rapid industrial development and urbanization in the last few decades. Usually, the increase in natural weathering in the watershed area would not cause obvious change in the ratios of Pb isotope. However, as discussed above, the ^{206}Pb/^{207}Pb ratios display obvious decline in the sediments of the last few decades (Fig. 3), implying that the increase in trace metal concentrations in the Liaodong Bay should mainly come from anthropogenic sources, such as rapid urbanizations and intensive industrial activity.

The heavy metal concentrations are often normalized by conservative elements in rocks to reduce the influence of granulometric and/or mineralogical variations of sediments on the concentrations of trace elements (Tam and Yao, 1998; Aloupi and Angelidis, 2001; Liu et al., 2003; Ip et al., 2004). The heavy metals are normalized by scandium in this study. The reason for choosing Sc instead of other conservative elements like Ti or Zr is its wide distribution in crustal rocks, unlike Ti and Zr, which are mainly concentrated in ilmenite and zircon, respectively (Frondl, 1970; Steinmann and Shotyk, 1997).

Before the 1950s, the areas around Liaohe Rvier and Liaodong Bay were mainly agricultural regions with very few industrial activities. At that time, the Liaodong Bay mainly received inputs from the natural environment. Consequently, the relative enrichment of heavy metals in the surface layers than those in the sediments before 1950s can provide a reliable assessment on the extent of anthropogenic contamination.

The enrichment factors in the two cores from the Liaodong Bay are calculated in order to identify the extent of anthropogenic heavy metal pollution. The enrichment factors are calculated by following equation:

$$\text{Enrichment factor} = (\text{X/Sc})_{\text{sample}}/(\text{X/Sc})_{\text{B}}$$

where $(\text{X/Sc})_{\text{sample}}$ is the ratio of element (X) to Sc for studied sample, and $(\text{X/Sc})_{\text{B}}$ is the average value of X/Sc ratios in sediments before 1950.

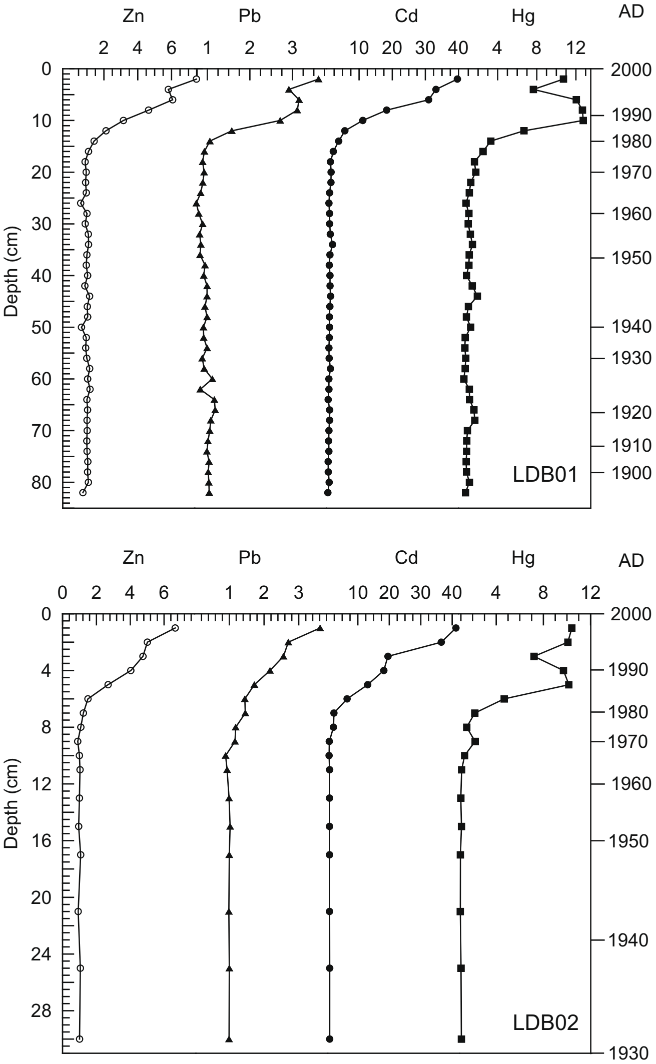

Fig. 5. Enrichment factors for the profiles of LDB01 and LDB02.

The enrichment factors show a consistent variation along the profiles of both LDB01 and LDB02 (Fig. 5). For the sediments deposited before 1950s, the enrichment factors of Zn, Pb, Cd, and Hg change little with an average value of ~1 (Fig. 5). The relative stable enrichment factors, together with geogenic $^{206}Pb/^{207}Pb$ ratios, suggest that these elements should have a similar origin reflecting their common natural background signature (Fig. 5). In contrast, the enrichment factors of Cd, Hg, Zn and Pb are more than 30, 10, 7 and 3.5, respectively, reflecting an abrupt increase in near surface sediments accumulated after late 1970s (Fig. 4).

5. Conclusion

Two cores from the Liaodong Bay are dated based on the method of the combination of ^{137}Cs and ^{210}Pb in the Liaodong Bay. The relative high values of $^{206}Pb/^{207}Pb$ ratios before 1950s together with the low industrial activities before 1950s indicate that the heavy metals in the sediments before 1950s were mostly lithogenic in origin, which were used as natural background signatures in the Liaodong Bay. The synchronous changes of the heavy metal concentration with decrease in $^{206}Pb/^{207}Pb$ ratios show clearly that the elevations of Zn, Pb, Cd, and Hg concentrations in the recent sediments were mostly due to anthropogenic activities. The enrichment factors of heavy metals in the surface sediments are more than 30, 10, 7, and 3.5 for Cd, Hg, Zn and Pb, respectively.

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