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Heavy metal enrichments in the Changjiang (Yangtze River) catchment and on the inner shelf of the East China Sea over the last 150 years

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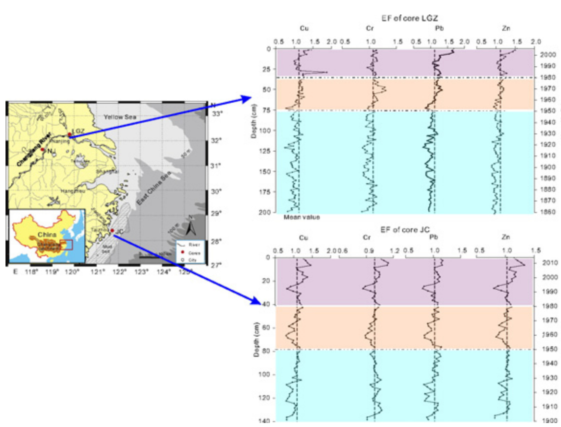
HIGHLIGHTS

- Three cores were collected from East China to evaluate the heavy metal enrichment.
- The major sources of heavy metals come from natural weathering detritus.
- Enrichment of Cu, Cr, Pb and Zn has increased over the last five decades.
- The heavy metal enrichment synchronizes with enhancing human activities.

GRAPHICAL ABSTRACT



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ABSTRACT

Compositions of heavy metals including Cu, Zn, Cr and Pb in three sediment cores recovered from the lower basin of the Changjiang (Yangtze River) and the inner shelf mud of the East China Sea were analyzed by traditional X-ray florescence (XRF) and XRF Core Scanner. This study aims to investigate the accumulation of heavy metals in the fluvial sediments and to decipher the influence of anthropogenic activities within the large catchment over the last 150 years. The data suggest that the heavy metals, especially Pb and Zn, show obvious enrichments in concentrations since 1950s, and the small and consistent variations of heavy metal concentrations before 1950s can represent geochemical background values. After removing the grain size effect on elemental concentrations, we infer that the sources of heavy metals predominantly come from natural weathering detritus, while human contamination has increased over the last half century. The calculations of both enrichment factor and geoaccumulation index, however, indicate that the pollution of these heavy metals in the fluvial and shelf environments is not significant. The rapid increase in human activities and fast socioeconomic development in the Changjiang catchment and East China over the last five decades accounts for the enrichments of heavy metals in the river and marine sediments. The inner shelf of the East China Sea, as the major sink of the Changjiang-derived fine sediments, provides a high-resolution sediment archive for tracing the anthropogenic impacts on the catchment.

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1. Introduction

Heavy metals of Cu, Cr, Pb and Zn accumulated in terrestrial and marine environments can cause serious problems to ecosystem due to their toxicity, persistence and bioaccumulation (Kelderman and Osman, 2007; Hu et al., 2013). There are two major sources of heavy metals in detrital sediments, i.e. natural inputs and anthropogenic contaminations, anthropogenic sources include biomass and fossil fuel combustion (coal, petroleum and natural gas), waste incineration, as well as mining and smelting industries (Nriagu and Pacyna, 1988; Pan and Wang, 2012). The relative contributions of anthropogenic sources to global emissions of heavy metals have considerably varied with time. Terrigenous sediment in fluvial and marine environments often serves as a major sink for heavy metals, and has become an environmental archive for the investigation of anthropogenic contamination in the past (Qiu et al., 2007; Krom et al., 2009). Geochemical composition of dated sediment cores has shown to be an excellent tool for evaluating the effects of anthropogenic and natural processes on depositional environments. A number of recent researches have used sediment cores from marine and lake environments to investigate and reconstruct historical records of contaminant inputs in these environments (Audry et al., 2004; Chen et al., 2004; Kelderman and Osman, 2007; Morelli et al., 2012; Townsend and Seen, 2012; Azoury et al., 2013; Duan et al., 2014; Vallius, 2014; Xu et al., 2014; Choi et al., 2015).

The Changjiang (Yangtze River) is the largest river in China and one of the largest in the word in terms of its huge water and sediment discharges, which plays a critical role on terrestrial material cycle and ecosystem health in the western Pacific marginal seas (Milliman et al., 1985; Saito et al., 2001; Yang et al., 2003; Wang et al., 2008). As the largest river in Asia, the Changjiang has the water and sediment discharges of about 896.4×10^9 m^3/year and 390×10^6 ton/year respectively, based on the multi-year observations at Datong gauge station (1950–2010) (Changjiang Water Resources Commission, http://www.cjw.com.cn/). Since the middle Holocene, a major portion of the Changjiang-derived sediments have been trapped in its estuary to build a large delta, and the remainder being mostly transported southeastward by the coastal currents, and formed a unique muddy depositional system on the inner shelf of the East China Sea (ECS), offshore the coastal Zhejiang and Fujiang Provinces (Qin, 1979; Liu et al., 2006; Liu et al., 2007; Xu et al., 2009; Yang et al., 2014). Thus, the sediment of the mud belt on the ECS shelf is predominantly from the Changjiang River.

In recent years, the Changjiang River is severely disturbed by anthropogenic activities, with the construction of the world's largest hydroelectric project (Three Gorges Dam, TGD) as a typical example. As a result, the sediment discharge to its estuary has been decreasing rapidly since the impoundment of TGD in 2003, averaging at only about 155 × 106 ton/year over the last ten years (2003–2013) (Changjiang Water Resources Commission, http://www.cjw.com.cn/). The Changjiang catchment has a population of about 500 million and has become one of the most important areas in the socioeconomic development of China. Thus, it is of great significance to evaluate the impact of anthropogenic activities on the fluvial and coastal sea environments.

Several studies have investigated the temporal and spatial distributions of heavy metal concentrations in the Changjiang catchment, which suggest that heavy metal enrichment has become serious over the last decade compared to the 1990s (Liu and Fan, 2011; Dong et al., 2012); the enrichments of organic pollutants and Pb in the Changjiang estuarine sediments are closely related to economic development (Shen et al., 2006; Guo et al., 2006). Generally, the estuary and coastal area have complicated hydrodynamic regimes subject to dynamic marine processes, and the sediments therein may be derived from both terrestrial and marine sources. Thus, it is difficult to reliably reveal the anthropogenic activity on the accumulation of heavy metals in the estuary and coastal ocean. However, the inner shelf mud of the ECS, as a major sink of the Changjiang-derived sediments during the mid-late Holocene (Liu et al., 2006; Liu et al., 2007; Xu et al., 2009), is characterized by continuous deposition with higher sediment accumulation rates (Gao and Wang, 2008; Yang et al., 2014), which thus provides a good archive for the high-resolution environmental study. Similarly, the lower valley of a river acts as the sink of sediment from the whole catchment, which makes it a desired area to evaluate the impact of human activity on the fluvial environment.

In this study, three short gravity cores with sediments ultimately from the Changjiang River were taken from the lower Changjiang mainstream (cores LGZ and NJ) and from the mud belt on the ECS inner shelf (core JC). The major purpose of this research is to investigate the anthropogenic impacts on the Changjiang catchment over the last 150 years. Based on the variations of geochemical elements and grain size of the core sediments, sources of heavy metals will be examined and the degree of heavy metal enrichment is assessed by using the proxies of enrichment factor and geoaccumulation index.

2. Materials and methods

The cores LGZ and NJ were taken from the lower mainstream of the Changjiang River in March 2008 and March 2010, respectively, and core JC was taken offshore the Zhejiang coast in April 2014 (Fig. 1). Core LGZ is located in a newly emerging bar in Yangzhong County, Jiangsu Province. The geographic coordinate is 32°18.393′ N and 119°45.218′ E. Core NJ was taken from the north bank of the Changjiang River near Nanjing City, with the geographic coordinate of 31°59.149′ N and 118°39.817′ E. Core JC was taken from the mud belt on the ECS inner shelf with the geographic coordinate of 28°39.017′ N and 121°41.300′ E, and the water depth of 10 m. No obvious agricultural and industrial activities are observed near the cores of LGZ and NJ, which makes them natural depositional environments in the Changjiang catchment and suitable for the study of environmental reconstruction.

Sediment cores LGZ and NJ were obtained by pushing about 200 cm long of PVC pipes into the ground, and subsequently pulled out manually. All the cores were taken to minimize disturbance and kept in a vertical position during transport from the field to the laboratory. This sampling technique has been used successfully in a range of sediment types and it yields undisturbed samples of sediment (Moura et al., 2004; Morelli et al., 2012). In laboratory, the cores were cut and split into two halves with a nylon string for minimizing metal contamination, and were stored at 4 °C until analysis.

The absolute and relative concentrations of elements of the core sediments were analyzed using X-ray fluorescence (XRF, PANalyticalAxiosMAX) and XRF Core Scanner (Avaatech Company). For the XRF Core Scanner analysis, the split-core surface was first flattened and covered with a thin Ultralene film to avoid contamination of the measurement prism of the core scanner, which allows continuous and non-destructive analysis of elements range from aluminum through to uranium (Richter et al., 2006). The relative concentrations of elements in the core sediments were acquired by scanning the core with a 0.5 cm resolution by the XRF Core Scanner. China Steam Sediment Reference Material (national geostandard GSD-15) was analyzed before and after the core scanning in order to confirm the stability of the equipment. The basic unit of the scanning elements is total counts or counts per second (cps). This unit implies the elemental intensity that is proportional to the chemical concentration (Tjallingii et al., 2007). In this study, the XRF-scan data will be presented as unprocessed intensities, i.e. cps.

After the XRF scanning, the cores LGZ, NJ and JC were sliced at 1–2 cm sampling intervals for the analyses of traditional XRF and grain size. A total of 101, 182 and 138 subsamples were respectively collected from cores LGZ, NJ and JC. For the XRF analysis, the subsamples were oven dried at 60 °C and ground to a fine powder with a size of about 200 mesh. The powder samples were heated again in the oven for 2 h at 120 °C and kept overnight at 60 °C before the XRF analysis. About 4 g samples were put into the tablet mold with boric acid prepared, and then the elemental concentrations were measured on the compressed disks.

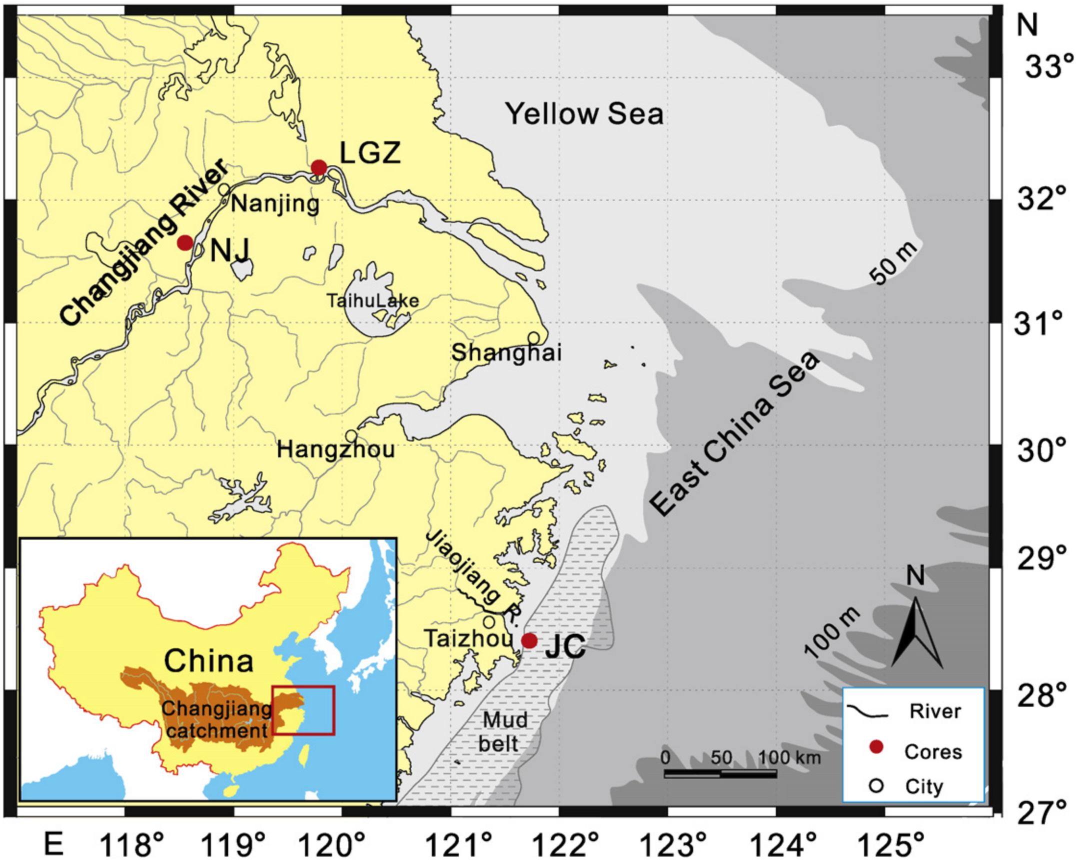

Fig. 1. Map showing the sampling locations in the lower valley of the Changjiang River (cores LGZ and NJ) and in the mud belt of the East China Sea shelf (core JC).

Blanks and China Steam Sediment Reference Materials (GSR-6 and GSD-15) are measured together with the unknown samples for data quality control, which yield the analytical precision of about 5%. The total organic carbon (TOC) was analyzed using a Vario Cube CN Elemental Analyzer (made by Elementar Company in Germany). For monitoring the analytic quality, the repetitive measurements of standards of cystine and sulphanilamide and unknown samples yielded a precision of about 0.5%.

Sediment samples prior to being ground were analyzed by the laser size analyzer (Coulter LS230, USA) for grain size composition after processing the samples with 10% H_2O_2 and 1 mol/L HCl to remove organic matter and carbonate, respectively. The measurement error is ≤1%. All of the above analyses were carried out in the State Key Laboratory of Marine Geology at Tongji University.

In order to estimate the depositional rates and establish the chronology of the cores, the samples of core LGZ were sent to Chungnam University in Korea for ^{210}Pb dating measurements (Zhan et al., 2010), and the samples of cores NJ and JC were measured for ^{210}Pb and ^{137}Cs dating at Nanjing Institute of Limnology and Geography, Chinese Academy of Sciences, with gamma spectrometry (GWL-120230, EG and G Ortec, USA). The dating subsamples were taken from the cores at 2–5 cm intervals for the measurements of ^{210}Pb, ^{226}Ra and ^{137}Cs radioisotope activities. Radioactivity level of ^{210}Pb was determined by gamma emission at 46.5 keV. ^{226}Ra was determined with the 295 keV and 352 keV γ-rays emitted by its daughter nuclide ^{214}Pb after 10 days storage in sealed containers to allow radioactive equilibrium. ^{137}Cs radioactivity was measured with the 662 keV photopeak. The standard sources and sediment samples of known activity provided by China Institute of Atomic Energy were used to calibrate the absolute efficiencies of the detectors. Supported ^{210}Pb in each sample was assumed to be in equilibrium with the in-situ ^{226}Ra, and the excess ^{210}Pb activities were determined from the difference between the total ^{210}Pb and supported ^{210}Pb activities.

3. Results

3.1. Geochronology of the studied cores

Dating of core LGZ using the ^{210}Pb and ^{137}Cs radioactive isotopes has been reported previously (Zhan et al., 2010). The average accumulation rate of core LGZ is about 0.97 cm/a based on the CIC (constant initial concentration) model, and then was corrected by the compaction ratio inside the sample PVC tube which is related to water content of the sediment and sorting coefficient (Wang et al., 2006). The average water content is about 25% and the sorting coefficient is 1.75, and accordingly, the compaction ratio is estimated to be about 1.39 based on the equation proposed by Wang et al. (2006). After correcting the compaction ratio, the actual sediment accumulation rate of core LGZ measured by the ^{210}Pb dating method was about 1.34 cm/a.

As for cores NJ and JC, the ^{210}Pb and ^{137}Cs depth profiles are shown in Fig. 2. The ^{137}Cs profiles display relatively well-resolved peaks at 45.5 cm and 56 cm, which may correspond to nuclear tests in early 1960s, with the major peak dated to the year 1963. Given that the complex hydrodynamic environment in the lower Changjiang mainstream and on the inner shelf of ECS, and furthermore, the cores of LGZ, NJ and JC are not long enough to obtain the ^{210}Pb equilibrium point, the CRS (constant rate of supply) model may not be applicable for this area. The CIC model used in this study assumes that an increased flux of sedimentary particles from the water column will be removed proportionally. In recent years, the CIC model has been widely used in dating the cores from the Changjiang catchment and inner shelf of ECS (Wang et al., 2013; Yu et al., 2014; Chen et al., 2014; Ge et al., 2015; Hu et al., 2015; Meng et al., 2015; Li et al., 2015).

In the CIC model, it is assumed that the incorporation of unsupported ^{210}Pb to the sediment is produced as a constant flow and that the sedimentation rate is also constant. According to the hypothesis, the ^{210}Pb

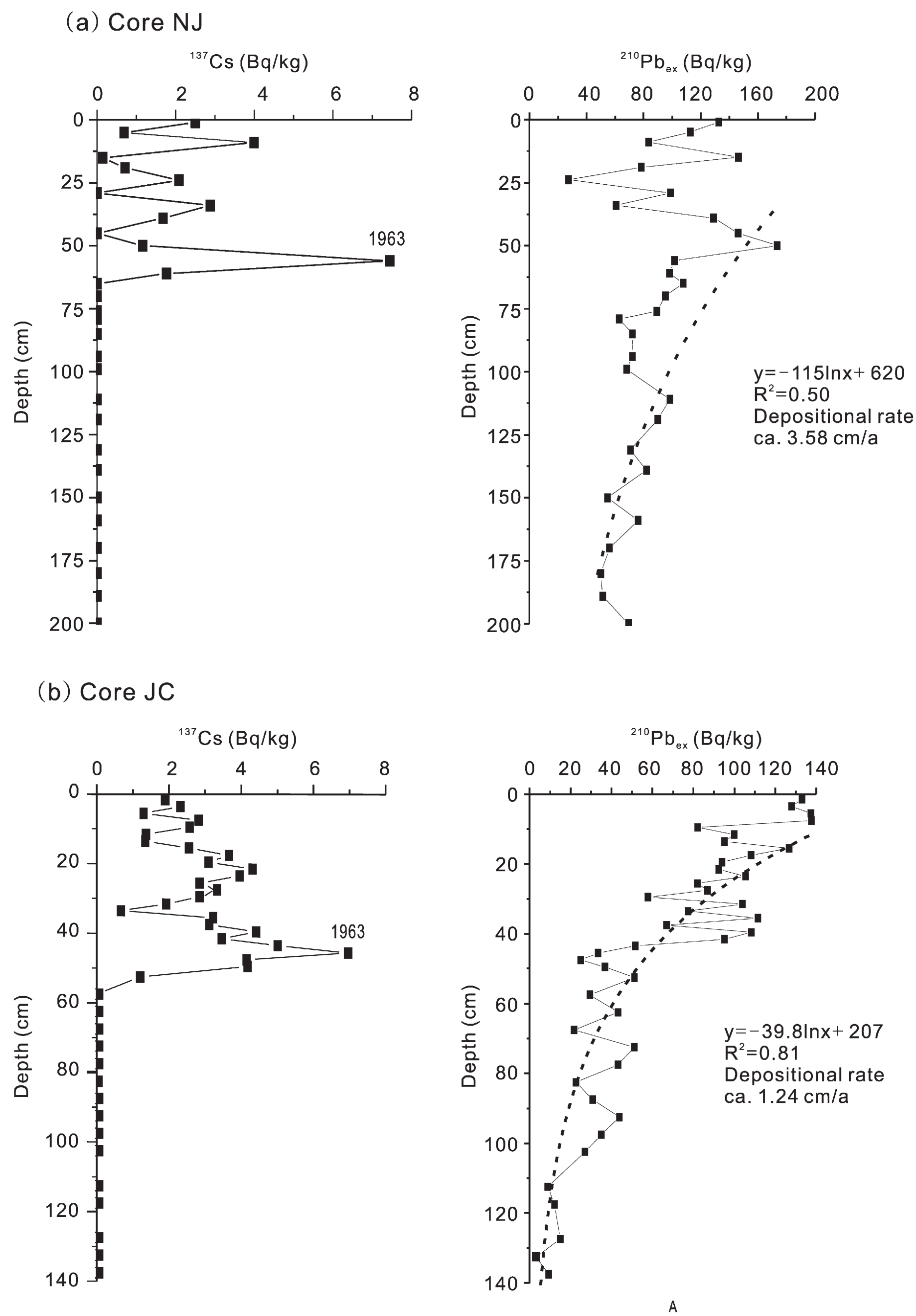

Fig. 2. Specific activities of $^{210}Pb_{ex}$ and ^{137}Cs with depths of the cores NJ and JC. Dotted lines indicate the regression result of ^{210}Pb chronology calculation.

excess activity in a layer Z (cm) deep, A (Bq/kg), is expressed by Appleby and Oldfield (1983) as,

$$\ln A = \ln A_0 - \frac{\lambda}{s} Z \quad (1)$$

where, A_0 (Bq/kg) is the ^{210}Pb excess activity in the top layer of the sediment core, λ is the ^{210}Pb decay constant (0.031/a), and s is the sedimentation rate (cm/a). The sedimentation rate s (cm/a) is calculated as follows:

$$s = \lambda / a \quad (2)$$

where, a is the slope of the linear regression of depth plotted against the logarithm of the unsupported ^{210}Pb according to Eq. (1), the regression results of core NJ and JC are shown Fig. 2. For the core JC, the excess ^{210}Pb overall displays an exponential decreasing trend, which indicates that the CIC model can be used to date the sediment samples and yields a mean sedimentation rate of 1.24 cm/a. While for the core NJ, considering the large fluctuation of ^{210}Pb activities at the top 50 cm, the ^{210}Pb dates are calibrated using the ^{137}Cs date as a dating marker, which yields a mean accumulation rate of 1.09 cm/a between the year 1963 and the sampling time, and of about 3.58 cm/a in the lower part.

3.2. Depth variations of grain size, TOC, and elements in the studied cores

The variations of grain size and major element contents in the core sediments of LGZ, NJ and JC are shown in Fig. 3. For all the three cores, silt is dominant with sand layers occurring throughout the profiles, and the mean grain size (Mz) of profiles range from 5.0 to 8.0 phi. The contents of TOC in three cores vary at 0.5–2.0% with small variations. As for the core LGZ, it is noteworthy that TOC increases upward significantly in the upper 10 cm and reaches the maximum at top.

Geochemically, concentrations of Fe, Al and Ti vary synchronously with depth in the cores, and the ratio of Al/Ti (relative contents, cps/cps) keeps relatively stable through the core sediments. At the depths of ~50 and ~100 cm of the core LGZ, Fe, Al and Ti all show pronounced changes in composition (Fig. 3). Given that Al, Fe and Ti are major metallic elements found in the continental crust and geochemically conservative in earth surface process, and rarely affected by anthropogenic activities, the abnormal changes of these elements in these samples could be caused by the changes in natural source such as the terrigenous input.

The depth profiles of heavy metal compositions in the sediments of cores LGZ, NJ and JC examined by XRF (units in ppm) and XRF Core Scanner (for Pb and Zn, units in cps) are shown in the Fig. 4. As for the core LGZ, Pb and Zn show overall increasing contents in the upper 50–70 cm and relatively low and stable contents in the lower part. While, the concentrations of Cu and Cr bear weak variations in the core but somewhat increasing trends are also observed at the depth of 75 cm corresponding to the depositional age of A.D. 1950 (Fig. 4a). The core JC displays similar trends in heavy metal compositions with core LGZ, showing relatively stable contents in the lower part but obvious fluctuation in the upper 80 cm section (Fig. 4c).

In this study, we did not measure the absolute concentrations of heavy metals in cores NJ by XRF but present the relative contents measured by XRF Core Scanning. The vertical variations of heavy metal

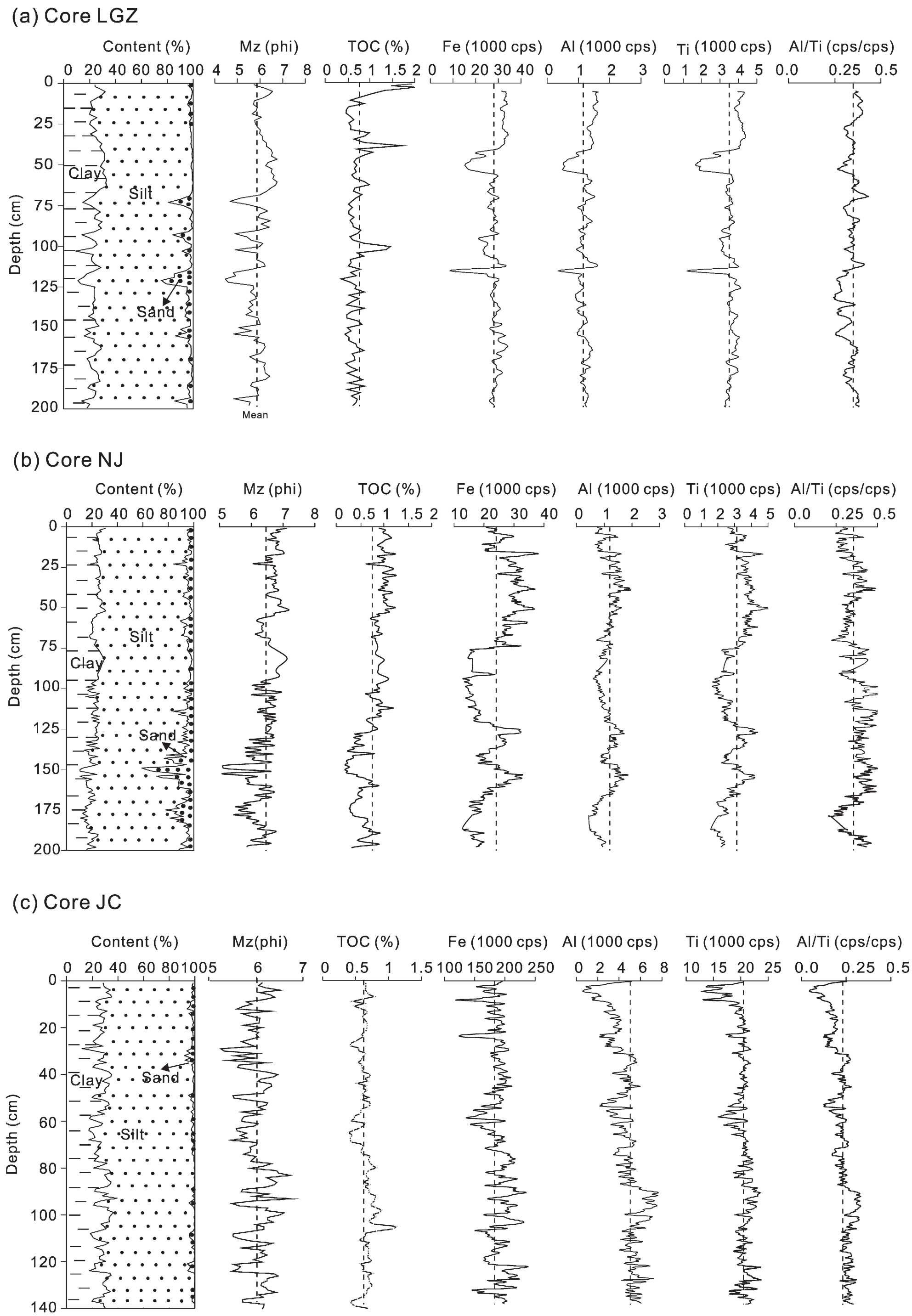

Fig. 3. Depth profiles of grain size parameters, TOC and major elemental contents of cores LGZ, NJ and JC. Mz: mean grain size (unit: phi), dotted lines indicate the mean values.

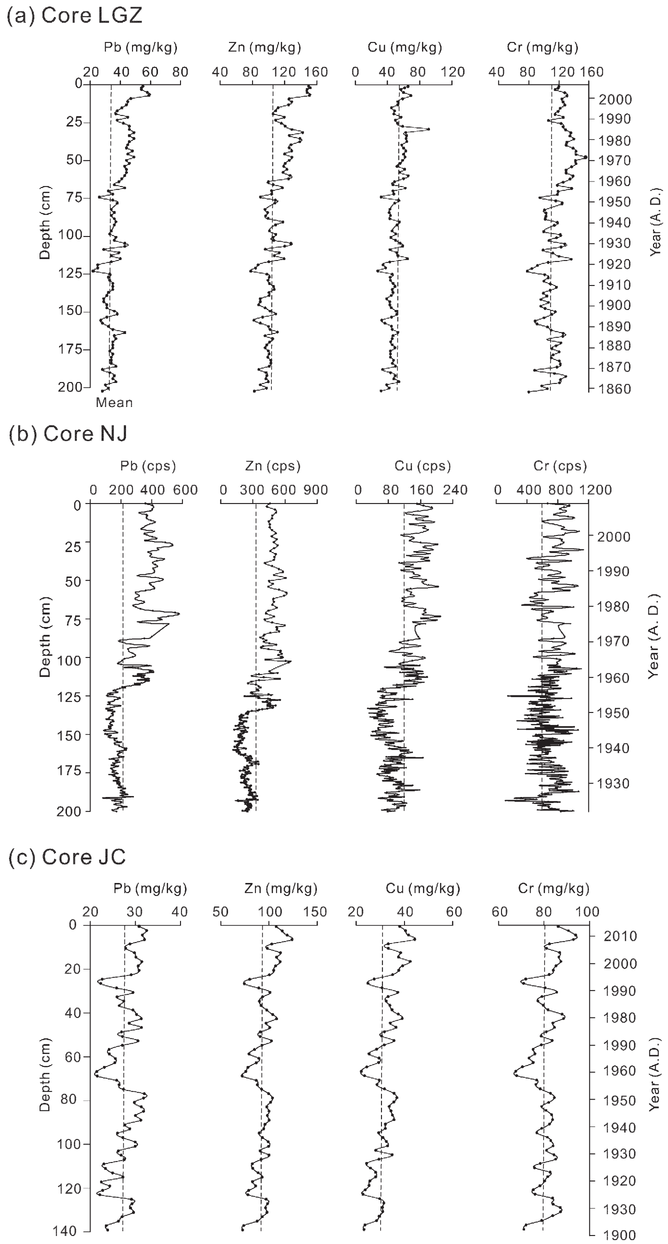

Fig. 4. Concentrations of heavy metals of cores LGZ, NJ and JC analyzed by XRF (unit: ppm) and XRF Core Scanner (unit: cps, counts per second). Dotted lines indicate the mean values.

contents in this core are overall similar with those of the other two cores, showing rapid increase in relative contents at about 123 cm (ca. A.D. 1950), and lower and relatively stable values below 123 cm (Fig. 4b). While, obvious increasing trends for Pb and Zn occurring at ~123 cm correspond to the time of 1950s (Fig. 4b), and whether this was caused by fast economic development after the national independence in 1949 will be discussed later. Given that the heavy metals in the three cores possess the similar trends in absolute and relative contents, the following discussions will focus on cores LGZ and JC.

4. Discussions

4.1. Sources of heavy metals in the core sediments

To explore the sources of heavy metals and examine the grain size effect on the cores LGZ and JC, correlations of the given elements with mean grain size, clay content and TOC content are shown in Table 1. For the core sediments, positive correlations exist between Al and other heavy metals. Previous studies suggest that Al in the Changjiang River sediment is primarily derived from aluminosilicates, and mostly resides in the clay fraction. The relatively constant ratios of Al/Ti in the sediments of three cores (Fig. 3) also imply that these core sediments have stable provenances, and are dominated by natural weathering detritus. Similarly, positive correlations are observed between the clay content and heavy metal concentrations, suggesting the relatively enrichments of heavy metals in clay. And also, these heavy metals show positive correlation with each other. Nevertheless, the TOC content has no obvious relationship with the heavy metals.

In order to further discern the sources of heavy metals, principal component analysis (PCA) was performed (Table 2). PCA is an effective method to identify the correlations between elements, to delineate the factors affecting sediment chemistry, to determine the source of sediment metals, and to distinguish between natural and human inputs (Boyle et al., 1999). For both of the cores LGZ and JC, two factors of PC1 and PC2 with the total variance of 74.8% and 77.9% are observed, respectively. All of the elements Al, Fe, Cu, Cr, Pb, Zn and Ti show higher loading in the PC1 factor, except for the clay content that has higher loading in PC2. Given that Al and Fe are primarily derived from the aluminosilicate minerals, we infer that the major source of heavy metals in cores LGZ and JC is the natural detritus input.

4.2. Assessment of anthropogenic impacts on heavy metal accumulation

4.2.1. Estimation of enrichment factor (EF)

A common approach to estimate the anthropogenic impact on sediment chemistry is to calculate a normalized enrichment factor (*EF*) for metal concentrations above uncontaminated background levels (Liaghati et al., 2004; Reimann and Caritat, 2005; Ip et al., 2007). *EF* is expressed as:

$$EF = \frac{(M/X)_{\text{sample}}}{(M/X)_{\text{background}}} \tag{2}$$

where M is the element investigated, X is the reference element, $(M/X)_{\text{sample}}$ and $(M/X)_{\text{background}}$ are the ratios of an evaluated element and the reference element in the interested and background samples respectively. Generally, five categories are recognized on the basis of the EF values: $EF < 2.0$, none to slight enrichment; $2 \le EF < 5$, moderate enrichment; $5 \le EF < 20$, significant enrichment; $22 \le EF < 40$, very high enrichment, and $EF > 40$, extremely high enrichment (Liaghati et al., 2004; Pekey, 2006).

The key for the *EF* calculation is the selection of a reference element that is not universal and depends on geological and physicochemical characteristics of the study area (Reimann and Caritat, 2005). Elements including Al, Fe, Li, Co, Sc, Ti and Cs have often been used as the reference elements (Rose et al., 2004). In this study, the concentrations of Ti are relatively stable and have positive correlations with Al and clay contents in the cores LGZ and JC, which suggests that Ti is predominantly derived from terrigenous detritus and can be used as the reference element.

Another factor to be taken into account in *EF* calculation is the establishment of geochemical background values. Normally, shale, upper continental crust, and fine-grained sediment are often used as reference materials. Abrahim and Parker (2008) suggested the use of local background values (e.g., from a deep sediment layer not affected by pollution) instead of the average crust composition. Heavy metal contamination in the sediment is usually relating to agricultural, industrial, mining or metallurgy activities (Bindler et al., 2011; Morelli et al., 2012). Different from the developed western countries, China started economic recovery in 1950s just after the end of the civil war in 1949, and has experienced rapid industrial development since the 1970s (Liu et al., 2009; Guan et al., 2011). According to the variations of heavy metal concentrations in cores LGZ, NJ and JC (Fig. 4), we infer

Table 1
Pearson correlations matrix of the elements and grain size of cores LGZ and JC (sample numbers: 101 for core LGZ and 70 for core JC).

	Al	Fe	Cu	Cr	Pb	Zn	Ti	Mz	Clay	TOC
Core LGZ										
Al	1									
Fe	0.64**	1								
Cu	0.56**	0.78**	1							
Cr	0.64**	0.91**	0.80**	1						
Pb	0.47**	0.77**	0.83**	0.78**	1					
Zn	0.46**	0.72**	0.85**	0.73**	0.95**	1				
Ti	0.60**	0.83**	0.76**	0.81**	0.62**	0.58**	1			
Mz	0.47**	0.68**	0.55**	0.68**	0.56**	0.50**	0.54**	1		
Clay	0.43**	0.65**	0.54**	0.64**	0.54**	0.48**	0.51**	0.97**	1	
TOC	0.12	0.27**	0.38**	0.22**	0.55**	0.57**	0.07	0.19	0.19	1
Core JC										
Al	1									
Fe	0.98**	1								
Cu	0.80**	0.83**	1							
Cr	0.85**	0.87**	0.84**	1						
Pb	0.88**	0.88**	0.91**	0.83**	1					
Zn	0.86**	0.87**	0.96**	0.91**	0.92**	1				
Ti	0.62**	0.68**	0.87**	0.66**	0.76**	0.68**	1			
Mz	0.18	0.19	0.61**	0.41**	0.39**	0.57**	0.35**	1		
Clay	0.53**	0.54**	0.48**	0.56**	0.53**	0.50**	0.37**	0.12	1	
TOC	0.52**	0.50**	0.25	0.47**	0.37**	0.36**	0.20	−0.16	0.39**	1

Mz: mean grain size.
** Correlation is significant at the 0.01 levels (two tailed).

that the average concentrations of heavy metals in the lower parts of these cores deposited before 1950 can represent pre-industrial levels and be used as the background values.

As shown in Fig. 5, The *EF* values of Cu, Cr, Pb and Zn of the cores LGZ and JC mostly vary between 0.5 and 1.5, and remain relatively stable at the depth of 200–75 cm (about 1860s–1950s) and 140–80 cm (about 1900s–1950s), respectively, again implying that the heavy metals in the cores are "none to slight enrichment", natural terrestrial weathering is the main source of these heavy metals in the sediments. It is clear that the *EF* values of these heavy metals all show increasing trends since 1950s albeit with different variations, suggesting that anthropogenic activities in the Changjiang catchment might have some influence on sediment compositions, which will be discussed further later.

Table 2
Statistical results from principal component analysis of cores LGZ and JC. The bold-faced numbers indicate the larger loadings between two principal components (PC1 and PC2).

Component	PC1	PC2
Core LGZ		
Al	**0.705**	0.061
Fe	**0.873**	0.301
Cu	**0.894**	0.119
Cr	**0.891**	0.258
Pb	**0.871**	0.137
Zn	**0.857**	0.085
Ti	**0.824**	0.145
Mz	0.607	**0.703**
Clay	0.519	**0.833**
Silt	0.128	−0.765
Sand	−0.663	−0.343
Eigenvalue	6.114	2.113
% total variance	55.6	19.2
% cumulative variance	55.6	74.8
Core JC		
Al	**0.836**	0.357
Fe	**0.857**	0.351
Cu	**0.967**	0.084
Cr	**0.884**	0.277
Pb	**0.912**	0.253
Zn	**0.969**	0.140
Ti	**0.763**	0.132
Mz	**0.616**	−0.371
Clay	0.400	**0.839**
Silt	−0.489	−0.643
Sand	0.059	−0.773
Eigenvalue	6.285	2.289
% total variance	57.1	20.8
% cumulative variance	57.1	77.9

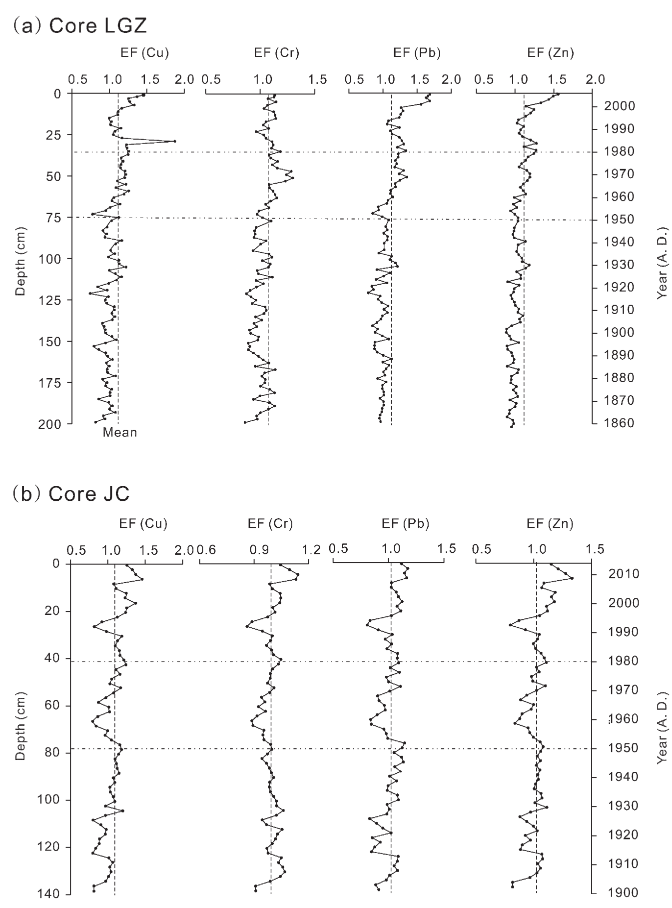

Fig. 5. Depth profiles of enrichment factor (*EF*) from the sediments of cores LGZ and JC. Dash lines indicate obvious changes in *EF* values. Dotted lines indicate the mean values.

Furthermore, the mean value of EF in the core LGZ is relatively higher than in the core JC. Core JC is located on the ECS inner shelf which is far away from the Changjiang river but is regarded as a major sink of the Changjiang-derived sediments. Combining the EF data with the PCA analysis, it is hypothesized that the metal contamination by human activity in marine environment may not be so serious as in terrestrial environment. In other words, the core LGZ may be more influenced by local anthropogenic input, which accounts for higher enrichments of heavy metals.

4.2.2. Indication of geoaccumulation index (I_{geo})

Geoaccumulation index (I_{geo}) is also often used to evaluate the pollution history of heavy metals (Muller, 1969). The method assesses the degree of metal pollution in terms of seven classes based on the increasing values of the index. The I_{geo} is calculated as the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5b_n} \quad (3)$$

where C_n is the measured concentration of the examined metal n, and b_n is the background concentration of the metal n, factor 1.5 used as the possible variation in background values due to lithogenic effect and weathering. The I_{geo} is associated with a qualitative scale of pollution intensity, being classified as unpolluted ($I_{geo} < 0$), unpolluted to moderately polluted ($0 < I_{geo} < 1$), moderately polluted ($1 < I_{geo} < 2$), moderate to strongly polluted ($2 < I_{geo} < 3$), strongly polluted ($3 < I_{geo} < 4$), strongly to extremely polluted ($4 < I_{geo} < 5$), and extremely polluted ($I_{geo} > 5$) (Farkas et al., 2007).

Given that the similar variations of heavy metal concentrations in the cores LGZ, NJ and JC, only cores LGZ and JC samples are considered for the I_{geo} calculation. In this study, the average concentrations of heavy metals before the year 1950 are also chosen as the background values. The I_{geo} values of all heavy metals vary between −1.0 and 0.5, with most samples below zero (Fig. 6), suggesting that the heavy metals in most of the samples studied can be classified as "none to moderately polluted". This observation is consistent with the result of *EF* estimation, all implying that the heavy metal enrichment in the investigated river and marine sediments is not severe and natural weathering dominates the sources of heavy metals. It is interesting to note that the I_{geo} values of Pb, Cu and Zn increase from around the year 1950 till the present, with a weak decrease in 1990s, which probably indicates the human contamination on these heavy metals.

4.3. Heavy metal accumulation and socioeconomic development in central China

According to the ^{210}Pb and ^{137}Cs dating results, the cores LGZ and NJ are roughly estimated to have depositional ages of 150, 100 and 110 years, respectively, which provide good archives for the reconstruction of anthropogenic impacts on heavy metal accumulation in the Changjiang catchment. Core JC was taken from the inner shelf mud of the ECS with sediment provenance predominantly from the Changjiang catchment during the mid-late Holocene (Liu et al., 2006; Liu et al., 2007; Xu et al., 2009; Yang et al., 2014). Therefore, all the three cores are good archives for tracing the anthropogenic contamination in the Changjiang catchment over the last hundred years.

Depth variations of heavy metal concentrations, *EF* and I_{geo} values as well all suggest that heavy metal pollution was not severe in the Changjiang catchment over the last 150 years, but the relative enrichments of heavy metals since 1950s may be caused by enhancing human activities over the large drainage basin (Figs. 3–5). China started economic recovery in the 1950s after the end of the civil war in 1949, and experienced rapid industrial development since the 1970s (Liu et al., 2009; Guan et al., 2011), which correspond well with the changes of *EF* and I_{geo} values in the LGZ and JC core sediments.

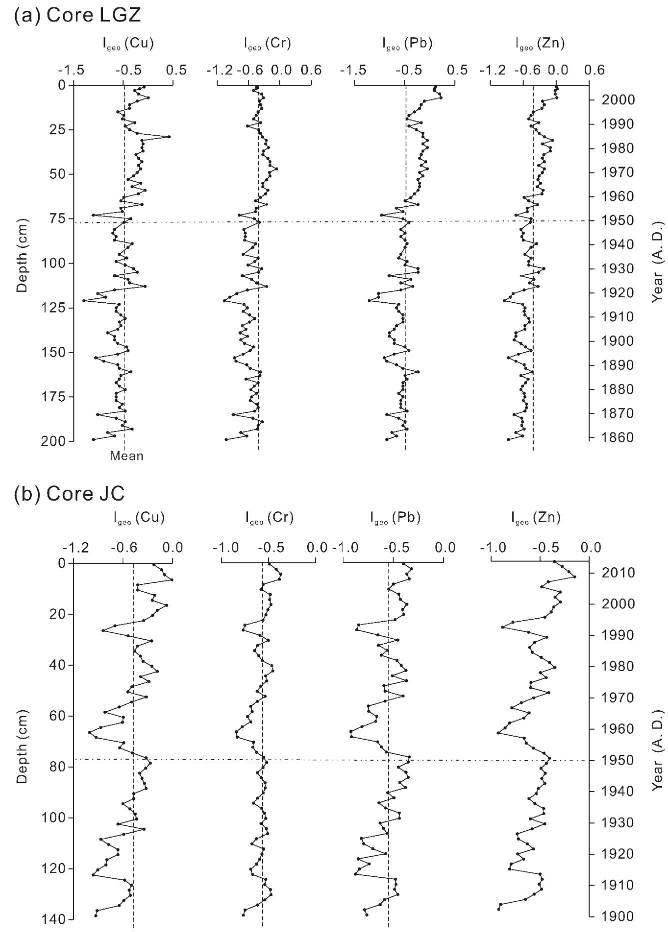

Fig. 6. Geoaccumulation index (I_{geo}) for Cu, Cr, Pb and Zn in the sediments of cores LGZ and JC. Dotted lines indicate the mean values.

Based on the changes of heavy metal accumulation in the cores, several stages can be identified:

(1) Pre-1950s: stable stage with natural weathering source.

Before the independence of China in 1949, industrial activities were very weak and dramatically slowdown because of the civil war. Therefore, the human activities in the large catchment exerted weak influence on river sediment quality and heavy metal accumulation as well. Natural weathering of provenance rocks predominantly determined the sediment chemistry of the Changjiang River.

(2) 1950s–1980s: increasing heavy metal accumulation.

The *EF* and I_{geo} values of Cu, Cr, Pb and Zn in the cores LGZ and JC all show increasing trends relative to the pre-1950s stage (Figs. 5, 6). Here, we compare the socioeconomic development with the accumulation of heavy metals in the Changjiang sediments in the last 50 years (Fig. 7). With the national independence in 1949 after the long civil war, China entered a period of social reconstruction and rapid economic recovery. As one of the most important economic zones in China, the Changjiang River basin witnessed the rapid socioeconomic development. The socioeconomic indices including population, energy consumption, gross regional product and steel production in the Changjiang catchment all exhibit gradual increase during the period of 1950s–1980s. Obviously, the enhancing human activities in the catchment, especially the industrial revolution, might result in the release of a large amount of heavy

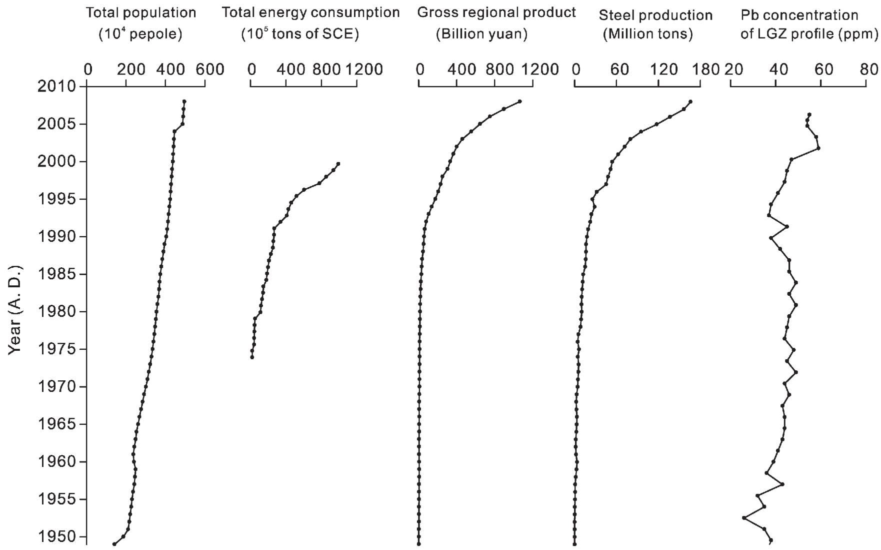

Fig. 7. Comparison of heavy metal enrichment (Pb) with total population, energy consumption, gross regional product and steel production in the Changjiang catchment from the year 1949 to 2008.
Data from China Compendium of Statistical 1949–2008 compiled by Department of Comprehensive Statistics of National Bureau of Statistics.

metals into the river environment, which caused the enrichment of heavy metals in the river sediments relative to pre-1950s.

During the Cultural Revolution in China (1966–1976), many of the manufacturing plants either ceased to operate or greatly reduced production especially in the later period of this political movement (Liu and Fan, 2011). Nevertheless, China's energy consumption increased at the same time, from 96 million tons in 1957 to 454 million tons in 1975 (China Statistical Yearbook, http://www.stats.gov.cn/tjsj/ndsj/information/njml.html). Fossil fuels such as coal, gas and oil consumption may be the main anthropogenic source of heavy metals in the river environment.

(3) 1980s to present: rapid increasing stage.

During this period, the *EF* and I_{geo} values of heavy metals in the cores rapidly increase despite the drop in 1990s. This stage corresponds to the period of reform and opening up of China since 1978. The socioeconomic indices such as total energy consumption, gross regional product and steel production in the Changjiang catchment all display rapid increase since 1990s (Fig. 6). In particular, the large increase in automobiles-using leaded gasoline since 1990s, which might cause the rapid accumulation of Pb in the sediments (Gan, 1998). Between the 1970s and 1980s, Pb released by human activity to the atmosphere is 33 times of the natural source, and for the Cu and Zn, the values vary between 2 and 5 (Callender, 2003). At the same time, the "Soil and Water Conservation" policy carried out in the upper valley of the Changjiang River since 1989 (Liao et al., 2010), which may considerably reduce the sediment supply from the upper basin to the lower Changjiang mainstream. Combining these factors, the intensifying anthropogenic activities in the large catchment can be taken into account for the increasing accumulation of heavy metals since 1980s till the present.

Furthermore, several flood events happened in the Changjiang River, especially in 1998, and the excessive stripping and leaching of soils in the basin by the flood water can supply more anthropogenic heavy metals to the Changjiang mainstream. Similarly, flood events have resulted in a noticeable increase of the particle-associated metals, such as As, Pb, Cu and Zn in the Dese River Estuary, Venice Lagoon, Italy (Zonta et al., 2005).

Another possible reason for the increase of heavy metal accumulation in the lower Changjiang mainstream is the construction of numerous dams in the watershed, including the Three Gorges Dam (TGD). With the impoundment of the TGD in June 2003, about 70% of the sediment derived from the upper valley has been trapped in the large reservoir, causing the significant decline of sediment discharge to the sea (Xu and Milliman, 2009). Meanwhile, the sediment grain size of the cores LGZ and NJ has decreased and TOC contents increased slightly in recent years (Fig. 3), which could be attributed to the TGD effect. After the construction of TGD, TOC contents in river sediments gradually increase in the middle and lower reaches (downstream of Yichang City), and the grain size composition can also be altered by the TGD water regulation (Zhang et al., 2014). Consequently, the decreasing grain size and increasing TOC contents after the TGD construction may result in the relative increase in heavy metal accumulation over the last ten years.

5. Conclusions

Three cores were taken from the lower basin of the Changjiang River and the mud belt of the ECS shelf for the examination of heavy metal accumulation in relation to anthropogenic activities over the last 150 years. The data clearly show that the major elements and heavy metals in the Changjiang-derived sediments are predominantly derived from the natural weathering detritus. Positive correlations between heavy metal concentrations and clay contents suggest the grain size effect on elemental composition, which has to be carefully considered before the evaluation of heavy metal pollution.

Principal component analysis further recognizes two major origins for heavy metal accumulation in the river and marine sediments, i.e. natural detritus and human contamination. The impacts of anthropogenic activities on heavy metal accumulation are evaluated by using enrichment factor and geoaccumulation index, with the pre-industrial (before 1950) sediment used as reference material for the calculation of geochemical background values. Both indices clearly indicate that Cu, Cr, Pb and Zn in the river sediments are mostly unpolluted, and only since 1950s enhancing human activities in the Changjiang catchment contribute the heavy metal accumulation over the last 50 years. Our study reveals that the changes of sediment quality in the Changjiang River are closely related to the socioeconomic development in China. The Changjiang catchment has always been one major center of cultural evolution and socioeconomic development in China, and thus, our study also provides a general spectrum of how anthropogenic activities influencing natural environment in China. Although about 500 million people currently live in the Changjiang catchment, our study suggests that heavy metals of Cu, Cr, Pb and Zn witness no obvious pollution over the last 150 years. It is an encouraging environmental finding for the public and the government as well, which implies that enhancing human activities have not caused serious environmental problems and/or environmental preservation policy is effective on environmental control. Nevertheless, more in-depth investigations on more heavy metals have to be carried out in the future.

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