Baseline

Fractionation, sources and budgets of potential harmful elements in surface sediments of the East China Sea

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ABSTRACT

Total concentrations, chemical fractions by BCR procedure and enrichment factors of nine potential harmful elements (V, Cr, Co, Ni, Cu, Zn, Mo, Cd and Pb) in surface sediments of the East China Sea (ECS) were investigated. Spatial distributions illustrated that PHEs (potential harmful elements) were mainly from the Changjiang River and the Jiangsu coastal current, except Pb which was influenced by atmospheric input. Sediments in the ECS were moderately polluted with Cd, Pb, Zn and Cu according to their enrichment factors (EFs). Distributions of EFs and labile fractions revealed that anthropogenic Cd and Cu were mainly input though the Changjiang, Pb pollutant was delivered from the Changjiang and atmosphere, while Zn was impacted by terrestrial pollution from the Changjiang and the Hangzhou Bay. Budget calculation showed that the Changjiang contributed 82–90% of PHE influxes. Thirty-eight to 77% of PHEs were buried in sediment, mainly along the inner shelf.

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The East China Sea (ECS) continental shelf is the largest marginal sea in the western Pacific Ocean, with a vast continental area of 0.5×10^{12} m². The Changjiang River is the major source of material to the ECS (Liu et al., 2007), annually delivering 3.97×10^{11} kg sediment into the ECS on average from 1953 to 2009, according to the Datong Hydrological station (625 km upstream of the river mouth). A good deal of researches reveal that Zn, Cu, Pb and Cd pollution are ubiquitous in the river, lakes, intertidal zones in the Changjiang watershed, and even in suspended particulate matter (SPM) of the coastal ECS in recent decades (Hsu and Lin, 2010; Liu and Li, 2011; Zhang and Shan, 2008; Feng et al., 2004). The Changjiang River and Qiantang River annually deliver 2.4×10^4 and 937 t of heavy metals (Cu, Pb, Zn, Cd and Hg) on average from 2002 to 2010 into the ECS, respectively (Bulletin of China's Marine Environmental Status of China for the year of 2002 to 2010, 2002–2010). Influenced by excess terrestrial metal input, sediments in the inshore ECS have shown evidences of Cu, Zn, Cd and Pb enrichment in recent years (Lin et al., 2002; Fang et al., 2009). However, previous studies on trace metals in the ECS mainly focused on their total concentrations in sediments (Lin et al., 2002; Fang et al., 2009). Chemical fractions of trace elements, which were effective indexes of pollution status and potential toxicity of trace metals in sediment (Backstrom et al., 2004), were rarely studied in the ECS.

A procedure proposed by the Community Bureau of Reference (BCR) is commonly used to fractionate trace elements in sedi-ments. It partitions trace elements into four fractions including acid soluble (exchangeable and carbonate bound metals), reducible metals bound to Fe/Mn oxides, oxidizable (metals bound to organic matter) and residual fractions (Kazi et al., 2005). Labile fractions (acid soluble, reducible and oxidizable) are usually deemed as an indication of anthropogenic or authigenic sources of trace elements, while residual fraction represents the lithogenic part of metals (Backstrom et al., 2004; Wang et al., 2004; Zhang et al., 1990). On the other hand, larger proportion of labile fraction also indicates greater mobility and potential toxicity of trace elements in sediments (Okbah et al., 2005; Rath et al., 2009).

Vanadium, Cr, Co, Ni, Cu, Zn, Mo, Cd and Pb are potential harmful elements (PHEs), which might pose harm to life with higher concentrations (N'guessan et al., 2009). In addition, these metals are the commonest pollution elements in coastal waters produced by various human activities (Buckley et al., 1995; Lambert et al., 2007). This study aimed to investigate the distributions, sources and pollution status of these elements in the ECS. Particularly, the application of chemical fractions in assessing the pollution status of PHEs and identifying the pathways of anthropogenic elements was highlighted.

Thirty-five surface sediment samples (0–2 cm) were collected using a box sampler in the ECS during a cruise in May 2009 (Fig. 1). Sediments were kept in pre-cleaned polyethylene bags and frozen until lab analysis. Aliquots of sediment samples were dried at 60 °C and ground for homogenization.

About 0.05 g ground sediment were digested in air tight Teflon vessel with a mixture of HF–HNO₃–HClO₄ at round 150 °C for

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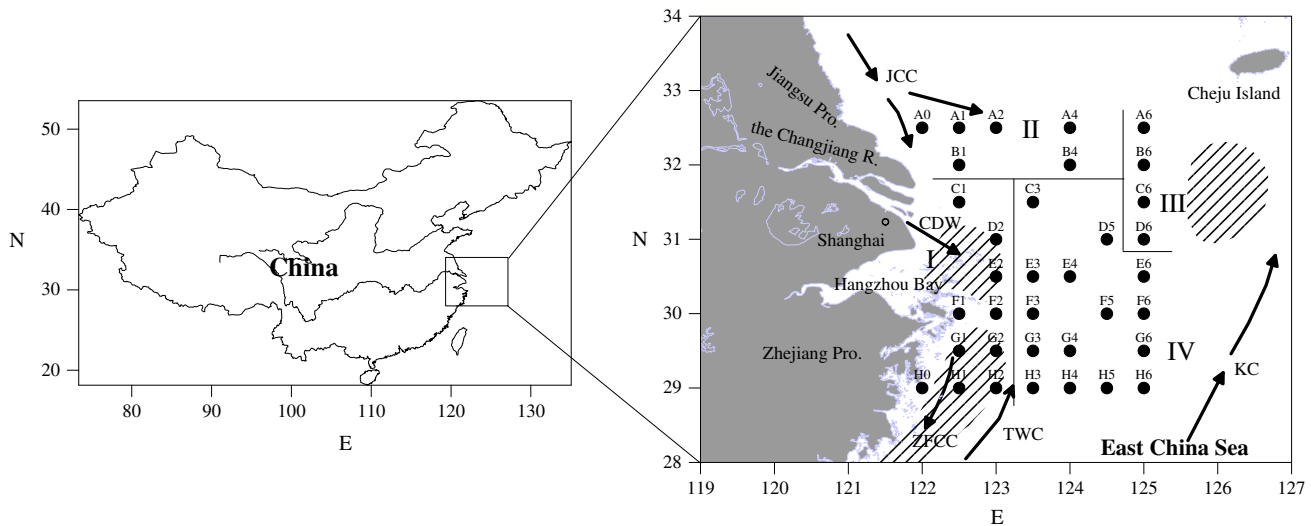
Fig. 1. Sampling sites (dots) and four geographically divided regions in this study. The current system (arrows) consists of the Changjiang Dilute Water (CDW), the Jiangsu Coastal Current (JCC), the Zhejian–Fujian Coastal current (ZFCC), the Kuroshio Current (KC) and the Taiwan Warm Current (TWC) (Liu et al., 2007; Zhu et al., 2011). There are three upwelling areas (shadows) in the ECS (Youn and Kim, 2011).

48 h. Concentrations of nine PHEs (V, Cr, Co, Ni, Cu, Zn, Mo, Cd and Pb) and Sc were determined with inductively coupled plasma-mass spectrometry (ICP-MS; Elan DRC II). A modified BCR procedure was conducted to fractionate PHEs in sediments (Kazi et al., 2005). Acid soluble, reducible and oxidizable fraction of metals were sequentially extracted with 0.11 M HAc (room temperature, 16 h), 0.5 M $NH_2OH·HCl$ (pH 1.5) (room temperature, 16 h) and 30% H_2O_2 (twice, 85 °C, 1 h every time) followed by 1 M NH_4Ac (pH 2) (room temperature, 16 h), respectively. After each step, the mixture was centrifuged for 15 min at 4000 rpm. The residual was washed with Milli-Q water, and the supernatant was discarded. Metal concentrations in extract from each step were determined using ICP-MS. Metal in residue fraction was calculated as the difference between total concentration and the sum of leachable fractions. All the chemicals and reagents used were of guarantee grade.

Total organic matter (TOC) in sediment was determined with a modified Walkley–Black method (Mebius, 1960). Carbonate in sediment was extracted with 10% HAc at 100 °C for 30 min. The slurry was filtered and the content of calcium in the filtrate was determined by titration with EDTA (Moss, 1961). The relative standard deviations (RSD) for TOC and carbonate measurement were less than 5%. Wet sediment samples treated with H_2O_2 (10%) and HCl (1 mol/l) were disaggregated by ultrasonic, and measured for grain size with a Laser Particle Size Analyzer (Cilas 940L). All the chemicals and reagents used were at least of analytical grade.

Blank, replicates and standard references were conducted to control the data quality. Blank samples were performed throughout the experiment of total concentration analysis and sequential extraction. Trace element concentrations in blank samples were below the detection limit of ICP-MS. Analytical precision was assured by duplicate analysis every 10 samples during total concentration analysis and every 8 samples during sequential extraction, with RSD less than 10% and 20%, respectively. Standard reference materials (GBW07315, GBW07316, BCR-2 and BHVO-2) were used to guarantee the accuracy of the total concentration (Table 1). The recoveries ranged from 90% to 110%. Ten samples of the residue after the sequential extraction were analyzed for metal concentrations with the same procedure as bulk concentration analysis. The recovery for sequential extraction of PHE is calculated as following (Kazi et al., 2005):

$$Recovery = (L_{acid\ soluble} + C_{reducible} + C_{oxidizable} + C_{residual})/C_{total} \times 100\%$$

The recoveries for the sequential extraction ranged from 85% to 98%.

Sediment grain size is a combined result of sediment input, depositional process and hydrodynamic conditions, and could be used to characterize depositional environments and sediment sources (Zhu et al., 2011). Median grain size of surface sediments in the ECS varied greatly from 1.75 to 7.68 Φ with a CV (coefficient of variation) of 45.8%, indicating diverse sedimentary environment in the northern ECS. Median grain size and mud content (clay and silt) displayed similar band-type distributions along the coast and they progressively decreased toward the sea (Fig. 2). Mud content decreased rapidly from more than 90% in the coast to 20–50% at 123°E, illustrating that terrestrial sediment was mainly deposited in the inner shelf west to 123°E. North to the estuary, mud content decreased southeastward from 90% in the Jiangsu coast to 20% in the northern middle shelf, revealing input of fine sediment by the JCC from old Huanghe delta. In the offshore upwelling area, sediment grain size progressively increased toward offshore reaching up to 7.7 Φ, with mud content increasing from 30% to 90%. High mud content and fine-grained sediment in the offshore where supply of terrestrial sediment was limited (Lim et al., 2007), indicated intense rework of sediment by offshore upwelling currents. It was noticed that, compared with less than 20% of mud in the northern middle shelf, mud content was still higher than 40% in the southern middle shelf. This distribution was attributed to more river sediment input into the southern area.

TOC in surface sediments of the ECS ranged from 0.09% to 0.60% with a CV of 40.3%. The distributions of TOC resembled that of mud content, with high values off the estuary, in the Zhejiang coast and in the offshore upwelling area and very low concentrations in the northern middle shelf (Fig. 2). TOC content showed seaward decreasing trends from 0.6% in the estuary to 0.28% in the middle shelf, revealing the impact of river input on the distribution of TOC. Carbonate in sediments varied between 2.6% and 19.6%. Maximum concentration (19.6%) existed in the southeast corner of the study area (Fig. 2). From this high value center, carbonate gradually decreased northwestward to less than 6% in vast areas in the inshore and the northern ECS. Carbonate of high content in the southern middle shelf was likely of biogenic source related to the intrusion of Taiwan warm current (TWC)-a branch of the KC (Lin et al., 2002).

To facilitate discussion, the investigated area is geographically divided into four regions (Fig. 1): zone-1, the estuary and