



Distribution and transport of heavy metals in estuarine–inner shelf regions of the East China Sea

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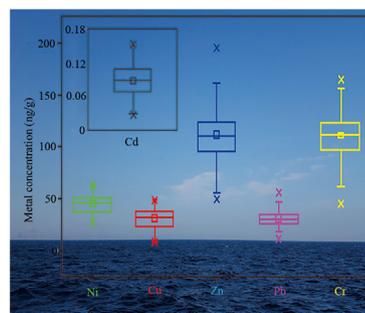
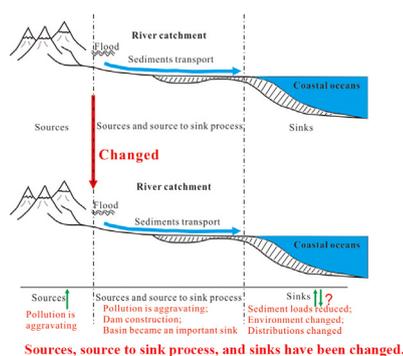
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HIGHLIGHTS

- Distribution patterns of heavy metals in the East China Sea are depicted.
- Hydrodynamics and sediment properties are the main factors affecting heavy metal distribution.
- Spatial patterns have drastically changed in the context of intensive human activities.

GRAPHICAL ABSTRACT



What will happen in the coastal ocean?

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ABSTRACT

This study analyzes the distribution and transportation of heavy metals in surface sediments by determining the concentrations of 6 heavy metals (Cr, Zn, Ni, Pb, Cu, and Cd) based on 164 surface sediments collected from the East China Sea (ECS). The results indicated that concentrations of heavy metals were higher in the south than the north with a clear boundary near 30° N. The distributions of the six heavy metals could be divided into four groups that corresponded well with different sediment components, suggesting that hydrodynamic sorting processes play an important role in the selective transportation of sedimentary heavy metals. In addition, the spatial distributions of heavy metals were more consistent with fine-grained sediments having a grain size lower than 32 μm. Heavy metal concentrations were slightly higher than found in previous studies conducted from 2002 to 2010. In addition, their spatial patterns have changed drastically compared to data from 2006, suggesting that intensive inland human activities have had a profound impact on heavy metal transportation and distribution in the estuarine & inner-shelf regions of the ECS.

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1. Introduction

Heavy metal pollution has been identified as one of the most concerning worldwide environmental crises in past decades. Seven of these (As, Cd, Cu, Pb, Ni, Se, and Zn) are regulated by the United States' Environmental Protection Agency due to their toxicity,

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abundance, and persistence (Ha et al., 2014). Although these heavy metals originate from both natural processes and anthropogenic activities (Chen et al., 2014; Huang et al., 2015), levels of anthropogenic heavy metals in the environment have increased dramatically since the Industrial Revolution (Chen et al., 2014; Guo and Yang, 2016). Once released, they are present throughout the environment including in air, water, soil, and sediment (Huang et al., 2018; Chowdhury et al., 2016; Birch, 2016; Wu et al., 2016), but most are eventually deposited into marine sediments via riverine runoff or atmospheric precipitation (Pan and Wang, 2012; Yin et al., 2016; Wu et al., 2018). Therefore, marine sediments are considered an important sink of heavy metals, especially in coastal ocean, due to rapid urbanization and industrialization (Xia et al., 2011; Yin et al., 2016; Ip et al., 2004; Chen et al., 2014).

Estuaries and their adjacent inner shelf regions are an important component of coastal oceans, receiving large amounts of terrestrial materials discharged via riverine input (such as heavy metals) (Yin et al., 2016). However, such transportation has been changed substantially by intensive human activity in river catchments including land-use changes, fertilizer use, dam construction, and water withdrawal. For example, dam construction intercepts large amounts of terrestrial material, resulting in sediment starvation in coastal oceans and erosion of river deltas including those of the Ebro, Nile, Mississippi, Mekong, and Colorado (Stanley, 1996; Blum and Roberts, 2009; Syvitski et al., 2005; Anthony et al., 2015). In some cases, the sedimentary environment in the estuarine-inner shelf regions had changed, resulting in coarser surface sediments (Luo et al., 2012; Yang et al., 2018). Such changes have also influenced the distribution and composition of heavy metals in riverine-estuary-shelf systems because their transportation is increasingly dominated by fine-grained sediments. Therefore, more

attention should be paid to the environment in estuarine, coastal, and shelf areas associated with large rivers in response to upstream changes.

The East China Sea (ECS) is a typical river-dominated marginal sea primarily influenced by the Changjiang River, the longest river (6370 km) in Asia with an annual sediment discharge of 4.78×10^8 t (Milliman and Farnsworth, 2013). A large subaqueous delta has developed near the Changjiang River Estuary (Liu et al., 2007) and a massive muddy sedimentary system has formed on the inner shelf of the ECS (Fig. 1b) (Gao and Collins, 2014). At the same time, intensive industrialization and urbanization in the catchment have resulted in large amounts of terrestrial pollutants (including heavy metals) being discharged into the Changjiang River and eventually into the ECS.

However, the transport of terrestrial materials from river catchments to estuaries and shelves has changed substantially due to human activities such as those noted above (Syvitski et al., 2005; Gao et al., 2015; Yang et al., 2018). For example, the impoundment of the Three Gorges reservoir has resulted in a rapid decrease in the downstream discharge of sediments (Yang et al., 2011; Gao et al., 2015; Wang et al., 2017) and associated materials (Li et al., 2014), including large amounts of heavy metals absorbed by fine-grained sediments. The rapid decrease in sediment size and discharge has significantly changed the sedimentary environment and dynamics in the estuarine-inner shelf regions of the ECS inducing channel erosion in the middle and lower reaches, altering the sediment composition substantially (Yang et al., 2011; Gao et al., 2015, 2017). These variations have inevitably changed the distribution and transportation of heavy metals in the Changjiang River Estuary and the inner shelf of the ECS.

Previous studies have demonstrated that the composition, origin, and dispersal paths of terrestrial material in the ECS changed after

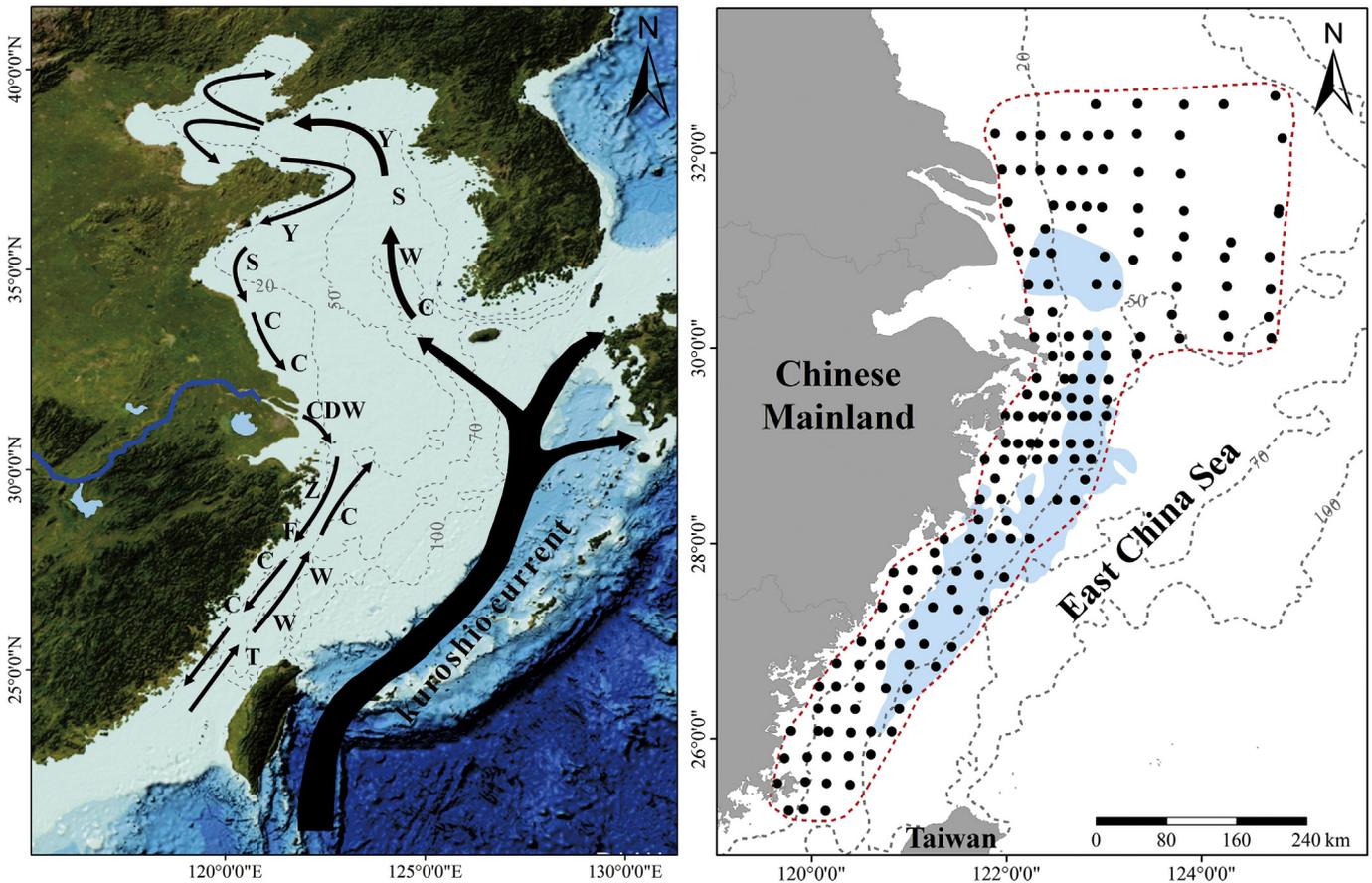


Fig. 1. Study area within the East China Sea showing (a) major oceanic currents including the Changjiang-diluted water (CDW), Zhejiang-Fujian coastal current (ZFCC), Taiwan warm current (TWWC), Yellow Sea coastal current (YSCC), Yellow Sea warm current (YSWC), and Kuroshio current; and (b) sampling sites along the Changjiang River Estuary and inner shelf regions. The red dotted line represents the delineations of the Changjiang Subaqueous Delta (CSD) and the Zhejiang-Fujian Coastal Mud Deposits (ZFCMD) by Su and Huh (2002).

completion of the Three Gorges Dam in 2003, though these changes did not clearly appear until 2006 (Hu et al., 2012; Li et al., 2014; Gao et al., 2017). These changes not only impacted the biogeochemical cycle and material distribution in the region, but also impacted its ecological security due to the ECS acting as a significant sink of pollutants such as heavy metals. Consequently, comprehensive research on the distribution and transportation of heavy metals in the estuarine-inner shelf regions of the ECS with regard to environmental changes is critical to improving sediment and water quality.

Several studies of heavy metal levels in surface sediments of the estuarine-inner shelf regions of the ECS have revealed a significant increase in heavy metal concentrations over recent decades (Liu and Fan, 2011; Guo and Yang, 2016; Chen et al., 2016). Most of these studies focused on the distribution, concentration, and ecological risk of these substances (Yu et al., 2013; Cao et al., 2015). However, less attention has been paid to the factors influencing the spatial patterns and dispersal paths of heavy metals in the ECS. Although fine-grained sediments are the main carriers of heavy metals and regional hydrodynamics are the main factors controlling their transportation, recently these factors have been altered by intensive human activities in the river basin. Therefore, the specific goals of this study were: 1) to determine the variability of heavy metals in the estuarine-inner shelf regions of the ECS with regard to intensive human activities in the river basin and 2) to explore the factors influencing the distribution patterns of heavy metals in this region.

2. Materials and methods

2.1. Study area and sample collection

The estuarine-inner shelf regions of the ECS receive large amounts of terrestrial sediment and form two large-scale mud deposits: the Changjiang Subaqueous Delta (CSD) and the Zhejiang-Fujian Coastal Mud Deposits (ZFCMD) (Gao et al., 2017). Previous studies have demonstrated that approximately 40% of Changjiang-derived sediments are trapped in the estuary north of 30° N while 32% are transported southward and deposited in the ZFCMD (Liu et al., 2007; Lin et al., 2013). At the same time, large amounts of heavy metals absorbed by fine-grained sediments are deposited in the estuarine-inner shelf regions.

Oceanic circulation in the study area is dominated by Changjiang diluted water, the Zhejiang-Fujian coastal current, the Taiwan warm current, and the Kuroshio Current (Fig. 1a) (Liu et al., 2006; Gao and Wang, 2008). The Changjiang diluted water is formed by the mixing of freshwater from the Changjiang River with offshore water and characterized primarily by low salinity and low density. During the summer, this flow first turns to the southeast and then expands northeastward toward Jeju Island (Chang et al., 2014). The Zhejiang-Fujian coastal current flows along the coasts of Zhejiang and Fujian Provinces and is controlled by the eastern Asian monsoon, moving northward in summer and southward in winter (Yuan and Hsueh, 2010). These currents' influence produce a natural shearing effect, limiting the export of Changjiang-derived sediments to the outer shelf and forming a mobile mud belt (Fig. 1b) (Liu et al., 2007; Xu et al., 2012). The Taiwan warm current, with its warm temperature and high salinity, flows northward to enter the ECS via the Taiwan Strait and is located seaward of the 50 m isobath (Yuan et al., 2008).

This study focused on the estuarine-inner shelf regions of the ECS. A total of 164 surface sediment samples (at 0–2 cm depth) were collected from 2013 to 2015 at sampling sites distributed throughout the study area (Fig. 1b). A stainless-steel grab sampler was used for collection, while a plastic shovel was used to excavate the sediments from the middle part of the sampler. Samples were kept in pre-cleaned polyethylene bags and frozen until lab analysis.

2.2. Laboratory analysis

Freeze-dried sediment samples were powdered and passed through a 200-mesh sieve. Homogenous sediment samples were digested by an

HCl-HNO₃-HF-HClO₄ mixture and total concentrations of Cr, Zn, Ni, Pb, Cu, and Cd were determined using an inductively coupled plasma-mass spectrometer (ICP-MS, PE ELAN9000, USA). All analytical data quality was controlled and assured subject to strict laboratory QA/QC methods. The standard curve was checked daily to ensure satisfactory linear regression coefficients ($R^2 > 0.999$). Reference materials were acquired from the National Research Center for Geoanalysis of China to ensure the precision and accuracy of the experiment. The recoveries of the six heavy metals in the reference materials ranged from 90 to 108%. Blank samples for digestion and analytical procedures were evaluated in duplicate with ten samples each. The relative deviation of the duplicate samples was <5% in all batch treatments.

Sediment grain size was analyzed using a Mastersizer 2000 instrument with a measurement range of 0.02–2000 μm and a relative error of <3% between replicate measurements (Gao et al., 2017). Surface sediments were placed into beakers with H₂O₂ solution (10%) added to digest the organic matter. Then sediment samples were dispersed in sodium metaphosphate for 24 h and vibrated in ultrasonic for 30 s to ensure full dispersion. Particle size parameters, including mean grain size, were calculated using specific formulas (McManus, 1988).

3. Results and discussion

3.1. Sorting and dispersal paths of Changjiang-derived sediments

The mean grain size of surface sediments in the estuarine-inner shelf regions of the ECS ranged from 7 to 101 μm , showing a distinct coarsening trend eastward and fining trend southward (Fig. 2a). The sediments deposited in the near-shore area of the Changjiang River Estuary and Hangzhou Bay were similar and primarily composed of fine-grained sediments. Together, these regions were considered to represent the CSD. The near-shore sediment was composed primarily of mud (silt + clay) and the mean grain size ranged from 9 μm to 101 μm with an average of 36 μm . In addition, the mean grain size of sediment samples collected north of 30° N revealed a distinct coarsening trend toward the sea and the sediment was composed primarily of sand and sandy silt east of 123° E (Fig. 2a).

South of 30° N, in the area considered to represent the ZFCMD, the sediment was relatively coarser than in the CSD, being composed mainly of silt and silty sand ranging from 6 to 43 μm with an average of 21 μm (Fig. 2a). Previous studies have reported that sediments in the ZFCMD primarily originate from the CSD under the influence of monsoons, coastal currents, upwelling, and tidal currents (Liu et al., 2007). This distribution pattern of surface sediments determined the distribution of heavy metals because of they are easily absorbed to fine-grained sediments.

To better understand the sorting and dispersal paths of Changjiang-derived sediment, spatial patterns of sediment components with different grain sizes were evaluated. Bulk sediments were divided into five components based on grain size: <4 μm , 4–16 μm , 16–32 μm , 32–63 μm , and >63 μm (Fig. 2b–f). The distribution of different components (coarse versus fine particles) in the sediment clearly indicated the processes of transportation, dispersal, and hydrodynamic sorting. Fine particles were transported further, whereas coarse particles were deposited near the estuary. The finest components (grain size <4 μm) were transported to the southernmost part of the ZFCMD (Fig. 2b). Sediments with grain sizes ranging from 4 to 16 μm were found in the CSD and partially transported to the southernmost part of the ZFCMD (Fig. 2c). A previous study indicated that finer silt (4–20 μm) might behave more like clay particles (Xu et al., 2009), which is consistent with the above results. Relatively coarser components with a grain size of 16–32 μm were deposited in the CSD and partially transported to the central region of the ZFCMD (Fig. 2d). Sediments with a grain size of 32–63 μm were primarily transported into the central part of the ZFCMD and partially trapped in the river's mouth (Fig. 2e).

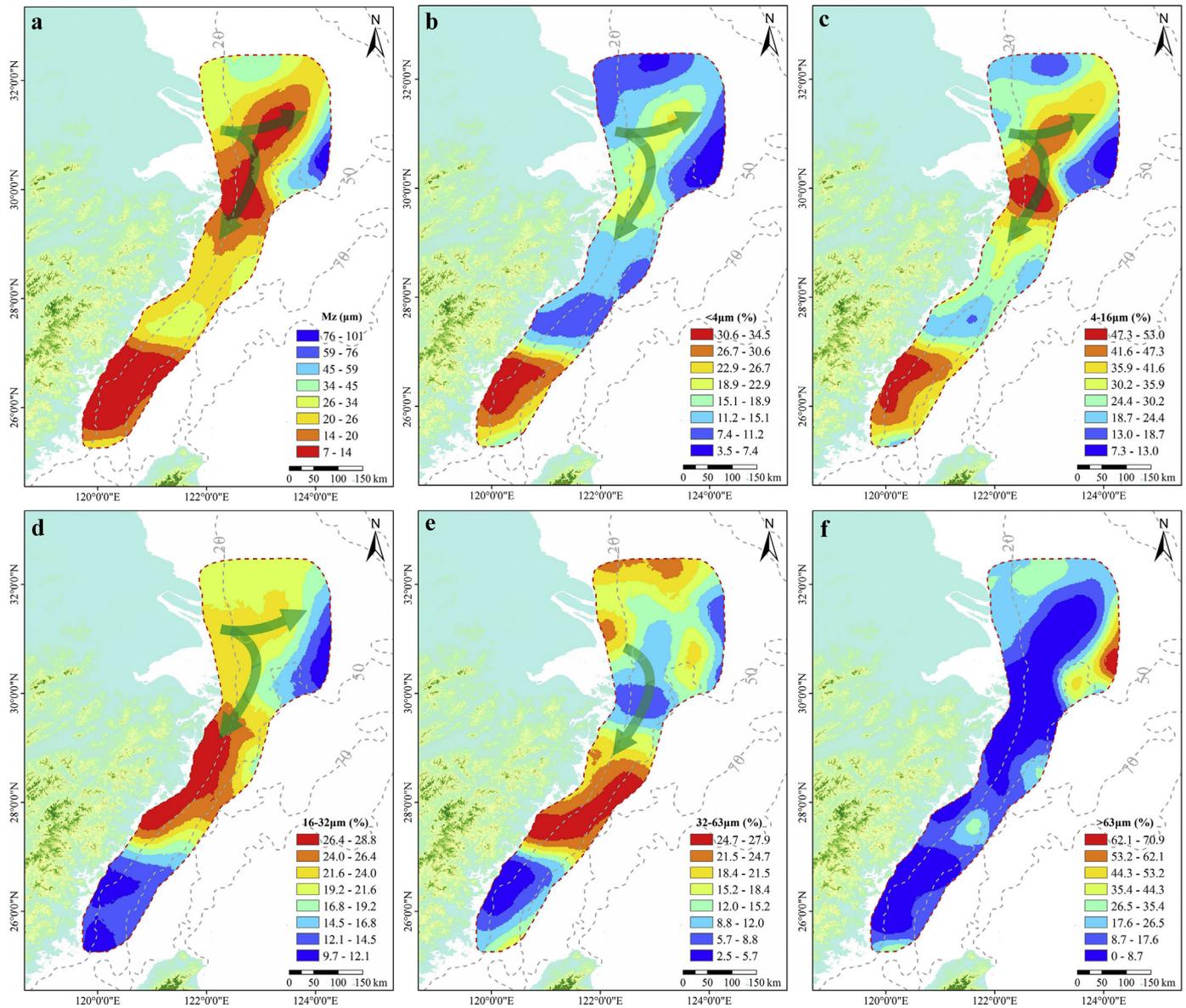


Fig. 2. Spatial patterns of sediment grain size in surface sediments from the estuarine-inner shelf regions of the East China Sea: (a) overall grain size (Φ), (b) $<4 \mu\text{m}$, (c) $4\text{--}16 \mu\text{m}$, (d) $16\text{--}32 \mu\text{m}$, (e) $32\text{--}63 \mu\text{m}$, and (f) $>63 \mu\text{m}$. Arrows note inferred directions of sediment transportation from the Changjiang River.

In addition to this southward transportation, another tongue-shaped dispersal path directed to the northeast was observed, in which sediment components with grain sizes lower than $32 \mu\text{m}$ appeared to be transported along the path of the Changjiang diluted water (Fig. 2). Overall, the distribution patterns of different sediment components were completely different, which could reflect the sorting and dispersal paths of Changjiang-derived sediment to a certain extent. In addition, previous studies have demonstrated that heavy metals are more easily absorbed by finer sediment fractions and mainly accumulate in clay and fine silt (Yao et al., 2016). Therefore, the distribution patterns of different sediment components also could be used to explore the transportation and distribution of heavy metals.

3.2. Spatial distribution of heavy metals and their influencing factors

3.2.1. Spatial patterns of heavy metals in the ECS

Table 1 summarizes the mean levels of the six heavy metals considered by this study in the estuarine-inner shelf regions of the ECS. The

mean concentrations were relatively higher in the ZFCMD than in CSD (except for Cd) and were slightly higher than those reported by previous studies conducted from 2002 to 2010 (Table S1), consistent with results recorded in sediment cores (Chen et al., 2014; Guo and Yang, 2016).

Table 1
Heavy metal concentrations in sediment from the estuarine-inner shelf regions of the ECS.

Sectors		Ni ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)
CSD n = 83	Max	53.90	63.30	137.90	0.38	51.25	142.48
	Min	22.50	7.09	50.02	0.03	14.78	45.67
	Average	39.47	26.79	94.34	0.09	26.55	100.01
	SD	7.78	10.40	19.82	0.04	5.48	19.62
ZFCMD n = 81	Max	63.38	87.50	225.22	0.23	162.00	202.99
	Min	6.43	4.03	47.82	0.01	12.90	21.10
	Average	48.21	33.98	129.26	0.08	37.69	121.27
	SD	8.98	10.74	29.71	0.04	16.88	25.73

The geographic distribution of heavy metal concentrations was quite variable and a clear boundary was observed near 30° N (Fig. 3). North of this is a primarily estuarine region with lower heavy metal concentrations compared to samples collected from the inner shelf region. However, a central area with relatively high concentrations was found in the estuarine region, suggesting that the occurrence of heavy metals in this region directly depends on input from the Changjiang River.

In addition, the spatial patterns of heavy metals in the inner shelf region can be divided into four groups. Group 1, including Cr and Zn, had an obvious increasing trend from the estuary region to the southernmost part of the ZFCMD (Fig. 3a,b) and a clear boundary observed near 27° N. The spatial patterns of Cr and Zn are more consistent with grain sizes <16 μm. Group 2 included Ni and Pb, which also displayed an obvious increasing trend southward from the estuary, but their highest values occurred over a much broader area and with a clear boundary near 28° N (Fig. 3c,d). Group 3 consisted of Cu, which was highest in the central ZFCMD and most consistent with grain sizes from 16 to 63 μm (Fig. 3e). Group 4 consisted of Cd, which displayed a distinct variation from the other groups with the highest values mainly occurred in the CSD (Fig. 3f). Overall, the distribution patterns of these

six heavy metals showed obvious differences and had clear correspondence to different sediment components.

3.2.2. Influence of regional hydrodynamics on the distribution of heavy metals

The correlation between the distribution patterns of heavy metal concentrations and sediment components suggests that hydrodynamic sorting processes could play an important role in the selectively transportation of heavy metals in the estuarine-inner shelf regions of the ECS. Complex hydrodynamic conditions with multiple currents (Fig. 1a) control the distribution patterns of surface sediment grain sizes in the study area (Liu et al., 2007; Gao and Wang, 2008). Previous studies have demonstrated that sediments and associated pollutants are highly concentrated in the CSD and ZFCMD, owing to the hydrodynamic conditions in the region (Lin et al., 2013; Wang et al., 2017). During flood season (May to October), >80% of the mean annual sediments from the Changjiang River are deposited in the CSD (Liu et al., 2006). Meanwhile, the southeast monsoon prevails in the summer, intensifying the northward Taiwan warm current and leading to the weakening and/or northward diversion of the otherwise southward Zhejiang-

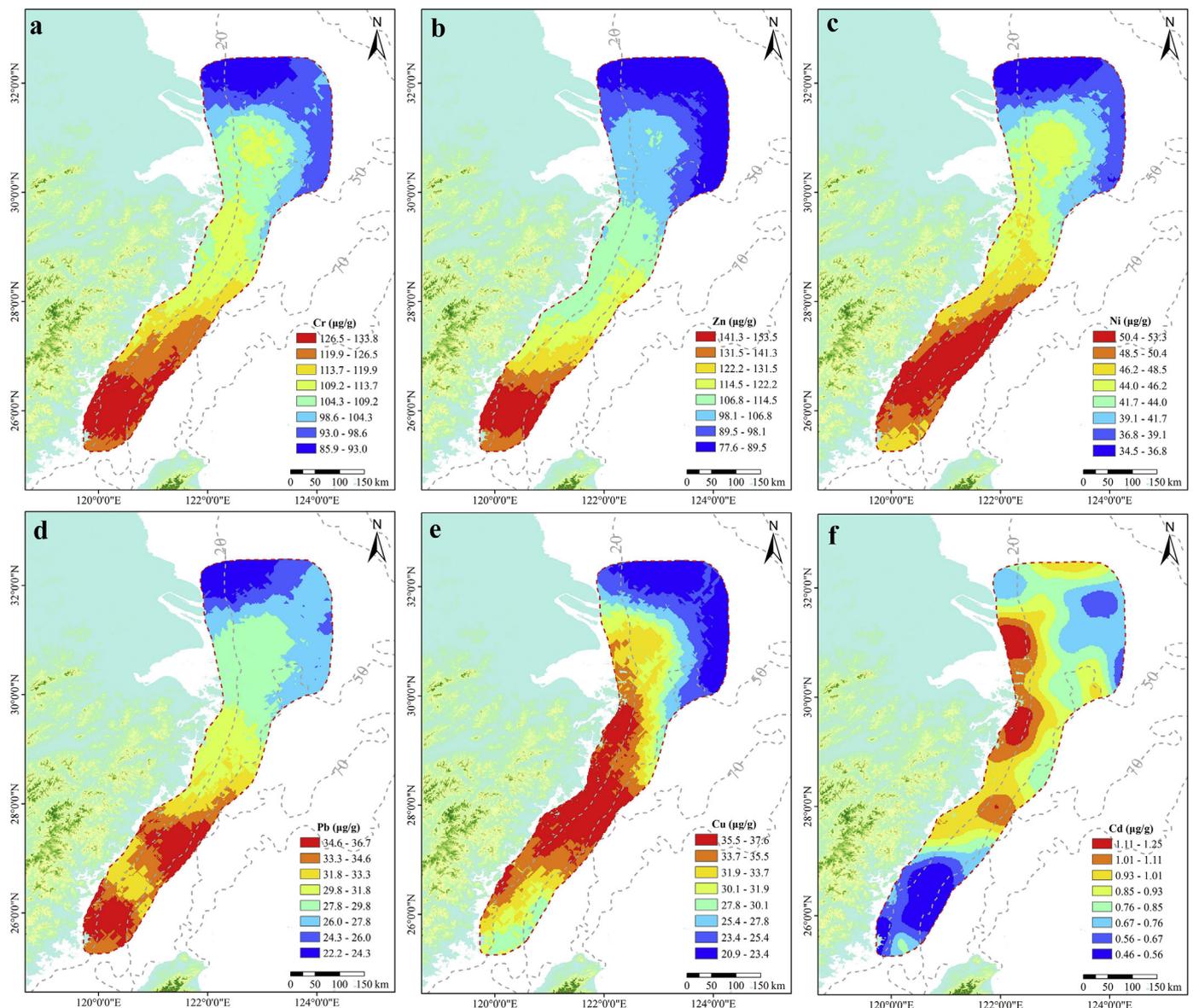


Fig. 3. Spatial patterns of six heavy metals in surface sediment in the ECS: (a) Cr, (b) Zn, (c) Ni, (d) Pb, (e) Cu, and (f) Cd.

Fujian coastal current (Liu et al., 2007). Variations in the Taiwan warm current and the Zhejiang-Fujian coastal current lead to the trapping of river-derived sediments in the CSD and the formation of mud deposits in this region. Therefore, under the influence of Changjiang-derived sediments and regional hydrodynamics, large amounts of heavy metals can be trapped and deposited in the CSD.

However, such deposition in the CSD is a short-term process, because the Zhejiang-Fujian coastal current re-intensifies and flows southward in winter due to the prevailing winter monsoon. Therefore, a large amount of fine sediment initially deposited near the CSD is resuspended and transported southward to be deposited along the coasts of Zhejiang and Fujian Provinces, transporting a significant portion of the associated heavy metals into this region. This matches the results of this study showing that heavy metal concentrations were relatively high in both the CSD and ZFCMD, consistent with the distribution pattern of fine sediments controlled by the hydrodynamic conditions.

In addition, during the processes of resuspension and transportation, heavy metals were attached to sediments with different grain sizes such that their transportation, dispersal paths, and sorting processes were different, leading to different distribution patterns (Fig. 3). In addition, the Changjiang diluted water can be very strong and reach 200 km from the river's mouth during flood season, bringing large amounts of fine-grained sediment into the open sea. Therefore, large amounts of heavy metals attached to the surface of fine-grained particles, especially those <32 μm due to their high surface area, are eventually transported and deposited along the axis of this flow.

3.2.3. Potential effects of grain size on the distribution of heavy metals

Previous studies have documented higher accumulations of heavy metals accumulated in the clay and fine silt fractions (Yao et al., 2016). This study's results showed spatial patterns of heavy metals that were more consistent with fine-grained sediment, particularly grain sizes >32 μm (Fig. 3). Furthermore, since the hydrodynamic sorting coupled with resuspension and along-shore transportation processes in the coastal ECS is significant, these heavy metals could also be enriched during this process by the similar sorption affinity associated with fine particles due to their large specific surface area.

Although the spatial patterns of sediment grain size and heavy metals concentrations were well-correlated overall (Figs. 2, 3), an individual assessment of the relationships between different sediment components and heavy metals concentrations was considered useful. Correlation analysis was thus applied to heavy metal concentrations and sediment grain size using SPSS 22.0 software.

The resulting correlation coefficient matrix suggested an obvious difference between the CSD and ZFCMD regions (Table 2). The calculated correlation between heavy metal concentration and grain size was relatively good in CSD, but very poor in ZFCMD, similar to results of other studies (Lin et al., 2013; Hu et al., 2012; Liu et al., 2017). The

dominant factor could be the continuous flow of the Changjiang River, which discharges large amounts of relatively homogenous sediment and associated heavy metals into the CSD. However, as the sediment deposited in the ZFCMD was mainly transported from the CSD, it was subject to a series of resuspension-deposition loops. This study's results suggest that heavy metals associated with the sortable silt fraction are modified and laterally dispersed, most likely via entrainment within benthic nepheloid layers. These sediments and associated heavy metals experienced dramatic transformation and were eventually trapped in the ZFCMD by regional hydrodynamic factors including tides, waves, coastal currents, winter storms, and offshore upwelling (Lin et al., 2013; Hu et al., 2011; Bian et al., 2013).

In addition, previous studies have demonstrated that a drastic decrease in Changjiang-derived sediments has induced quick and intensive variations in the sedimentary environment of the estuarine-inner shelf regions of the ECS (Hu et al., 2012; Gao et al., 2017), which would also deeply influence the distribution patterns of heavy metals in the study area. This further suggests that material input processes and regional hydrodynamics likely impact the equilibrium between sediment grain size and heavy metal concentrations in the estuarine-inner shelf region of the ECS.

To better understand the potential effects of sediment grain size on the distribution patterns of heavy metals, the percentage of the clay, silt, and sand components in each bulk sample was calculated and their individual correlations with heavy metals concentration were examined. Good correlations only occurred between heavy metal concentrations and fine-grained sediments, which usually have relatively large surface areas and can absorb more pollutants (Table 2). The weaker dependence of heavy metals on clay content, compared with silt content and mud content (clay + silt), suggests that the sorption of heavy metals has definite selectivity and that the finest particles do not necessarily possess the strongest adsorption capacity.

Studies have shown that different heavy metals have better correspondence with different grain sizes. For example, Cr and Zn are linked to grain sizes lower than 16 μm , while Cu tends to prefer grain sizes from 16 to 63 μm . To better understand this phenomenon, the percentage of different grain size components (<4 μm , 4–16 μm , 16–32 μm , 32–63 μm , and >63 μm) in each bulk sample were calculated and correlation analysis was applied to the heavy metal concentrations and grain size components to identify the fraction with the strongest adsorption capacity (Table 2). The highest correlation coefficient was observed in the fine silt fraction (4–16 μm), while the correlation coefficients had a decreasing trend as grain size increases, becoming a negative correlation when the grain size was coarser than 63 μm . This confirmed that finer particles have a stronger absorption capacity for heavy metals.

Correlation analysis for the six heavy metals revealed good correlation with fine sediments in the CSD, except for Cd (Table 2). In addition, the distribution pattern of Cd in the estuarine-inner shelf region was

Table 2
Correlation coefficient matrix of heavy metals and sediment grain size (μm) in the two study regions within the East China Sea.

		0–4	4–16	16–32	32–63	>63	Mud	Sand	Clay	Silt
CSD	Ni	0.587 ^a	0.607 ^a	0.510 ^a	−0.023	−0.664 ^a	0.653 ^a	−0.667 ^a	0.603 ^a	0.663 ^a
	Cu	0.611 ^a	0.647 ^a	0.604 ^a	0.036	−0.739 ^a	0.713 ^a	−0.739 ^a	0.634 ^a	0.739 ^a
	Zn	0.663 ^a	0.652 ^a	0.483 ^a	−0.030	−0.704 ^a	0.711 ^a	−0.706 ^a	0.684 ^a	0.697 ^a
	Cd	0.309 ^b	0.354 ^a	0.483 ^a	0.170	−0.482 ^a	0.439 ^a	−0.476 ^a	0.336 ^a	0.484 ^a
	Pb	0.460 ^a	0.479 ^a	0.277 ^b	−0.211	−0.433 ^a	0.441 ^a	−0.445 ^a	0.452 ^a	0.437 ^a
	Cr	0.502 ^a	0.525 ^a	0.360 ^a	−0.181	−0.504 ^a	0.529 ^a	−0.513 ^a	0.512 ^a	0.505 ^a
ZFCMD	Ni	0.259 ^b	0.162	−0.323 ^a	−0.218	0.000	0.175	−0.013	0.250 ^b	−0.074
	Cu	−0.208	−0.159	0.266 ^b	0.212	−0.005	−0.158	0.011	−0.208	0.062
	Zn	0.549 ^a	0.466 ^a	−0.470 ^a	−0.506 ^a	−0.223	0.472 ^a	−0.251 ^b	0.534 ^a	0.108
	Cd	−0.632 ^a	−0.537 ^a	0.638 ^a	0.618 ^a	0.166	−0.525 ^a	0.207	−0.612 ^a	−0.027
	Pb	0.101	0.035	−0.186	−0.042	0.030	0.056	0.032	0.089	−0.070
	Cr	0.419 ^a	0.303 ^a	−0.372 ^a	−0.335 ^a	−0.151	0.346 ^a	−0.166	0.422 ^a	0.047

^a Correlation is significant at the 99% confidence interval.

^b Correlation is significant at the 95% confidence interval.

different from the other five heavy metals and by sediment grain size (Fig. 3f). In aquatic environments, Cd primarily exists in a dissolved form with exchangeable states, resulting in easy migration and transformation. Suspended particles generally have a weak binding capacity with respect to Cd, causing any Cd attached to such particles to disassociate and dissolve into the water. Therefore, complicated dynamics (the resuspension-deposition loops discussed above) in the estuarine-inner shelf regions lead to an obvious spatial variability of cadmium.

3.3. Anthropogenic impacts

The CSD acts as an important sink for heavy metals from the Changjiang River and is also an important source of heavy metals for the ZFCMD (Liu et al., 2017; Chen et al., 2016). Before the impoundment of the Three Gorges Dam in 2003, the CSD was generally in a stable depositional state with continuous accumulation of sediment, and significant spatial variation was observed in the distribution of heavy metals in surficial sediments (Cao et al., 2015). However, after 2003, the depositional environment of the CSD changed greatly due to the decrease in sediment load from the Changjiang River (Yang et al., 2011; Dai et al., 2014) and the distribution of heavy metals in the CSD also changed significantly. In addition, the total contribution of heavy metals originating from anthropogenic sources was increased by rapid socio-economic development in the Changjiang River catchment. Therefore, changes caused by anthropogenic activities in the catchment, including reduction of sediment load and increasing heavy metals input, could also affect the spatial patterns of heavy metals in the estuarine-inner-shelf regions of the ECS.

To understand the influences of anthropogenic activities in the catchment on the spatial patterns of heavy metals in the estuarine-inner shelf regions of the ECS, a dataset of heavy metals from 2006 (Cao et al., 2015) was compared with the results of this study. The concentrations of heavy metals in 2006 were somewhat lower than the levels detected in this study, with metals such as Cr, Zn, Pb, and Cu being found at levels that were half those observed in this study. To investigate this difference, levels of Chinese coal and oil consumption from 2006 to 2015 were compared; both showed an obvious increase of about 50% (Fig. 4). As fossil fuel combustion is one important source of heavy metal emissions, this increase in use may be an important cause of the significant rise in heavy metal concentrations in this region.

In addition, spatial patterns of heavy metals in the estuarine-inner shelf regions have changed significantly over time. The distribution of heavy metals in 2006 indicated a continuous gradient between CSD and ZFCMD (Cao et al., 2015) and decreased away from the coast in the entire region, indicating the important influence of riverine inputs. However, this pattern disappeared in the current study and an isolated “deposition center” for Cr, Zn, Ni, and Pb was observed north of 31° N (Fig. 3).

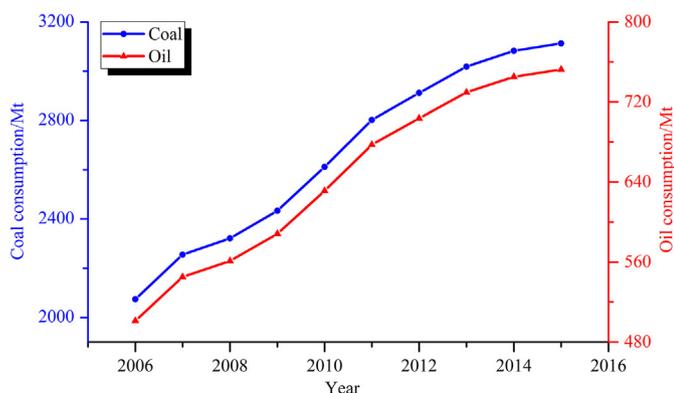


Fig. 4. Annual consumption of coal and oil in China from 2006 to 2015.

Based on previous studies, variations in sediment discharge from the Changjiang River related to human activities (particularly dam construction) could be one of the most significant factors influencing the dispersal of materials in the ECS (Yang et al., 2011; Gao et al., 2017). More than 50,000 reservoirs have been constructed in the Changjiang catchment (Yang et al., 2011); these reservoirs intercept sediment at a rate of 453 Mt yr⁻¹ (Gao et al., 2015) which is approximately four times the sediment load discharged into the ECS. Therefore, large amounts of heavy metals must also have been intercepted in these reservoirs, which have thus become an enormous sink of heavy metals in the Changjiang catchment (Bing et al., 2016). Although such variations in the catchment did not decrease the heavy metal concentrations in the ECS, it influenced their spatial patterns to a certain extent. After the 2003 impoundment of the Three Gorges Dam, the depositional environment of the CSD changed greatly due to the decrease in sediment load from the Changjiang River (Yang et al., 2011; Dai et al., 2014).

Other evidence was also provided by a study showing that the ²¹⁰Pb activity of surface sediments after 2003 was relatively lower than before and that this exhibited a relatively uniform spatial pattern in the estuarine-inner shelf regions of the ECS (Gao et al., 2017). The same study suggested that the depositional environment of the Changjiang estuary changed greatly after 2003, causing intensified sediment redistribution, and weakening the material transfer functions of the CSD (Gao et al., 2017). All these changes suggest that the sedimentary environment in the estuarine-inner shelf regions of ECS has changed along with the distribution of heavy metals.

4. Conclusions

The spatial distributions of six heavy metals (Cr, Zn, Ni, Pb, Cu, and Cd) in the estuarine-inner shelf regions of the East China Sea were studied in detail based on 164 surface sediment samples. The results showed that heavy metal concentrations were relatively high in the CSD and ZFCMD zones, consistent with the distribution pattern of fine sediment controlled by hydrodynamic conditions. Mean concentrations of the six heavy metals were found to be slightly higher compared to previous results from 2002 to 2010. In addition, spatial patterns have changed drastically in the past decade compared to 2006, suggesting that recent intensive human activities in the river basin have had a profound impact on the distribution patterns of heavy metals in this region.

The observed distribution patterns of heavy metals and grain sizes suggest that hydrodynamic sorting processes play an important role in the selective transportation of sedimentary heavy metals in this region. A correlation analysis between heavy metal concentrations and grain size showed that the highest correlation coefficient was observed for the fine silt fraction (4–16 μm). Correlation decreased as grain size increased, becoming negative for grain sizes coarser than 63 μm. In addition, the absorption capacity may have an additive effect with regard to certain grain size fractions, leading to higher correlation coefficients for silt than clay.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.06.383>.

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