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Distribution and contamination of trace metals in surface sediments of the East China Sea

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The distributions, contamination status and annual sedimentation flux of trace metals in surface sediments of the East China Sea (ECS) were studied. Higher concentrations of the studied metals were generally found in the inner shelf and the concentrations decreased seaward. The sequences of the enrichment factor (EF) of the studied metals are $\text{Cu} > \text{Mn} > \text{Ni} > \text{Zn} > \text{Pb} > \text{Fe}$. The values of EF suggest that the metals contamination in the middle and outer shelves of the ECS is still minor. The annual sedimentation fluxes of trace metals in the ECS were: Fe, 3.48×10^7 t/y; Mn, 9.07×10^5 t/y; Zn, 1.08×10^5 t/y; Ni, 4.48×10^4 t/y; Pb, 4.32×10^4 t/y; and Cu, 3.1×10^4 t/y, respectively. Approximately 55-70% and 10-17% of the sedimentation fluxes of trace metals were deposited in the inner shelf and the Changjiang estuarine zone. (Keywords: continental shelf; East China Sea; enrichment factor; trace metals; sediments; sedimentation flux)

1. Introduction

The East China Sea, located between 26° – 31° N and 121° – 126° E, is one of the

largest marginal seas in the western Pacific of the northern hemisphere, and it is also the main discharge area of the Changjiang River which is the world's fourth largest river when reviewed in terms of suspended load. The annual transportation of suspended load of the Changjiang River is approximately 4.61×10^8 t/y (Zhang and Liu, 2002). In addition, there are another four middle size rivers, namely the Jiaojiang, the Qiantangjiang, the Jiulongjiang and the Minjiang, which together discharge 2.36×10^7 tons/y of suspended load into the ECS (Zhang and Liu, 2002). Along the coast there are many developed cities, such as Shanghai and Ningbo, and a number of factories have also been set up there. Because of the over-emphasis on the economic development and the lack of environmental regulations since China embarked on the "Reform and Open Policy" from 1978, many studies have indicated that the Hangzhou Bay was contaminated by trace metals (Huh and Chen, 1999; Yuan et al., 2004) and polycyclic aromatic hydrocarbon (Guo et al., 2006). A recent study conducted in August 2003 uncovered a hypoxic area (dissolved oxygen concentrations $< 2\text{--}3$ mg/l) greater than $12,000 \text{ km}^2$ extending from the Changjiang River plume to the ECS (Chen et al., 2007). Thus, our current understanding is that the water quality of the ECS has been getting worse. However, the distribution and contamination status of trace metals for the whole ECS has not been established (Shi et al., 2005). In order to establish such a knowledge, the present study investigates the spatial distribution of trace metals in surface sediments of the ECS. In addition, based on the mass accumulation rates published in the literature for the ECS, the annual sedimentation fluxes of the studied metals in the ECS are also estimated.

46

47 **2. Sampling and methods**48 **2.1 Study area**

49 Twenty-five sediment cores were collected with a box core during a cruise
50 onboard the R/V *Ocean Research-I* from 6-16 November, 2006. The box core was
51 designed to obtain undisturbed sediments and the core samples were sealed and kept
52 frozen for subsequent processing and analyzing in the university laboratory. The
53 sampling stations (Fig.1) were located outside of the mouth of the Changjiang River
54 and extended to the outer shelves of the ECS with water depths < 150 m. Stations
55 I1-I6 were located in the inner shelf and along the coast of China. Stations M1-M11
56 were situated in the middle shelf and extended southwards to the northern Taiwan
57 Strait. Stations O1-O6 were located along the Okinawa Trough, through which the
58 Kuroshio Water flows. To facilitate interpretation of the results, the sampling stations
59 were divided into three groups based on their locations and bathymetry of the
60 sampling sites: stations I1-I8 in the inner shelf (depth < 50 m); stations M1-M11 in
61 the middle shelf (50 m < depth < 100 m); and stations O1-O6 in the outer shelf (100
62 m < depth < 150 m).

63

64 The major source of the fine-grained sediment to the ECS continental shelf is from
65 the Changjiang River, which discharges 4.61×10^8 t/y fine-grained sediment and
66 accounts for 73% of the terrestrial export of suspended matter carried by rivers
67 (Zhang and Liu, 2002). Most of the suspended sediments consist of silt and clay. A

large portion of this sediment supply is moved southward by the Jian-Su coastal current (Cao et al., 1989). A small portion of the suspended sediments is transported east and northeastwards to the ESC (Sternberg et al., 1985). From the examination of ^{210}Pb profiles in sediment DeMaster et al. (1985) obtained a sedimentation rate of up to 4.5cm/y near the mouth of the Changjiang River. In a recent study based on measurements of ^{137}Cs throughout the ECS, Huh and Su (1999) indicated that the sedimentation rates in the ECS varied by two orders of magnitude, from 2 to 0.02 cm/y, and generally decreased southwards along the inner shelf and eastwards offshore. Based on the spatial distributions of the grain size, carbonate, organic carbon contents, metals/aluminum ratios and the δC^{13} content of organic carbon, the ECS continental shelf was divided into five major regions: the Delta, inner shelf, middle shelf, outer shelf and northeast outer shelf (Lin et al., 2002). Major types of sediments occurring there include terrigenous sediments from the Changjiang River, relict sediment from the middle shelf, biogenic carbonate from the outer shelf and sediments from the Yellow Sea (Lin et al., 2002).

2.2 Analytical method

After thawing, the cores samples were extruded vertically with a hydraulic jack and sampled at 1 cm thickness at the surface. The outer rim (~ 0.5cm) of each sediment slab was trimmed off to avoid contamination between layers. Approximately 10-20 g of each surface sample (0-1 cm) was freeze-dried, ground and

homogenized with a mortar and pestle. The processed sample was stored in acid-cleaned polypropylene tubes for further analysis. The bulk sediment samples were divided into two sub-samples for the determinations of total organic carbon and trace metals.

Total organic carbon analysis

Total organic carbon (TOC) contents in the sediment samples were measured by a Horbia carbon analyzer 8210 after the samples were smoked with concentrated HCl acid in a closed container for 48 hours to remove the inorganic C content. The detailed analytical procedure of TOC can be found in Fang and Hong (1999).

Trace metals analysis

The trace metals contents in the surface sediments were totally digested with hydrofluoric acid (HF) in combination with aqua regia and heated on a hot plate at 200 °C for about 8 hours and evaporated to dryness. After cooling, the residue was dissolved with 0.5ml HNO₃ and the solution was made up with Milli-Q water to a volume of 25 ml in a volumetric tube. The final acidic solution was transferred into a 50ml centrifuge tube and was centrifuged at a speed of 4000 rpm for 5 minutes. The clear supernatant was stored in acid-cleaned polypropylene tubes and was analyzed for trace metals (Cu, Fe, Mn, Ni, Pb and Zn) by flame atomic absorption spectrometry using a Perkin-Elmer Analyst 800A.

Analytical quality assurance was performed by measurements of the PACS-2 reference material (National Research Council of Canada). The concentrations (n=6) of trace metals measured in the PACS-2 reference material (one standard deviation) were as follows: Cu, 286 ± 14 $\mu\text{g/g}$; Mn, 412 ± 18 $\mu\text{g/g}$; Ni, 38.8 ± 1.5 $\mu\text{g/g}$; Pb, 167 ± 3 $\mu\text{g/g}$; and Zn, 340 ± 11 $\mu\text{g/g}$, respectively. The ratio of the measured concentration to the certified value and precision (one standard deviation) was as follow: Cu, $92.6 \pm 4.0\%$; Mn, $94.5 \pm 4.4\%$; Ni, $98.3 \pm 4.0\%$; Pb, $91.7 \pm 1.8\%$; and Zn, $93.4 \pm 3.4\%$.

3. RESULTS AND DISCUSSION

3.1 *Spatial distribution*

The concentration ranges of TOC and trace metals in surface sediments of the ECS were as follows: TOC, 0.10-0.61%; Cu, 4.3-41.5 $\mu\text{g/g}$; Mn, 152-1152 $\mu\text{g/g}$; Ni, 8.2-48.6 $\mu\text{g/g}$; Pb, 10.0-44.8 $\mu\text{g/g}$; Zn, 18.2-114 $\mu\text{g/g}$; Fe, 0.62-3.97 % and Al, 4.35-8.49 %, respectively. The concentrations of TOC and trace metals found at each station are listed in Table 1. The spatial distributions of TOC and trace metals are shown in Fig.2. Higher concentrations of TOC and trace metals were generally found on the inner shelf, especially the area off Hangzhou Bay. Away from the Hangzhou Bay area, concentrations (except for Mn) decreased in both a southerly (along the inner shelf) and south-easterly (middle and outer shelves) direction. This finding is in good agreement with TOC decreasing along transects radiating outwards from the mouth of the Changjiang River. Therefore, it supports the view that Changjiang River

is a dominant factor resulting in elevated trace metals and TOC concentrations on the ECS (Lin et al., 2002). The spatial distributions of trace metals and TOC in the ECS generally exhibited similar patterns and the concentration of TOC correlated well with trace metals (Fig.3). It is well established that natural organic matter (NOM) has a high affinity for trace metals in the aquatic environment (Stumm and Morgan, 1996). As a consequence, it affects the geochemical behavior of trace metal in the aquatic environment. The coupling between the cycles of TOC and trace metals is ultimately reflected in the chemical composition of marine sediments (Basaham and El-Sayed, 1998; Fang and Hong, 1999; Lin et al., 2002).

In addition, the distribution of Mn showed a distinct peak situated between the middle and outer shelves at approximately located at 27° N and 123.5° E. The mechanism caused such a distribution is probably due to the sediment of this area being dominated by biogenic carbonate (Lin et al., 2002). Previous studies have shown that dissolved manganese can become adsorbed on, or incorporated into, freshly precipitated CaCO_3 in seawater (e.g. Wartel et al., 1990). Wartel et al. (1990, 1991) used suspended particulate matters from the English Channel, which is high in carbonate minerals, to study the interaction of Mn^{+2} in the CaCO_3 structure. They concluded that the adsorption on and substitution in calcite are the major mechanisms controlling the dissolved concentration of Mn in seawater along the French coast of the English Channel. Recent studies on suspended particulate matter from the Seine Estuary have also indicated that the majority of particulate Mn is bound to carbonate

(Boughriet et al., 1992; 1994). A good correlation between concentrations of Mn and carbonate in marine sediments has been reported off the southwestern coast of Taiwan (Fang and Hong, 1999).

Total concentrations of trace metals in the inner shelf sediment found in the present study were in good agreement with the report by Yuan et al. (2004) who used the four-step sequential extraction procedure to analyze coastal sediments outside of the Changjiang Estuary. Their results also indicated that more than 90% of Fe and 60-80% of Cu, Ni and Zn total concentrations were present in the residual fraction. In contrast, the concentrations of Mn and Pb were dominant in the non-residual fraction, accounting for more than 60% of the total concentrations. A comparison of trace metals concentrations in shelf sediments around the world is given in Table 2. It can be seen that the concentrations of trace metals, except Mn, found in the continental shelves, such as the Arabian Gulf, the Mediterranean Sea, the Aegean Sea and the Laptev Sea, around the world are quite comparable. However, the average concentration of Mn found in the ECS is two-three folds higher than those of the above continental shelves. Comparably high concentrations of Mn have been reported by Nolting et al. (1996) who indicated that Mn lateral distribution in surface sediments showed an increase from 1000 $\mu\text{g/g}$ in the mouth of the Lena River to > 5000 $\mu\text{g/g}$ in the eastern part of the Laptev Sea. They attributed these higher concentrations to the diagenetic process in sediments which caused large upward fluxes of Mn. The findings of Nolting et al. (1996) elucidate that trace metal, especial

the redox sensitive metal like Fe and Mn, contents in marine sediments may increase several folds through the naturally geochemical process regardless of the anthropogenic influence.

3.2 *Enrichment factor*

Trace metals concentrations in marine surface sediments can vary widely (Luoma, 1990). As a result, it is difficult to evaluate whether the observed concentration in marine sediments is influenced by anthropogenic sources or not without normalizing the result. Some normalising procedures are widely used to compensate for differences in grain size variations and carbonate content, and thus provide a means of separating anthropogenic sources from natural inputs (Luoma, 1990). Normalization to a background level of metals in samples with different characteristics can be accomplished by calculating an enrichment factor (EF) relative to the reference sample. In the equation

$$EF = (M/Al)_S / (M/Al)_R ,$$

$(M/Al)_S$ and $(M/Al)_R$ are the ratio of metal to Al concentrations in sample and in reference sample, respectively. It is found that the metal concentrations at stations of the outer shelf in the ECS were the least among the study areas, which may indicate that the disturbance of the outer shelf was relatively minor. In order to avoid the natural differences of sediment textures in different environments, the reference sample is taken from the data of outer shelf stations in the present study. The average concentrations of each metal and Al at all stations of outer shelf are considered as the

reference values which are used to calculate the EF and assess the contamination status of the ECS. The EF range of the studied metals was as follow: Fe, 0.43-1.93 (average 1.22); Cu, 0.67-5.83 (average 1.96); Mn, 0.54-3.76 (average 1.47); Ni, 0.52-2.57 (average 1.42); Pb, 0.56-2.07(average 1.29); and Zn, 0.51-2.89 (average 1.42). Contour plots of EF distribution for each metal are shown in Fig.4. Surprisingly, the EF values of Cu are the highest and indicate a marked anthropogenic burden, suggesting that Cu was the most contaminated metal among the studied metals. However, it can be seen in Fig.4 that the contour values of each metal greater than 2 generally distributed in the inner shelf. While, the contour values in the middle and outer shelves are within the range of 1-2 and approach to 1, respectively. The EF values suggest the inner shelf of the ECS was mildly contaminated by trace metals. Such a metal contamination did not further extend to the middle and outer shelves.

An EF value of 1 indicates a predominantly natural origin for the element in sediment, while values greater than 1.5 indicate enrichment by either natural processes (e.g. biota contributions) or anthropogenic influences (Zhang and Liu, 2002). EF values lower than 0.5 can reflect mobilization and loss of these elements relative to Al, or indicate an overestimation of the reference metal contents (Zhang, 1995; Mil-Homens et al., 2006).

3.3 *Trace metals sedimentation flux*

Huh and coworker employed the radionuclide method (^{210}Pb , ^{137}Cs and $^{239,240}\text{Pu}$) to comprehensively evaluate the sedimentation rates and mass accumulation rates in the East China Sea (Huh and Su, 1999; Su and Huh, 2002). Based on their data and trace metals concentrations in surface sediment found in the present study, an attempt is made to calculate the trace metals sedimentation fluxes in the ECS. To facilitate the calculation, the calculated area is divided into five boxes: estuary (box I), inner shelf (box II), middle shelf (box III and IV), and outer shelf (box V) (Fig. 5), according to the value of mass accumulation rate (MAR) in each box observed by Huh and coworker (Huh and Su, 1999; Su and Huh, 2002). The middle shelf area is divided into two boxes because the MAR in the northern middle shelf slightly differed from the southern middle shelf.

Due to the ECS being adjacent to the Yellow Sea to the north and with the North Pacific Ocean to the east, its total area is difficult to determine. Two widely accepted values are $0.74 \times 10^6 \text{ km}^2$ for the total area of the ECS and $0.51 \times 10^6 \text{ km}^2$ for the area with a water depth $< 200\text{m}$ (Wong et al., 2000, and references cited therein). The calculated area of the present study is approximately $0.376 \times 10^6 \text{ km}^2$, which accounts for about 50% of the whole ECS area provided by Wong et al. (2000) and about 74% of the continental shelf area. Table 3 shows the area, the concentration range of trace metals obtained in the present study and the mass accumulation rate (MAR) in each box.

There are three values for each metal-related parameter: minimum, maximum and average. The minimum value of the annual metals sedimentation flux was calculated from the minimum concentration of metals multiplied the minimum value of MAR in each box. The maximum and average values were calculated in a similar manner. The average annual sedimentation fluxes of trace metals in the calculated area were as follow: Fe, 34800×10^9 g/y; Mn, 907×10^9 g/y; Cu, 31.0×10^9 g/y; Ni, 44.8×10^9 g/y; Pb, 43.2×10^9 g/y; and Zn, 108×10^9 g/y. Most of the sedimentation fluxes of trace metals were concentrated in the inner shelf (box II), accounting for 55-70% of the total fluxes of each metal. The second important area was the estuarine zone (box I), contributing from 10 to 17% of the total fluxes of each metal. These results indicate that the suspended loads of metals exported from the Changjiang River catchment were mostly deposited on the inner shelf. It is well known that the continental shelf sediments originate primarily from the riverine suspended load. The suspended load of the Changjiang River is the major contribution and the four middle size rivers, namely the Jiaojiang, the Qiantangjiang, the Jiulongjiang and the Minjiang, contribute minor inputs to the ECS (Zhang and Liu, 2002). The upper part of Table 4 summarizes the annual flux of particles to the coast and their trace metal contents. The calculated annual chemical fluxes of particulate metals from these rivers are listed in the lower part of Table 4. These fluxes are as follows: Fe, 24456×10^9 g/y; Mn, 386.6×10^9 g/y; Cu, 29.97×10^9 g/y; Ni, 30.67×10^9 g/y; Pb, 19.87×10^9 g/y; and Zn, 46.67×10^9 g/y.

These riverine fluxes of particulate metals are generally lower than, but with the same magnitude as, the calculated sedimentation fluxes. The reason for this phenomenon may attribute to the anthropogenic influence as indicated in the enrichment factor values. The calculation bias of sedimentation fluxes could also be another reason because the difference of maximum and minimum values may vary one order of magnitude. However, the data accuracy of the riverine sediment transportation fluxes and properties shown in literature (Zhang and Liu, 2002, and references cited therein) should be taken into account when calculating the riverine annual transportation fluxes. Since the riverine data were established in the early 1990s. It is known that China launched its modernization campaign from 1980 and substantially increased its economic development in the last two decades (Guo et al., 2006). The rapid economic development of China may alter the environment. One of the evidences is that the Asian dust storm which occurred since 2000 (Mori et al., 2003). Thus, in order to obtain a more accurate calculation of the riverine annual fluxes of trace metals, the updating riverine data are necessary to be used. Unfortunately, it is not able to find the updating data in the literature.

3.4 *Atmospheric trace metals flux*

Owing to its rapid industrial development and urbanization since 1980, the frequency and scale of dust events giving rise to dust storm aerosols has increased rapidly in the east Asian region since 2000 (Mori et al., 2003). Thus, Asian countries suffer from the dust storms which annually occur in the late winter and spring in this

decade. Asian dust storms, generated when the surface soil in the arid region of the Asian continental landmass is lifted by winds, move southeastward out of the China continent, the northeasterly monsoon prevails south of 30 °N following the passage of the cold front (Hsu et al., 2008). Zhang et al (1997) estimated China's annual emission of dusts to be Tg, 50% of which is subject to long-range transport to the Pacific Ocean and beyond. The East China Sea is situated the right pathway of the Asian dust storms. As a result, it is expected that the atmospheric dry deposition may provide a substantial amount of chemical constituents to the East China Sea.

Research into Asian dust storms impact on the biogeochemistry of the ECS, especially with respect to biological bloom and budget balance of nutrients and trace metals, has been conducted by several research groups (Yuan and Zhang, 2006; Hsu et al., 2008). A comprehensive study carried out by Hsu et al (2008) who conducted several cruises to collect the marine aerosols from the ECS during the spring of 2005 and 2007. They analyzed marine aerosol samples for both the water-soluble and the total concentration of 27 trace elements and calculated the dry deposition fluxes. Their results for trace metals dry deposition fluxes were as follows: Fe, $39 \pm 50 \mu\text{g}/\text{m}^2/\text{d}$; Cu, $12 \pm 14 \mu\text{g}/\text{m}^2/\text{d}$; Mn, $6.7 \pm 14.3 \mu\text{g}/\text{m}^2/\text{d}$; Ni, $0.24 \pm 0.29 \mu\text{g}/\text{m}^2/\text{d}$; Pb, $2.5 \pm 6.7 \mu\text{g}/\text{m}^2/\text{d}$; and Zn, $19 \pm 39 \mu\text{g}/\text{m}^2/\text{d}$. We used these values to calculate 120-day and 180-day of the aerosol dry deposition fluxes of these metals in same area, $0.376 \times 10^6 \text{ km}^2$, as the calculation of metals sedimentation fluxes in the ECS, as shown above. The calculated result for the aerosol dry deposition fluxes and the riverine

annual transportation fluxes of these metals are depicted together in Fig. 6. Surprisingly, the aerosol dry deposition fluxes of these metals are relatively small compared with the riverine annual fluxes. The percentage of 120-day aerosol dry deposition fluxes of these metals to the riverine annual fluxes is as follows: Cu and Zn, 1.8%; Pb, 0.56%; Mn, 0.08%; Ni, 0.035%; and Fe, 0.007%. This result may suggest that the aerosol dry deposition fluxes of Fe, Mn, Ni and Pb can be ignored, and of Cu as well as Zn contribute a small amount of fluxes to the ECS when comparing with the riverine fluxes.

4. Conclusions

The water quality of the ECS has been getting deleterious due to the rapid industrial development and urbanization of China since 1980. However, the results of this study find that the surface sediment of the inner shelf of the East China Sea was mildly contaminated by trace metals. Elevated concentrations of trace metals were generally found in the Hangzhou Bay and along the inner shelf of the ECS. Trace metals contamination did not extend further to the middle and outer shelves of the ECS. The combination of two effects may explain this finding. First, more than 80% the sedimentation fluxes of trace metals are deposited in the inner shelf and the Changjiang estuarine zone. Secondly, the atmospheric dry deposition fluxes of trace metals to the ECS are relatively small compared with the riverine annual fluxes.

Finally, the estimated annual sedimentation fluxes of trace metals in this study

are generally higher than those of the riverine annual transportation fluxes of particulate metals. The anthropogenic source is probably the major mechanism. However, the use of the old published data of the riverine particulate composition and flux in literature to calculate the riverine annual fluxes may cause under estimation because the environmental changes may occur substantially due to the rapid industrial development and urbanization in China.

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Figures captions

Fig.1. Map showing sampling stations in the East China Sea.

Fig.2. Spatial variation of trace metals concentrations in the surface sediment in the study area of the East China Sea.

Fig.3 Scatter plot between concentrations of TOC and trace metals and their correlation

Fig.4. Spatial variation of enrichment factor of trace metals in the study area of the East China Sea.

Fig.5. Sub-areas, as defined on the basis of sedimentation rates, and trace metal content. These sub-areas are: (I) estuary; (II) inner shelf; (III) middle shelf; (IV) middle shelf; and (V) outer shelf

Fig.6. Comparison of the riverine annual transportation fluxes of trace metals with Asian dusts dry deposition fluxes of trace metals (120-day and 180-day) to the East China Sea.

Fig.1

Fig.2

Fig.2 Continue

Fig. 3

Fig.4

Fig.5

Fig. 6

20

21 Table 1. The concentrations of trace metals in surface sediments at the study stations
 22 in the East China Sea.

23

Station	Long.(E)	Lat. (N)	TOC (%)	Al (%)	Fe (%)	Cu ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
I1	123°8.75'	31°37.49'	0.25	5.12	1.73	8.83	251	22.4	33.8	31.8
I2	123°55.00'	31°20.00'	0.20	5.47	2.17	9.61	376	19.3	33.7	33.9
I3	122°40.00'	31°10.00'	0.44	5.67	1.67	32.1	594	39.7	33.8	96.9
I4	123°15.00'	30°27.50'	0.28	5.84	2.00	11.2	328	22.4	26.3	51.3
I5	122°35.00'	29°35.00'	0.61	8.49	3.97	41.5	730	48.6	44.8	114.2
I6	122°2.50'	28°40.00'	0.58	5.33	3.08	40.8	1152	44.0	40.6	112.6
I7	121°30.00'	27°45.00'	0.43	5.83	2.70	29.0	958	33.7	26.3	86.2
I8	120°5.00'	26°10.00'	0.51	7.44	3.19	28.9	1085	32.6	30.0	90.0
M1	124°41.25'	31°2.50'	0.29	6.03	1.89	11.1	418	26.2	26.0	54.1
M2	125°27.50'	30°45.00'	0.40	5.63	2.19	13.6	436	39.7	37.5	110.4
M3	126°13.75'	30°27.50'	0.37	6.03	1.99	12.0	490	26.5	22.5	28.7
M4	124°16.67'	30°4.17'	0.24	5.48	1.47	9.56	368	23.3	26.1	49.5
M5	123°4.17'	28°16.67'	0.31	5.75	2.42	16.8	412	27.4	30.0	35.5
M6	124°5.84'	27°53.33'	0.29	5.66	1.68	8.84	324	20.4	26.3	52.4
M7	122°16.25'	27°27.50'	0.26	4.75	2.18	10.4	369	22.4	22.5	56.3
M8	123°48.75'	26°52.50'	0.10	5.35	1.97	6.45	757	25.6	26.4	52.3
M9	121°43.96'	26°37.09'	0.33	5.77	2.56	16.1	488	27.5	26.3	75.9
M10	120°47.45'	25°55.00'	0.37	5.76	1.99	11.2	417	27.5	22.5	69.9
M11	121°29.90'	25°40.00'	0.30	5.65	2.25	17.7	413	27.6	22.6	66.1
O1	127°0.01'	30°10.00'	0.27	4.35	1.42	8.82	293	19.3	26.3	44.6
O2	126°20.00'	29°17.50'	0.16	5.24	1.32	7.43	332	16.2	18.8	33.0
O3	125°40.00'	28°25.00'	0.23	5.37	2.05	7.24	389	19.4	18.8	42.2
O4	125°7.50'	27°30.01'	0.14	5.15	1.80	6.40	360	20.3	22.4	46.4
O5	124°35.00'	26°35.00'	0.16	5.34	1.84	5.60	216	14.2	15.0	37.1
O6	123°31.88'	25°56.26'	0.15	4.87	0.62	4.29	152	8.17	10.0	18.2

Table 2. Comparison of trace metals concentrations in surface sediment in the various continental shelves around the world. (Concentration unit is in $\mu\text{g/g}$, except Al and Fe in %)

Location	Digested Reagent	Al	Fe	Mn	Cu	Ni	Pb	Zn	Reference
East China Sea	HCl/HNO ₃ /HF	4.4-8.5 (5.7)	0.62-4.0 (2.1)	152-1152 (484)	4.3-42 (15)	8.2-49 (26)	10-49 (27)	18-114 (60)	This study
Arabian Gulf	HCl/HNO ₃ /HF	0.1-3.5 (0.69)	0.1-2.5 (0.69)	18-415 (165)	2-21 (9)	2-101 (30)	ND	4-58 (22)	Basaham & El-Sayed, 1998
Mediterranean, Israel coast	HNO ₃	2.0-6.4	0.94-5.94	300-900	5.9-28.5	ND	9.9-20.2	22.6-88.6	Goldsmith et al., 2001
Aegean Sea	HCl/HNO ₃ /HF	2.8-5.3 (4)	0.8-2.8 (1.8)	171-323 (251)	5.3-30.5 (17)	ND	20.7-44.2 (34)	13-77 (50)	Aloupi and Angelidis, 2001
Banc d'Arguin, Mauritania	HCl/HNO ₃ /HF	1.19-4.66	0.63-2.34	27-112	2-18	5-32	2.8-8.9	19-65	Nolting et al., 1999
Campeche shelf, Gulf of Mexico	HCl/HNO ₃	ND	<0.5-7.9 (1.84)	12.5-449 (111)	3.8-18.7 (7.5)	0.56-76.9 (23.0)	0.22-20.2 (4.3)	0.04-79.6 (18.5)	Macias-Zamora et al., 1999
Laptev Sea, Siberia	HCl/HNO ₃ /HF	5.0-7.6	1.9-5.2	187-5398	2-20	16-33	12-22	56-120	Nolting et al., 1996
Chukchi Sea, Alaska	HNO ₃ /HF	1.6-8.3 (4.7)	0.7-8.1 (3)	96-610 (252)	8-31 (17)	10-38 (22)	ND	23-106 (61)	Naidu et al., 1997
Pechora Sea, Russia	ND	2.97-6.88 (4.7)	0.51-6.88 (3)	154-684 (377)	4-25 (13)	6-47 (25)	9-22 (14)	7-97 (47)	Loring et al., 1995

ND: no data. Value in parentheses is an average.

Table 3. The area, ranges of metals concentration, mass accumulation rate (MAR), and annual sedimentation flux for each box of the East China Sea.

Box	Area (km ²)	MAR* (g/cm ² /y)	Fe	Mn	Cu	Ni	Pb	Zn
metals concentration (Fe in %; all others in µg/g)								
I	31900	0.40-1.09(0.75)	1.66-2.00 (1.80)	251-593 (391)	8.8-32.1 (17.4)	22.4-39.7(28.2)	26.3-33.8 (31.3)	31.8-96.9 (60.0)
II	98600	0.28-1.17(0.73)	1.99-3.97 (2.99)	417-1152 (869)	11.2-41.5(30.3)	27.5-48.6 (37.3)	22.5-44.8 (32.9)	69.9-114 (94.6)
III	53000	0.06-0.98(0.32)	1.47-2.19 (1.93)	368-436 (400)	9.6-13.7 (10.9)	19.3-39.8(27.1)	26.0-37.5 (30.8)	33.9-110 (62.0)
IV	86600	0.07-0.61(0.26)	0.65-2.56 (1.96)	152-757 (417)	4.3-17.7 (11.5)	8.2-27.6 (22.7)	10.0-30.0 (23.4)	18.2-75.9 (51.0)
V	105800	0.03-0.13(0.072)	1.32-2.05 (1.74)	216-490 (347)	5.6-12.0 (7.92)	14.2-26.5 (19.3)	15.0-26.2 (20.6)	28.7-46.4 (38.7)
annual metals sedimentation flux (10 ⁹ g/y)								
I			2120-7000(4300)	32-207(93.6)	1.13-11.2 (4.2)	2.9-13.8(6.70)	3.4-11.7(7.5)	4.1-33.7 (14.4)
II			5500-45800(21500)	115-1330(625)	3.1-47.9 (21.8)	7.6-56.1(26.9)	6.2-51.7(23.6)	19.3-131(68.1)
III			470-11400(3270)	11.7-227(68.0)	0.3-7.1 (1.9)	0.6-20.6(4.60)	0.8-19.5(5.2)	1.1-57.4 (10.5)
IV			370-14500(4400)	9.2-400(93.8)	0.3-9.4 (2.6)	0.5-14.6(5.1)	0.6-15.8(5.3)	1.1-40.1 (11.5)
V			390-2800(1320)	6.4-67.0(26.4)	0.2-1.7 (0.6)	0.4-3.6(1.5)	0.4-3.6(1.6)	0.9-6.4 (2.9)
Total			8850-80500(34800)	175-2230(907)	5.0-77.1(31.0)	12.0-109(44.8)	11.5-102(43.2)	26.4-269 (108)

Value in parentheses is an average.

*: data taken from Huh and Su (1999), Su and Huh (2002)

Table 4. The annual suspended load, the concentration of riverine particulate metals and annual transportation flux of particulate metals of the major Chinese rivers entering to the East China Sea.

River	Suspended Load (10 ⁶ t/yr)	Fe	Mn	Cu	Ni	Pb	Zn	Reference
Riverine particulate metals conc. (Fe in %; all others in µg/g)								
Changjiang	461.4	5.2	811	62.3	64.2	39.9	97.7	Zhang and Liu, 2002
Qiantangjiang	4.4			89.3	92.6	76		
Jiaojiang	8.4	3.62	878	36.5	46.1	54.8	105	
Minjiang	7.7			51.8		62.5		
Jiulongjiang	3.1	5.12	1620	39.5	81	60.6	228	
Annual flux (10 ⁹ g/yr)								
Changjiang		23993	374.20	28.75	29.62	18.41	45.08	
Qiantangjiang				0.39	0.41	0.33		
Jiaojiang		304.1	7.38	0.31	0.39	0.46	0.88	
Minjiang				0.40		0.48		
Jiulongjiang		158.7	5.02	0.12	0.25	0.19	0.71	
Total Flux		24456	386.59	29.97	30.67	19.87	46.67	