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

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2 The distributions, contamination status and annual sedimentation flux of trace
3 metals in surface sediments of the East China Sea (ECS) were studied. Higher
4 concentrations of the studied metals were generally found in the inner shelf and the
5 concentrations decreased seaward. The sequences of the enrichment factor (EF) of the
6 studied metals are $\text{Cu} > \text{Mn} > \text{Ni} \cdot \text{Zn} > \text{Pb} > \text{Fe}$. The values of EF suggest that the
7 metals contamination in the middle and outer shelves of the ECS is still minor. The
8 annual sedimentation fluxes of trace metals in the ECS were: Fe, 3.48×10^7 t/y; Mn,
9 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, $3.1 \times$
10 10^4 t/y, respectively. Approximately 55-70% and 10-17% of the sedimentation fluxes
11 of trace metals were deposited in the inner shelf and the Changjiang estuarine zone.
12 (Keywords: continental shelf; East China Sea; enrichment factor; trace metals;
13 sediments; sedimentation flux)

22 1. Introduction

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

24 largest marginal seas in the western Pacific of the northern hemisphere, and it is also
25 the main discharge area of the Changjiang River which is the world's fourth largest
26 river when reviewed in terms of suspended load. The annual transportation of
27 suspended load of the Changjiang River is approximately 4.61×10^8 t/y (Zhang and
28 Liu, 2002). In addition, there are another four middle size rivers, namely the Jiaojiang,
29 the Qiantangjiang, the Jiulongjiang and the Minjiang, which together discharge $2.36 \times$
30 10^7 tons/y of suspended load into the ECS (Zhang and Liu, 2002). Along the coast
31 there are many developed cities, such as Shanghai and Ningbo, and a number of
32 factories have also been set up there. Because of the over-emphasis on the economic
33 development and the lack of environmental regulations since China embarked on the
34 "Reform and Open Policy" from 1978, many studies have indicated that the
35 Hangzhou Bay was contaminated by trace metals (Huh and Chen, 1999; Yuan et al.,
36 2004) and polycyclic aromatic hydrocarbon (Guo et al., 2006). A recent study
37 conducted in August 2003 uncovered a hypoxic area (dissolved oxygen
38 concentrations $<2-3$ mg/l) greater than $12,000 \text{ km}^2$ extending from the Changjiang
39 River plume to the ECS (Chen et al., 2007). Thus, our current understanding is that
40 the water quality of the ECS has been getting worse. However, the distribution and
41 contamination status of trace metals for the whole ECS has not been established (Shi
42 et al., 2005). In order to establish such a knowledge, the present study investigates the
43 spatial distribution of trace metals in surface sediments of the ECS. In addition, based
44 on the mass accumulation rates published in the literature for the ECS, the annual
45 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

68 large portion of this sediment supply is moved southward by the Jian-Su coastal
69 current (Cao et al., 1989). A small portion of the suspended sediments is transported
70 east and northeastwards to the ESC (Sternberg et al., 1985). From the examination of
71 ^{210}Pb profiles in sediment DeMaster et al. (1985) obtained a sedimentation rate of up
72 to 4.5cm/y near the mouth of the Changjiang River. In a recent study based on
73 measurements of ^{137}Cs throughout the ECS, Huh and Su (1999) indicated that the
74 sedimentation rates in the ECS varied by two orders of magnitude, from 2 to 0.02
75 cm/y, and generally decreased southwards along the inner shelf and eastwards
76 offshore. Based on the spatial distributions of the grain size, carbonate, organic
77 carbon contents, metals/aluminum ratios and the δC^{13} content of organic carbon, the
78 ECS continental shelf was divided into five major regions: the Delta, inner shelf,
79 middle shelf, outer shelf and northeast outer shelf (Lin et al., 2002). Major types of
80 sediments occurring there include terrigenous sediments from the Changjiang River,
81 relict sediment from the middle shelf, biogenic carbonate from the outer shelf and
82 sediments from the Yellow Sea (Lin et al., 2002).

83

84

85 ***2.2 Analytical method***

86 After thawing, the cores samples were extruded vertically with a hydraulic jack
87 and sampled at 1 cm thickness at the surface. The outer rim (~ 0.5cm) of each
88 sediment slab was trimmed off to avoid contamination between layers.

89 Approximately 10-20 g of each surface sample (0-1 cm) was freeze-dried, ground and

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

94

95 **Total organic carbon analysis**

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

100

101 **Trace metals analysis**

102 The trace metals contents in the surface sediments were totally digested with
103 hydrofluoric acid (HF) in combination with aqua regia and heated on a hot plate at
104 200 °C for about 8 hours and evaporated to dryness. After cooling, the residue was
105 dissolved with 0.5ml HNO₃ and the solution was made up with Milli-Q water to a
106 volume of 25 ml in a volumetric tube. The final acidic solution was transferred into a
107 50ml centrifuge tube and was centrifuged at a speed of 4000 rpm for 5 minutes. The
108 clear supernatant was stored in acid-cleaned polypropylene tubes and was analyzed
109 for trace metals (Cu, Fe, Mn, Ni, Pb and Zn) by flame atomic absorption
110 spectrometry using a Perkin-Elmer Analyst 800A.

111

112 Analytical quality assurance was performed by measurements of the PACS-2
113 reference material (National Research Council of Canada). The concentrations (n=6)
114 of trace metals measured in the PACS-2 reference material (one standard deviation)
115 were as follows: Cu, $286 \pm 14 \mu\text{g/g}$; Mn, $412 \pm 18 \mu\text{g/g}$; Ni, $38.8 \pm 1.5 \mu\text{g/g}$; Pb, 167
116 $\pm 3 \mu\text{g/g}$; and Zn, $340 \pm 11 \mu\text{g/g}$, respectively. The ratio of the measured
117 concentration to the certified value and precision (one standard deviation) was as
118 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,
119 $93.4 \pm 3.4\%$.

120

121 3. RESULTS AND DISCUSSION

122 3.1 *Spatial distribution*

123 The concentration ranges of TOC and trace metals in surface sediments of the ECS
124 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,
125 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,
126 4.35-8.49 %, respectively. The concentrations of TOC and trace metals found at each
127 station are listed in Table 1. The spatial distributions of TOC and trace metals are
128 shown in Fig.2. Higher concentrations of TOC and trace metals were generally found
129 on the inner shelf, especially the area off Hangzhou Bay. Away from the Hangzhou
130 Bay area, concentrations (except for Mn) decreased in both a southerly (along the
131 inner shelf) and south-easterly (middle and outer shelves) direction. This finding is in
132 good agreement with TOC decreasing along transects radiating outwards from the
133 mouth of the Changjiang River. Therefore, it supports the view that Changjiang River

134 is a dominant factor resulting in elevated trace metals and TOC concentrations on the
135 ECS (Lin et al., 2002) The spatial distributions of trace metals and TOC in the ECS
136 generally exhibited similar patterns and the concentration of TOC correlated well
137 with trace metals (Fig.3). It is well established that natural organic matter (NOM) has
138 a high affinity for trace metals in the aquatic environment (Stumm and Morgan,
139 1996). As a consequence, it affects the geochemical behavior of trace metal in the
140 aquatic environment. The coupling between the cycles of TOC and trace metals is
141 ultimately reflected in the chemical composition of marine sediments (Basaham and
142 El-Sayed, 1998; Fang and Hong, 1999; Lin et al., 2002).

143
144 In addition, the distribution of Mn showed a distinct peak situated between the
145 middle and outer shelves at approximately located at 27° N and 123.5° E. The
146 mechanism caused such a distribution is probably due to the sediment of this area
147 being dominated by biogenic carbonate (Lin et al., 2002). Previous studies have
148 shown that dissolved manganese can become adsorbed on, or incorporated into,
149 freshly precipitated CaCO₃ in seawater (e.g. Wartel et al., 1990). Wartel et al. (1990,
150 1991) used suspended particulate matters from the English Channel, which is high in
151 carbonate minerals, to study the interaction of Mn⁺² in the CaCO₃ structure. They
152 concluded that the adsorption on and substitution in calcite are the major mechanisms
153 controlling the dissolved concentration of Mn in seawater along the French coast of
154 the English Channel. Recent studies on suspended particulate matter from the Seine
155 Estuary have also indicated that the majority of particulate Mn is bound to carbonate

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

159

160 Total concentrations of trace metals in the inner shelf sediment found in the present
161 study were in good agreement with the report by Yuan et al. (2004) who used the
162 four-step sequential extraction procedure to analyze coastal sediments outside of the
163 Changjiang Estuary. Their results also indicated that more than 90% of Fe and
164 60-80% of Cu, Ni and Zn total concentrations were present in the residual fraction. In
165 contrast, the concentrations of Mn and Pb were dominant in the non-residual fraction,
166 accounting for more than 60% of the total concentrations. A comparison of trace
167 metals concentrations in shelf sediments around the world is given in Table 2. It can
168 be seen that the concentrations of trace metals, except Mn, found in the continental
169 shelves, such as the Arabian Gulf, the Mediterranean Sea, the Aegean Sea and the
170 Laptev Sea, around the world are quite comparable. However, the average
171 concentration of Mn found in the ECS is two-three folds higher than those of the
172 above continental shelves. Comparably high concentrations of Mn have been reported
173 by Nolting et al. (1996) who indicated that Mn lateral distribution in surface
174 sediments showed an increase from 1000 $\mu\text{g/g}$ in the mouth of the Lena River to >
175 5000 $\mu\text{g/g}$ in the eastern part of the Laptev Sea. They attributed these higher
176 concentrations to the diagenetic process in sediments which caused large upward
177 fluxes of Mn. The findings of Nolting et al. (1996) elucidate that trace metal, especial

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

181

182 **3.2 Enrichment factor**

183 Trace metals concentrations in marine surface sediments can vary widely (Luoma,
184 1990). As a result, it is difficult to evaluate whether the observed concentration in
185 marine sediments is influenced by anthropogenic sources or not without normalizing
186 the result. Some normalising procedures are widely used to compensate for
187 differences in grain size variations and carbonate content, and thus provide a means
188 of separating anthropogenic sources from natural inputs (Luoma, 1990).
189 Normalization to a background level of metals in samples with different
190 characteristics can be accomplished by calculating an enrichment factor (EF) relative
191 to the reference sample. In the equation

$$192 \quad EF = (M/Al)_S / (M/Al)_R ,$$

193 $(M/Al)_S$ and $(M/Al)_R$ are the ratio of metal to Al concentrations in sample and in
194 reference sample, respectively. It is found that the metal concentrations at stations of
195 the outer shelf in the ECS were the least among the study areas, which may indicate
196 that the disturbance of the outer shelf was relatively minor. In order to avoid the
197 natural differences of sediment textures in different environments, the reference
198 sample is taken from the data of outer shelf stations in the present study. The average
199 concentrations of each metal and Al at all stations of outer shelf are considered as the

200 reference values which are used to calculate the EF and assess the contamination
201 status of the ECS. The EF range of the studied metals was as follow: Fe, 0.43-1.93
202 (average 1.22); Cu, 0.67-5.83 (average 1.96); Mn, 0.54-3.76 (average 1.47); Ni,
203 0.52-2.57 (average 1.42); Pb, 0.56-2.07(average 1.29); and Zn, 0.51-2.89 (average
204 1.42). Contour plots of EF distribution for each metal are shown in Fig.4.
205 Surprisingly, the EF values of Cu are the highest and indicate a marked
206 anthropogenic burden, suggesting that Cu was the most contaminated metal among
207 the studied metals. However, it can be seen in Fig.4 that the contour values of each
208 metal greater than 2 generally distributed in the inner shelf. While, the contour values
209 in the middle and outer shelves are within the range of 1-2 and approach to 1,
210 respectively. The EF values suggest the inner shelf of the ECS was mildly
211 contaminated by trace metals. Such a metal contamination did not further extend to
212 the middle and outer shelves.

213

214 An EF value of 1 indicates a predominantly natural origin for the element in
215 sediment, while values greater than 1.5 indicate enrichment by either natural
216 processes (e.g. biota contributions) or anthropogenic influences (Zhang and Liu,
217 2002). EF values lower than 0.5 can reflect mobilization and loss of these elements
218 relative to Al, or indicate an overestimation of the reference metal contents (Zhang,
219 1995; Mil-Homens et al., 2006).

220

221 **3.3 Trace metals sedimentation flux**

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

233
234 Due to the ECS being adjacent to the Yellow Sea to the north and with the North
235 Pacific Ocean to the east, its total area is difficult to determine. Two widely accepted
236 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
237 with a water depth $< 200\text{m}$ (Wong et al., 2000, and references cited therein). The
238 calculated area of the present study is approximately $0.376 \times 10^6 \text{ km}^2$, which accounts
239 for about 50% of the whole ECS area provided by Wong et al. (2000) and about 74%
240 of the continental shelf area. Table 3 shows the area, the concentration range of trace
241 metals obtained in the present study and the mass accumulation rate (MAR) in each
242 box.

243

244 There are three values for each metal-related parameter: minimum, maximum and
245 average. The minimum value of the annual metals sedimentation flux was calculated
246 from the minimum concentration of metals multiplied the minimum value of MAR in
247 each box. The maximum and average values were calculated in a similar manner. The
248 average annual sedimentation fluxes of trace metals in the calculated area were as
249 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;
250 Pb, 43.2×10^9 g/y; and Zn, 108×10^9 g/y. Most of the sedimentation fluxes of trace
251 metals were concentrated in the inner shelf (box II), accounting for 55-70% of the
252 total fluxes of each metal. The second important area was the estuarine zone (box I),
253 contributing from 10 to 17% of the total fluxes of each metal. These results indicate
254 that the suspended loads of metals exported from the Changjiang River catchment
255 were mostly deposited on the inner shelf. It is well known that the continental shelf
256 sediments originate primarily from the riverine suspended load. The suspended load
257 of the Changjiang River is the major contribution and the four middle size rivers,
258 namely the Jiaojiang, the Qiantangjiang, the Jiulongjiang and the Minjiang,
259 contribute minor inputs to the ECS (Zhang and Liu, 2002). The upper part of Table 4
260 summarizes the annual flux of particles to the coast and their trace metal contents.
261 The calculated annual chemical fluxes of particulate metals from these rivers are
262 listed in the lower part of Table 4. These fluxes are as follows: Fe, 24456×10^9 g/y;
263 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;
264 and Zn, 46.67×10^9 g/y.

265

266 These riverine fluxes of particulate metals are generally lower than, but with the
267 same magnitude as, the calculated sedimentation fluxes. The reason for this
268 phenomenon may attribute to the anthropogenic influence as indicated in the
269 enrichment factor values. The calculation bias of sedimentation fluxes could also be
270 another reason because the difference of maximum and minimum values may vary
271 one order of magnitude. However, the data accuracy of the riverine sediment
272 transportation fluxes and properties shown in literature (Zhang and Liu, 2002, and
273 references cited therein) should be taken into account when calculating the riverine
274 annual transportation fluxes. Since the riverine data were established in the early
275 1990s. It is known that China launched its modernization campaign from 1980 and
276 substantially increased its economic development in the last two decades (Guo et al.,
277 2006). The rapid economic development of China may alter the environment. One of
278 the evidences is that the Asian dust storm which occurred since 2000 (Mori et al.,
279 2003). Thus, in order to obtain a more accurate calculation of the riverine annual
280 fluxes of trace metals, the updating riverine data are necessary to be used.
281 Unfortunately, it is not able to find the updating data in the literature.

282

283 3.4 *Atmospheric trace metals flux*

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

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

296

297 Research into Asian dust storms impact on the biogeochemistry of the ECS,
298 especially with respect to biological bloom and budget balance of nutrients and trace
299 metals, has been conducted by several research groups (Yuan and Zhang, 2006; Hsu
300 et al., 2008). A comprehensive study carried out by Hsu et al (2008) who conducted
301 several cruises to collect the marine aerosols from the ECS during the spring of 2005
302 and 2007. They analyzed marine aerosol samples for both the water-soluble and the
303 total concentration of 27 trace elements and calculated the dry deposition fluxes.
304 Their results for trace metals dry deposition fluxes were as follows: Fe, 39 ± 50
305 $\mu\text{g}/\text{m}^2/\text{d}$; 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,
306 $2.5\pm 6.7 \mu\text{g}/\text{m}^2/\text{d}$; and Zn, $19\pm 39 \mu\text{g}/\text{m}^2/\text{d}$. We used these values to calculate 120-day
307 and 180-day of the aerosol dry deposition fluxes of these metals in same area, $0.376 \times$
308 10^6 km^2 , as the calculation of metals sedimentation fluxes in the ECS, as shown
309 above. The calculated result for the aerosol dry deposition fluxes and the riverine

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

318

319 **4. Conclusions**

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

330

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

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

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Figures captions

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

518 Fig.2. Spatial variation of trace metals concentrations in the surface sediment in the

519 study area of the East China Sea.

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

521 correlation

522 Fig.4. Spatial variation of enrichment factor of trace metals in the study area of the

523 East China Sea.

524 Fig.5. Sub-areas, as defined on the basis of sedimentation rates, and trace metal

525 content. These sub-areas are: (I) estuary; (II) inner shelf; (III) middle shelf; (IV)

526 middle shelf; and (V) outer shelf

527 Fig.6. Comparison of the riverine annual transportation fluxes of trace metals with

528 Asian dusts dry deposition fluxes of trace metals (120-day and 180-day) to the

529 East China Sea.

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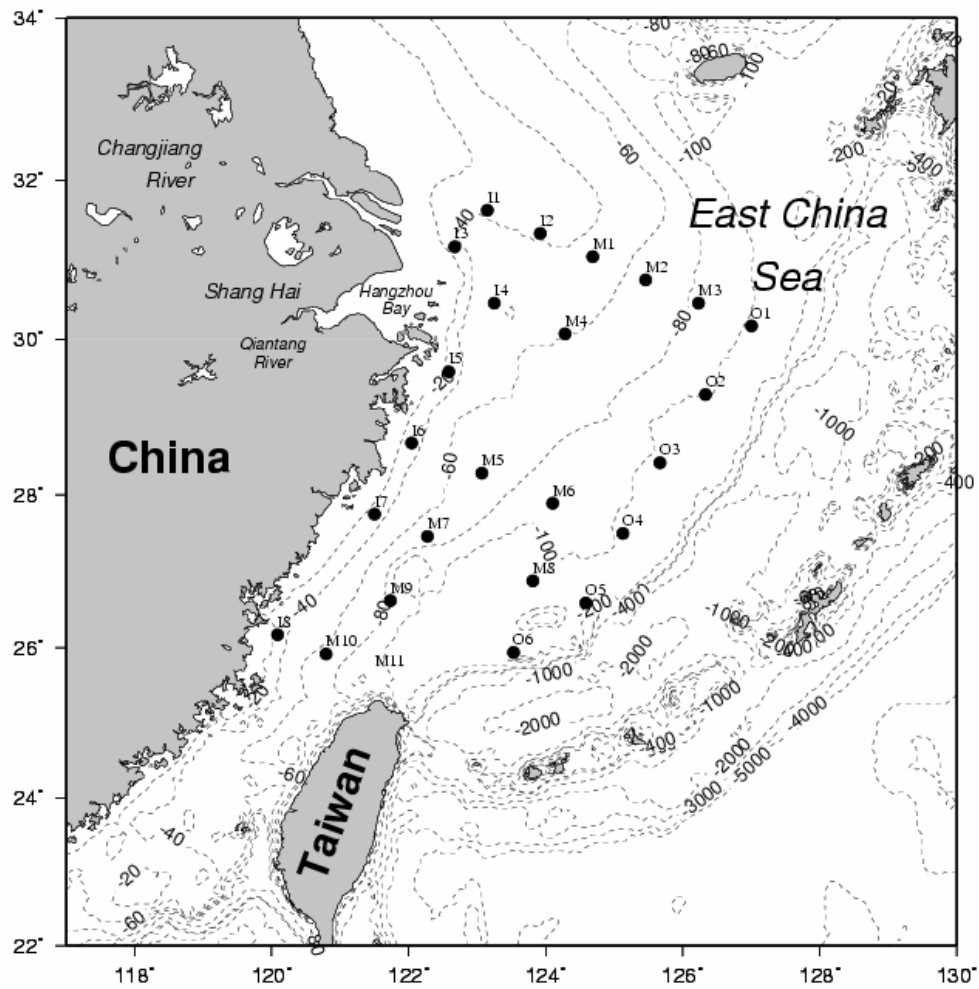


Fig.1

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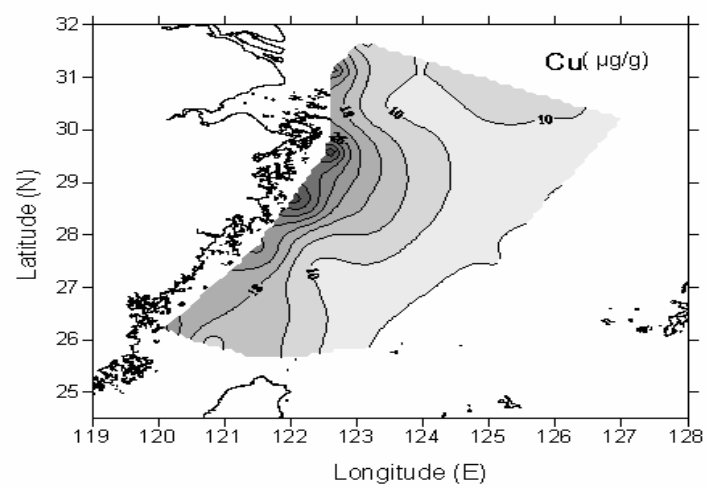
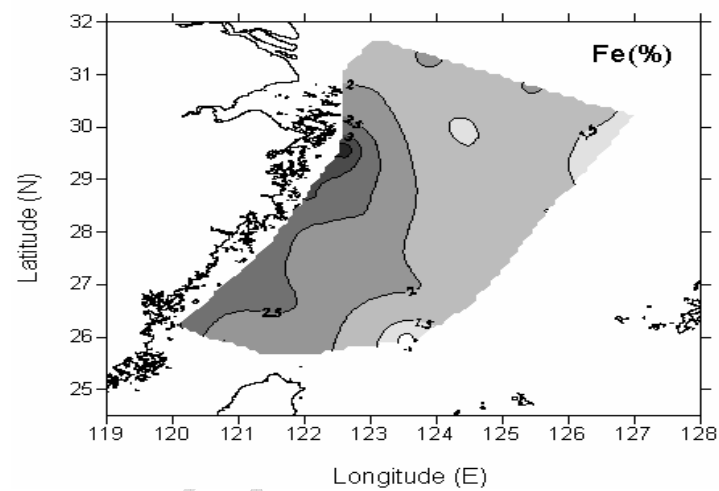
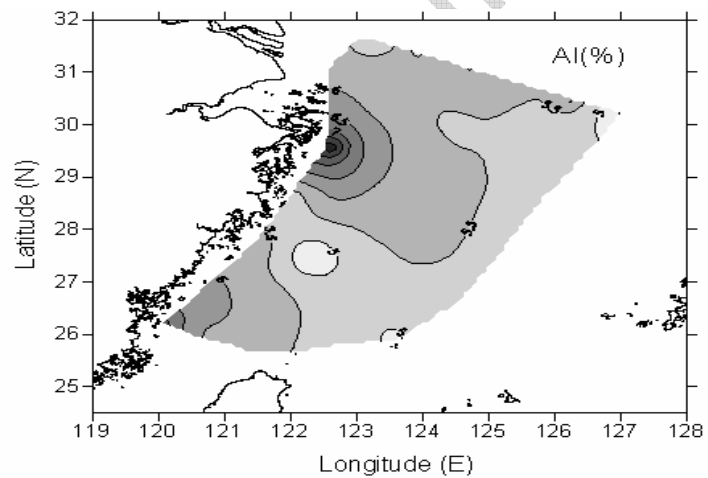
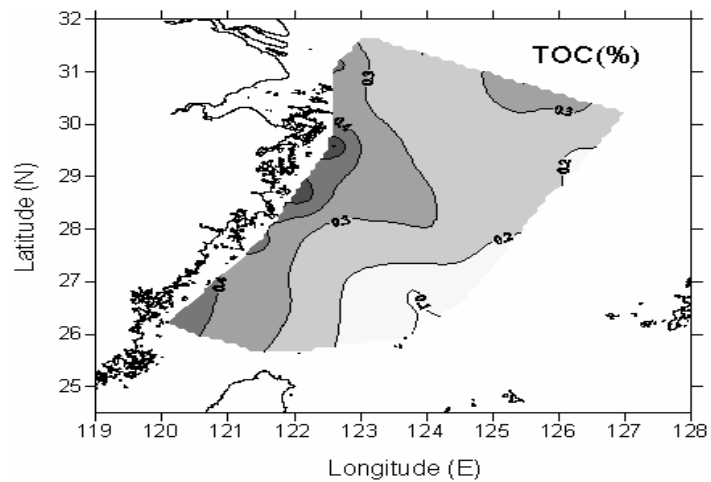


Fig.2

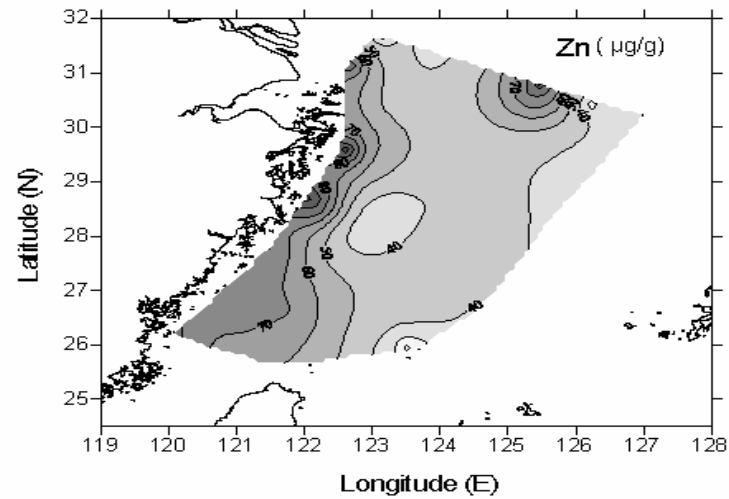
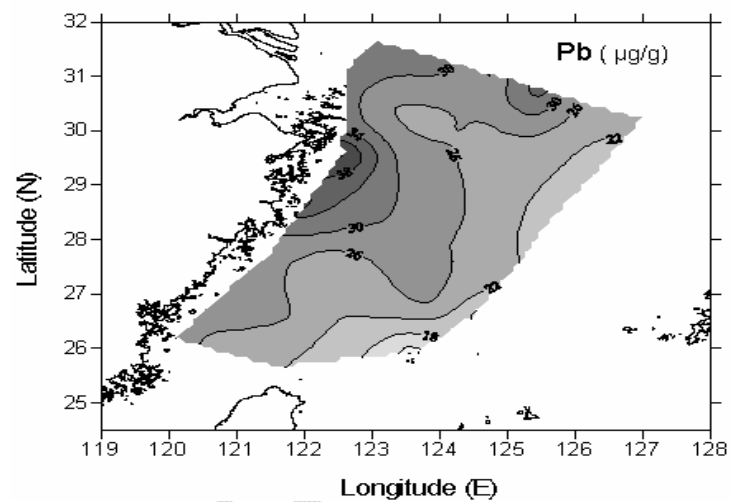
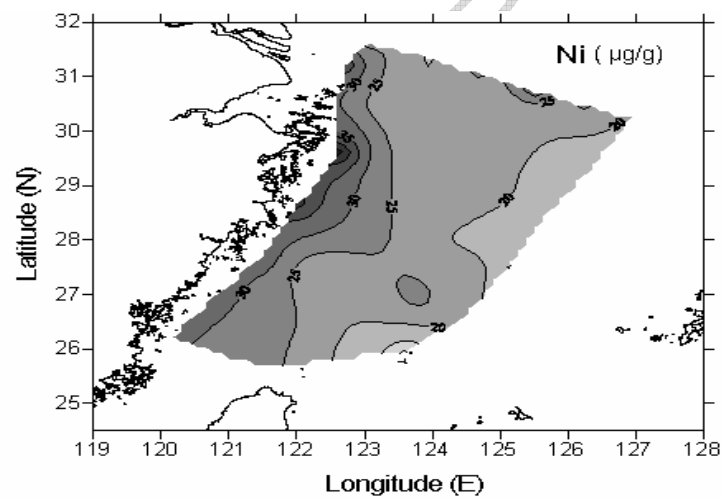
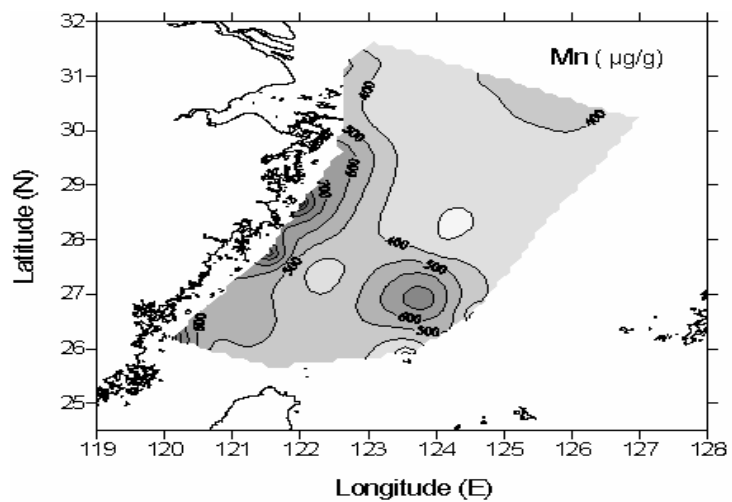


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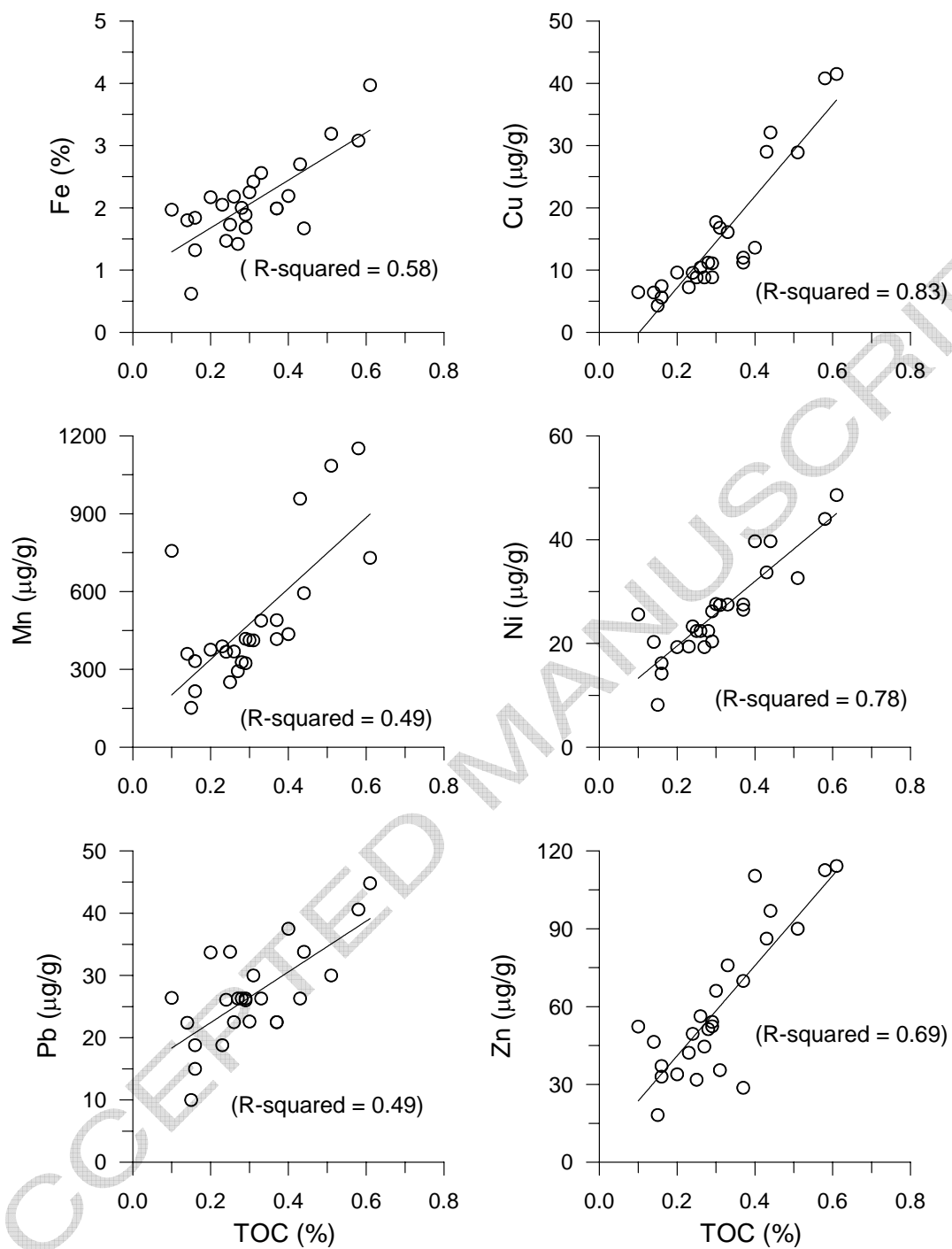


Fig. 3

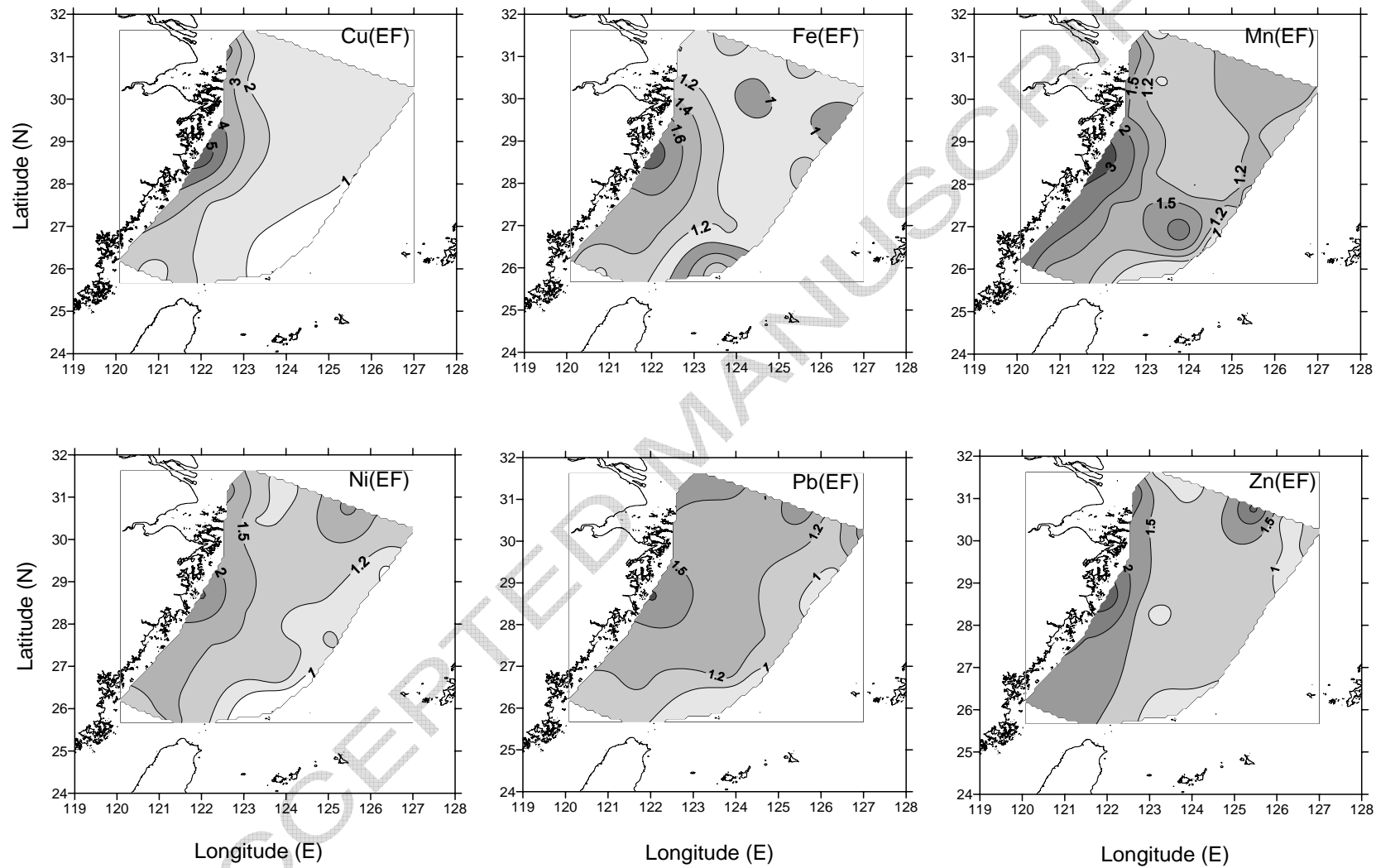


Fig.4

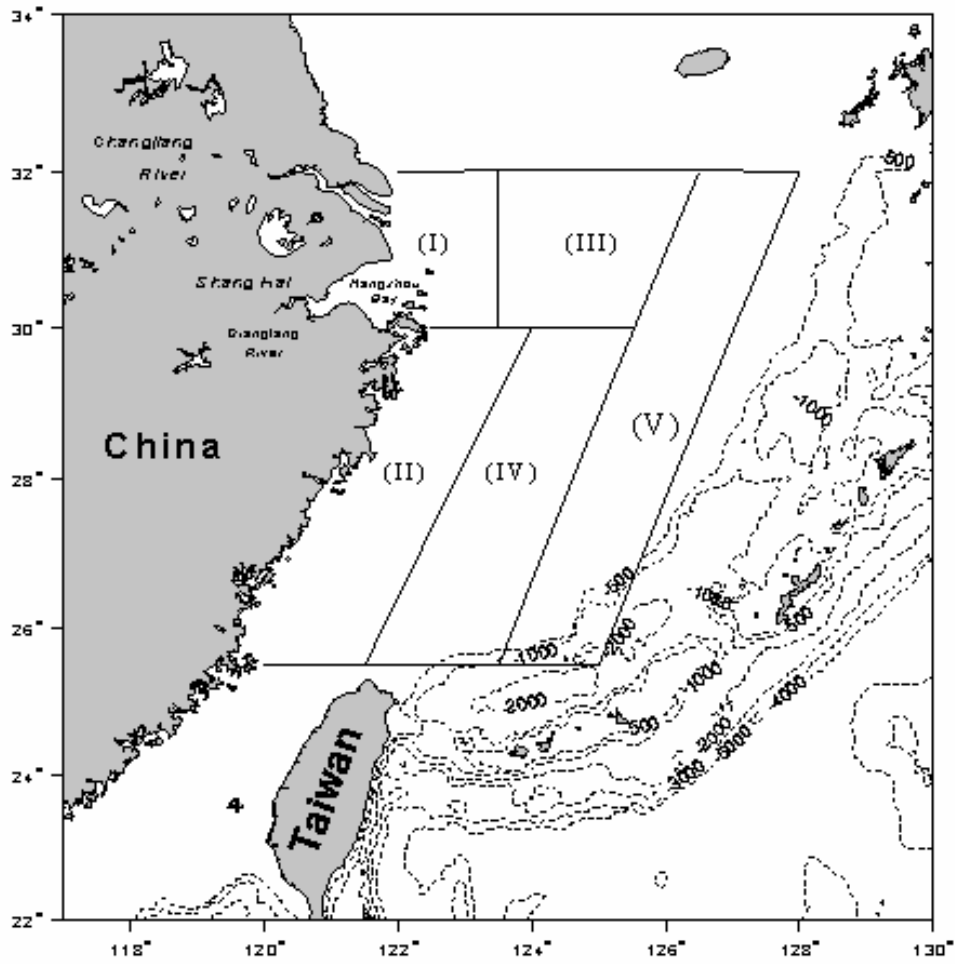
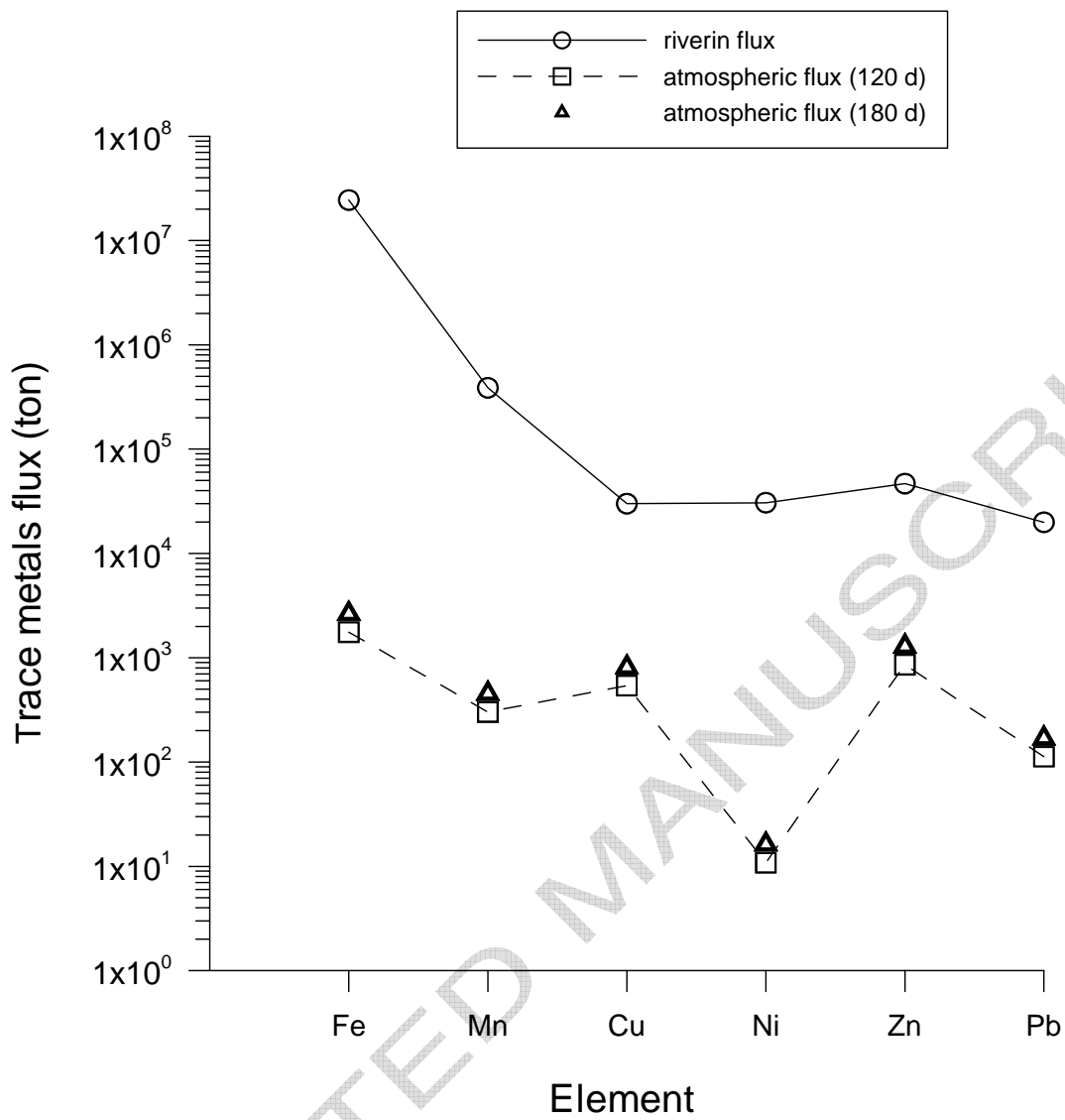


Fig.5

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Fig. 6

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

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Station	Long.(E)	Lat. (N)	TOC (%)	Al (%)	Fe (%)	Cu (μg/g)	Mn (μg/g)	Ni (μg/g)	Pb (μg/g)	Zn (μg/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	