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Heavy metals in surface sediments from Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas

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Abstract: The concentrations of Cu, Pb, Zn and Cd in surface sediments from Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas of China were investigated during 1995—1996. The concentration ranges of Cu, Pb, Zn and Cd in the Minjiang Estuary-Mazu sea area were 16.4—37.2, 33.4—69.6, 92.1—128, 0.087—0.336 mg/kg(dry wt.), respectively; those for Xiamen-Jinmen sea area were 11.0—24.5, 36.0—80.3, 77.5—161, 0.135—0.285 mg/kg(dry wt.), respectively. The concentrations and distributions of Cu, Pb, Zn and Cd in surface sediments of Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas were analyzed and evaluated. The results showed that the values of Zn and Pb exceeded those of sediment quality criteria. The average concentration of Cu in Minjiang Estuary-Mazu sea area was higher than that in Xiamen-Jinmen sea area. The obviously higher concentrations of Cu, Pb, Zn and Cd were found at outlets of Minjiang and Jiulong River. From the estuaries to open sea, the concentrations of Cu, Pb, Zn and Cd had a decreasing trend, and then elevated in the sea areas near Mazu and Jinmen, suggesting that Cu, Pb, Zn and Cd in Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas may come from both the mainland and Taiwan of China.

Keywords: heavy metal; sediment; concentration; distribution; Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas

Introduction

The pollution of heavy metals, being of wide sources, uneasiness to decompose, accumulation, and toxicity to the bodies of human being and life-form, are considered to be one kind of the main pollutants in the environment. Trace metals that enter into aquatic system tend to be sorbed on sediments (Wang, 2000). The sorption intensity and capacity of metals on sediments have been studied intensively since the 1970s (Forstner, 1981; Horrowitz, 1991; Wang, 1997a).

After decades of intensive industrial development accompanied by the production of thousands of different chemicals, there is worldwide concern with the preservation of existing natural resources and with possible harmful effects resulting from contamination of air, soil and water. The quality of aquatic ecosystems is of great interest to the entire world (Li, 2000). The waste products into rivers and estuaries, especially those in industrial and population centers, have led to a significant increase in metal contamination (Forstner, 1983; Tessier, 1988; Buckley, 1995).

The sea areas of Xiamen-Jinmen and Minjiang Estuary-Mazu belong to both the mainland and Taiwan and lack the data about some pollutants such as heavy metals, organochlorines and so on because of the historic reason. Thus, we collaborated with Taiwan Scientists to make the combined sampling and simultaneous investigation in sea areas of Minjiang Estuary-Mazu and Xiamen-Jinmen during 1995—1996. This paper attempts to address the deficit of heavy metal data detected in these sea areas and to know the sources and trend of change of the specific pollutants.

The results will help to assess the environmental impacts of the pollutants and make corresponding measures in protection and regulation of environment and oceanic resources.

1 Materials and methods

1.1 The study area

The sea areas of Xiamen-Jinmen and Minjiang Estuary-Mazu were the study areas for the present study and sampling locations are shown in Fig.1.

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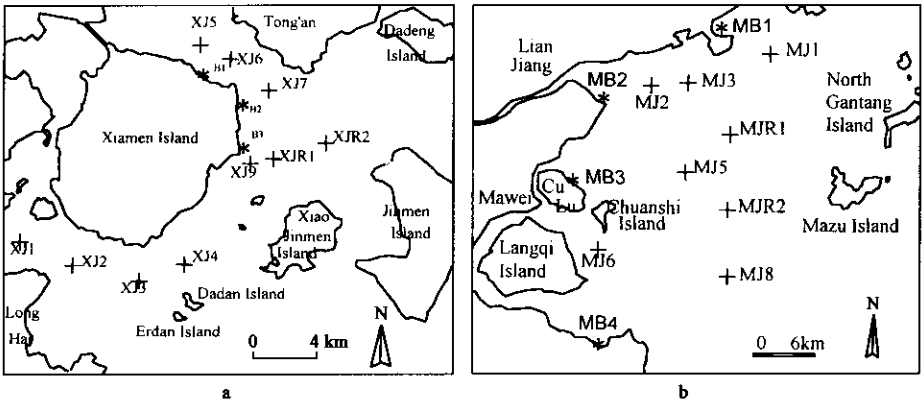

Fig.1 Map of sampling locations
(a) Xiamen-Jinmen sea area (24°24'—24°34'N, 118°02'—118°15'E); (b) Minjiang Estuary-Mazu sea area (26°04'—26°26'N, 119°39'—119°51'E)

There are wide sources of pollution and complex effecting factors in Minjiang Estuary-Mazu sea area that belongs to both Fuzhou City and Mazu Island. Minjiang River, the largest river in Fujian Province, is 54.1 km in length, has a drainage area of 60992 km^2 and an average discharge of 5.84×10^{10} m^3 in flux per year (Lin, 1989), and contains large amounts of silt and sand which have great adherence to the pollutants. Different processes in the area of Minjiang Estuary cause changes in quantity of heavy metals contained in flows through the estuary. Changes of the condition of aquatic kinetics may transport the sediment to its overlying waters and the surface sediments in the bottom may become the second pollution sources (Qi, 1990).

Xiamen Island, from which Jinmen Island is, east-toward 10 km faraway, lies on the west shore of the Taiwan Straits. The "Xiamen-Jinmen sea area" refers to, in this paper, the sea areas in south and east of Xiamen-Island, Tongan Bay and Jinmen-Xiamen channel. Jiulong River estuary lies in southwest of Xiamen Harbor. Jiulong River is the second largest river in Fujian Province, with 11909 km^2 in drainage area and 1148 km in the total length of its water system(Yang, 1996). The condition of aquatic kinetics in Xiamen-Jinmen sea area is complicated, because of contributions of river flows in addition to tidal currents and ocean waves. The sources of its sediments are various.

1.2 Sampling procedure

7 samples of surface sediment were collected at Stations MJ1-MJR2 in Minjiang Estuary-Mazu sea area and 10 samples at Stations XJ1-XJR2 in Xiamen-Jinmen sea area (Fig.1). The sampling sites were positioned by GPS. The samples were collected using a grab sampler and stored in glass bottles, then freeze-dried after being brought back to the laboratory.

1.3 Chemical analysis

The dried samples were sieved with a 0.18 mesh, then with 63 μm mesh. The former was used for measuring the concentrations of heavy metals in surface sediments and the latter for the sediment with partial size lower than 63 μm.

The samples are dissolved in mixed acid HNO_3 + $HClO_4$ under a temperature of 150℃. The concentrations of each heavy metal are measured with the atomic absorption spectrometer. The detected limits of Cu, Pb, Zn and Cd were 0.001, 0.003, 0.001 and 0.001 mg/L, respectively, with a relative standard deviation of 3.7%, 5.2%, 3.5% and 12.7%, respectively. The recovery rates for Cu, Pb, Zn and Cd from the standard reference material were around 85%—121%.

2 Results and discussions

2.1 Concentrations of Cu, Pb, Zn, Cd and evaluation

The concentrations of Cu, Pb, Zn and Cd in the surface sediments from Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas are listed in Table 1. The concentration ranges of Cu, Pb, Zn, Cd in the Minjiang Estuary-Mazu sea area were 16.4—37.2, 33.4—69.6, 92.1—128, 0.087—0.336 mg/kg(dry wt.), respectively; those for Xiamen-Jinmen sea area were 11.0—24.5, 36.0—80.3, 77.5—161, 0.135—0.285 mg/kg(dry wt.), respectively.

Table 1 Concentrations (mg/kg dry wt.) of Cu, Pb, Zn and Cd in surface sediments from Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas

Sample	Surface sediments									
Minjiang Estuary-Mazu										
Station	MJ1		MJ2	MJ5		MJ6	MJ8		MJR1	MJR2
Cu	28.3		16.4	22.2		37.2	24.2		34.4	32.6
Pb	34.4		35.2	39.4		69.6	42.4		43.2	42.5
Zn	92.1		95.4	92.7		128	93.0		101	100
Cd	0.138		0.087	0.112		0.336	0.157		0.170	0.154
Xiamen-Jinmen										
Station	XJ1	XJ2	XJ3	XJ4	XJ5	XJ6	XJ7	XJ9	XJR1	XJR2
Cu	19.0	24.5	22.0	14.5	14.8	16.6	17.0	11.0	14.2	12.5
Pb	70.8	80.3	64.0	47.5	40.3	42.0	52.8	43.8	48.8	36.0
Zn	115	136	161	91.5	85.5	85.3	104	77.5	94.4	89.3
Cd	0.232	0.285	0.250	0.181	0.143	0.222	0.227	0.135	0.230	0.150

The results showed that the values of Zn and Pb exceeded those of sediment quality criteria. This can be attributed to the effects of small metal mines(Xu, 1993). Some mines, which reserve Fe, Mn, Pb, Zn etc. were found by the end of 1983 in the coastal areas of Fujian Province and may result in high background values of Zn and Pb comparatively. Heavy metals abound in the Minjiang drainage area and the concentrations of Cu, Pb, Zn and Cd are relatively high in the whole country, according to the results of soil investigation of background-value in Fujian Province in 1987. Therefore, the metal elements may be taken into the rivers by rainwater runoff and finally aggregated into the Minjiang Estuary. Because of a series of reaction occurring in the area of the estuary, they were deposited into the bed sediment of the sea area. On the other hand, the fertilizers containing Zn in agricultural application can possibly be released into the survey sea area.

Compared to the survey data in 1993 (Table 2), it is found the concentrations of Zn and Cd remained almost unchanged, while that of Cu increased a little and that of Pb decreased in Minjiang Estuary-Mazu sea area. However, the concentrations of Cu, Pb, Zn, Cd evidently increased in Xiamen-Jinmen sea area, 2.01—21.53 times higher than the data (Xu,1986). The economy of Xiamen and Southern Fujian Delta has improved rapidly since 1990's, which has brought big environmental pressure to the coastal sea areas of Fujian Province. Besides, there are the influxes of Jiulong River and the western bay to the southern part of Xiamen-Jinmen sea area. While in the northern part of the sea area, the pollution of the aquatic breeding, and the construction of Tongan District such as Shi-xun industry area and so on, cause the environmental condition of the sea area to change in some extent. So, we can draw the conclusion that the anthropological pollution is not negligible. It was reported that artificial increase of Cu, Pb, Zn and Cd in the surface sediments in western sea area of Xiamen was 30.1%, 39.4%, 27.7% and 34.4% respectively(Liu, 1995). Even so, the results obtained in this study were relatively low compared to the data of Pearl River Estuary(Li, 2000), Victoria Harbor in Hong Kong(Zhuang, 1994), Narragansett Bay (Goldbery, 1977) and Harifax Harbor(Buckley, 1995).

The average concentrations and the relevant statistical analysis were applied to evaluate contamination levels of Cu, Pb, Zn and Cd in two sea areas. The data are listed in Table 3. Of which the calculation formula of t (Hu, 1986) is as follows:

$$t = (M_1 - M_2) \Bigg/ \sqrt{\frac{\sum(X_1 - M_1)^2 + \sum(X_2 - M_2)^2}{(n_1 - 1) + (n_2 - 1)}} \times \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}. \qquad (1)$$

Table 2 Comparison of Cu, Pb, Zn, Cd concentrations (mg/kg) in surface sediments collected from different estuaries and bays

	Cu	Pb	Zn	Cd
Minjiang Estuary-Mazu sea area(This study)	27.9	43.7	100.3	0.165
Mazu sea area(Taiwan Univ.)	40.0	24.1	53.2	0.280
Xiamen-Jinmen sea area(This study)	16.6	52.6	104	0.205
Jinmen sea area(Taiwan Univ.)	14.7	34.3	69.2	0.110
Minjiang Estuary(1993)(1)	22.6	50.8	101.0	0.140
Xiamen Harbour(Xu *et al*., 1986)	2.2	22.9	5.9	0.056
Meizhou Bay (1993)(1)	14.5	30.2	70.0	0.033
Pearl River Estuary(Li *et al*., 2000)	40.9	59.5	115	/
Victoria Harbour, Hong Kong (Zhuang *et al*., 1994)	29.2	123.9	/	6.89
Narraganest Bay, USA(Goldberg *et al*., 1977)	163	121	227	/
Halifax Harbour, Canada(Buckley *et al*., 1995)	88	206	249	/
Sediment Quality Criteria(2)	30	25	80	0.5

(1) The research reports on the environmental quality of Fujian Province Islands, 1993; (2) simple regulations of resource investigation on coastal zone in China

Table 3 Data about statistical analysis

		Cu	Pb	Zn	Cd
Xiamen-Jinmen	$M_1(n_1 = 10)$	16.6	52.6	104	0.205
Minjiang Estuary-Mazu	$M_2(n_2 = 7)$	27.9	43.7	100.3	0.165
t^*		−4.02	1.34	0.34	1.26
$t_{0.05}^{**}$		2.13	2.13	2.13	2.13

Notes: * calculated value according to Equation (1) in the text; ** critical value when $\alpha = 0.05$ from t-distribution table

In above Eq. (1), X_1 and X_2 mean the determined value in Xiamen-Jinmen and Minjiang Estuary-Mazu sea areas; M_1 and M_2 mean the corresponding average; n_1 and n_2 are the corresponding sample number. It can be seen from Table 3 that the absolute values of t for Pb, Zn and Cd are all smaller than the critical value $t_{0.05}$, while Cu is higher, meaning that evident difference in Cu mean between two sea areas existed but those for Pb, Zn, Cd did not. The results suggested the contamination levels of Pb, Zn and Cd in two sea areas were similar, whereas Cu contamination level in Minjiang Estuary-Mazu sea area was higher than that in Xiamen-Jinmen sea area in general.

Considered in the same station, the concentrations of Cu, Pb, Zn and Cd in the fine particles (< 63 μm) of sediments were all higher than those in the surface sediments (Table 1, 4), indicating that the smaller particles of sediment have more evident capacity to enrich heavy metals. Chen *et al*. (Chen, 1994) found that the grain size effect was obvious because of difference in relative surface area.

Table 4 Concentrations (mg kg^{-1} dry wt.) of Cu, Pb, Zn and Cd in fine fraction (< 63 μm) of surface sediments from Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas

Sample	(< 63μm) surface sediments						
	Minjiang Estuary-Mazu				Xiamen-Jinmen		
Station	MJ2	MJ5	MJ8	Mean	XJ1	XJ9	Mean
Cu	21.7	27.3	27.8	25.6	22.8	11.0	16.9
Pb	42.0	49.0	45.4	45.5	80.3	50.8	65.6
Zn	105	101	106	104	129	95.5	112.2
Cd	0.162	0.180	0.182	0.175	0.288	0.143	0.215

2.2 Spatial distribution

No investigation had been done at stations MJR1, MJR2 in Mazu sea area and stations XJR1 and XJR2 in

Jinmen-Xiamen channel before this study. The concentration distributions of Cu, Pb, Zn and Cd in the surface sediments in these areas are shown in Fig. 2 and 3. On the whole, the significantly higher concentrations of Cu, Pb, Zn and Cd were found at outlets of the Minjiang and Jiulong rivers. From the estuaries to open sea, the concentrations of Cu, Pb, Zn and Cd decreased, and then elevated in the sea areas near Mazu Island and Jinmen Island. For Minjiang Estuary-Mazu sea area, the peak values of Cu, Pb, Zn and Cd were found at station MJ6. The concentrations obviously decreased from station MJ6 in the estuary to stations MJ5, MJ8 near the outer sea, and then increased to stations MJR1, MJR2. The values were both relatively low at stations MJ1, MJ2 that are far away from Minjiang Estuary and near the Aojiang mouth. For Xiamen-Jinmen sea area, the concentrations of Cu, Pb, Zn and Cd were relatively high in the southern part(stations XJ1-XJ4), then in the northern part (stations XJ5-XJ7), and the relatively low concentrations in the eastern part (stations XJ9, XJR1, XJR 2).

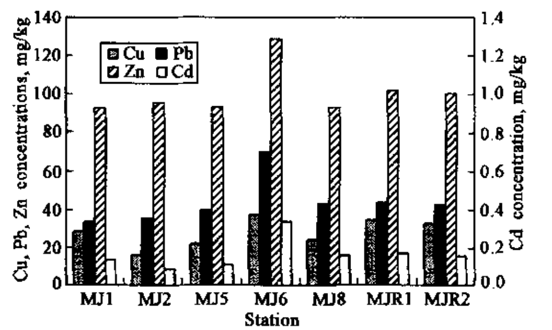

Fig. 2 Concentration distributions of Cu, Pb, Zn and Cd in surface sediments from Minjiang Estuary-Mazu sea area

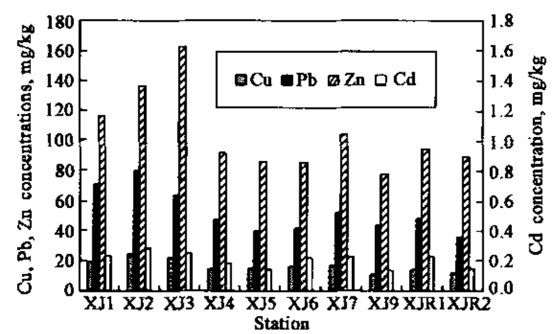

Fig. 3 Concentration distributions of Cu, Pb, Zn and Cd in surface sediments from Xiamen-Jinmen sea area

2.3 Source analysis

The concentrations of Cu, Pb, Zn and Cd at station MJ6 in Minjang Estuary were obviously higher than at other stations. The distribution character showed that Minjiang Estuary-Mazu sea area was mainly influenced by the flow of Minjiang River, including the inputs from territorial sources of Minjiang basin area and aquaculture along the bank of Minjiang Estuary. Therefore, it is of great importance to reinforce the control in total pollutants of Minjiang River to the sea, compositive recovery of mine exploitation in the basin area of Minjiang River, environmental regulation along the banks and pollution treatment of the corresponding industries.

The obvious decrease of Cu, Pb, Zn and Cd concentrations from station MJ6 to MJ5, MJ8 in the Minjiang Estuary is related to the dilution and diffusion of the seawater and tidal current. The concentrations of the heavy metals will ordinarily decrease from MJ6 to MJ5, MJ8 and to MJR1, MJR2, supposing that the heavy metals of the sea area only come from Minjiang River. However, the distribution character revealed in the results of this investigation was not so, showed that concentrations at stations MJR1 and MJR2 were higher than at MJ5, MJ8. This can be explained the heavy metals at MJR1 and MJR2 might come from both Minjiang Estuary and Mazu. The data reported by Taiwan University also revealed that there were maximum concentrations of heavy metals at Station MJR1 .

In the case of Xiamen-Jinmen sea area, the infusion of Western Bay is an important factor as well as the contribution of the flux of Jiulong River. Jiulong River, the second largest river in Fujian Province, is the main source of drinking water for the inhabitants of its basin area. Unfortunately, it became highly polluted because of the sewage discharge from the agriculture, industry, counties and towns. So that the water quality seriously deteriorates, even accessing the standards. Therefore, it is very important to tighten environmental management of the basin area. Xiamen City, which lies at the end of Jiulong River, will have long-term and onerous work in its compositive recovery. The concentrations of heavy metals in the northern part of the survey area were higher than those in the eastern part, due to the poor exchanging ability of the water body in the Tongan Bay which being a semi-close bay. It was also influenced by human activity directly, while the eastern part of the sea area is on a relatively widen environment. At stations XJ9, XJR1 and XJR2 in the eastern part of the sea area, the concentrations of Cu, Pb, Zn and Cd increased a bit from XJ9 to XJR1 and XJR2, which were relatively near to Jinmen area. For the similar reason referred above, the concentrations of Cu, Pb, Zn and Cd will decrease ordinarily, from XJ9 to XJR1, XJR2, supposing that the heavy metals at stations XJR1 and XJR2 only come from Xiamen. However, the distribution character revealed in the results of this investigation is contrary to this, for the concentrations at station XJR1 are highest. Therefore, it needs further analysis and discussion to know the sources. The data reported by Taiwan University also indicated that there were relatively higher concentrations of Cu, Pb, Zn and Cd in the Jinmen sea area .

Some mussel samples were collected at stations MB1-4 and XB1-3 (Fig.1) when we investigated the surface sediments in Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas. The monitoring results (Hong, 2000; 2001) showed that the concentrations of the heavy metals in bivalves were generally higher than in the sediments. It was reported that marine organisms can enrich the pollutants such as heavy metals, micro-organic pollutants and so on from their environment with the enrichment factors from several to hundreds times (Phillis, 1976). The bivalves alongside the shores can be used as bio-indicator for the pollution monitoring of Cu, Zn and Cd (Liu, 1995; Weng, 1996).

3 Conclusions

The mean concentrations of Cu, Pb, Zn and Cd in the Minjiang Estuary-Mazu sea area were 27.9, 43.7, 100.3 and 0.165 mg/kg(dry wt.), respectively, those for the Xiamen-Jinmen sea area were 16.6, 52.6, 104 and 0.205 mg/kg(dry wt.), respectively. The results showed that the values of Zn and Pb exceeded those of sediment assessment criteria, which was mostly relative to the inputs of territorial sources.

The significantly higher concentrations of Cu, Pb, Zn and Cd were found at outlets of Minjiang and Jiulong River, suggesting an important input from Minjiang to Minjiang Estuary-Mazu sea area and from Jiulong River to Xiamen-Jinmen sea area.

From the estuaries to open sea, the concentrations of Cu, Pb, Zn and Cd had a decreasing trend, and then increased in the sea areas near Mazu and Jinmen. The results suggesting that Cu, Pb, Zn and Cd in Minjiang Estuary-Mazu and Xiamen-Jinmen sea areas may come from both the mainland and Taiwan of China.

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