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Fe_2O_3 as indicator of heavy metal enrichment in Zhujiang (Pearl River) estuary sediments*

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Abstract: A part of the heavy metals in estuary and coastal zone occurs naturally in the environment; the other part is due to human activity; so the directly measured concentration of heavy metal does not automatically indicate anthropogenic enrichment. Fe_2O_3 was used in this study as conservative tracer to distinguish natural components from anthropogenic components of heavy metal sediment concentration in the Zhujiang estuary. Compared with clay and Al_2O_3, Fe_2O_3 is more suitable as reference element. The final results showed that two zones in the Zhujiang estuary were seriously contaminated by heavy metals. One nearby the Humen mouth; the other around the west coast of the estuary. The horizontal distribution of heavy metals indicates that Zn, Ni and Cu have wider contaminating areas than TiO_2, V and Cr in the estuary.

Key words: Heavy metal pollution, Reference element, Zhujiang (Pearl River) estuary
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INTRODUCTION

The Zhujiang River's delta region is one of China's most densely populated areas. Several economic and industrial centers such as Hong Kong, Guangzhou, Zhuhai, Shenzhen and Macao are around the Lingdingyang. In recent years, along with economic development in the delta region, a large amount of waste was released into the Zhujiang estuary, which may deteriorate the environmental quality of this region (Hills et al., 1998; Li et al., 2000). Knowledge of the degree of heavy metal pollution in the sediments, recognized as comprising a most important pollutant sink, can lead to better understanding the Zhujiang delta region's environmental changes.

The anthropogenic enrichment of heavy metals in the estuary, together with these that occur naturally in the silt- and clay-bearing minerals of terrestrial and marine geologic deposits there, complicates assessments of potentially contaminated estuarine sediments, as measurable quantities of heavy metals do not automatically infer anthropogenic enrichment in the estuary. For assessing heavy metal enrichment, some researchers developed a variety of normalizing techniques to provide baseline relationships. For example, aluminum, iron, rare earth element, lithium, grain size and radioisotope tracers were used as normalizers (Daskalakis et al., 1995; Din et al, 1992; Loring et al., 1990; Schropp et al., 1990). In this study, Fe_2O_3 was used as a normalizer to assess Cu, Ti, Ni, Cr, Zn, V enrichment in the Pearl River estuary.

MATERIALS AND METHODS

1. Study area

The Zhujiang River is the largest river system flowing into the northern part of the

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South China Sea. The estuary is located in a subtropical area with annual rainfall of 1600 to 2300 mm. Lingdingyang where the turbidity maximum zone exists is the major part of the Zhujiang estuary. In this investigation, Lingdingyang was our main study zone (see Fig.1). The N-S distance of Lingdingyang is about 49 km and E-W width is 4 to 58 km. The whole study area within the subtidal zone with strong freshwater and marine water interaction, is influenced by alongshore current; circulation currents flow mainly along the west coast in the Zhujiang estuary all year round except part of summer.

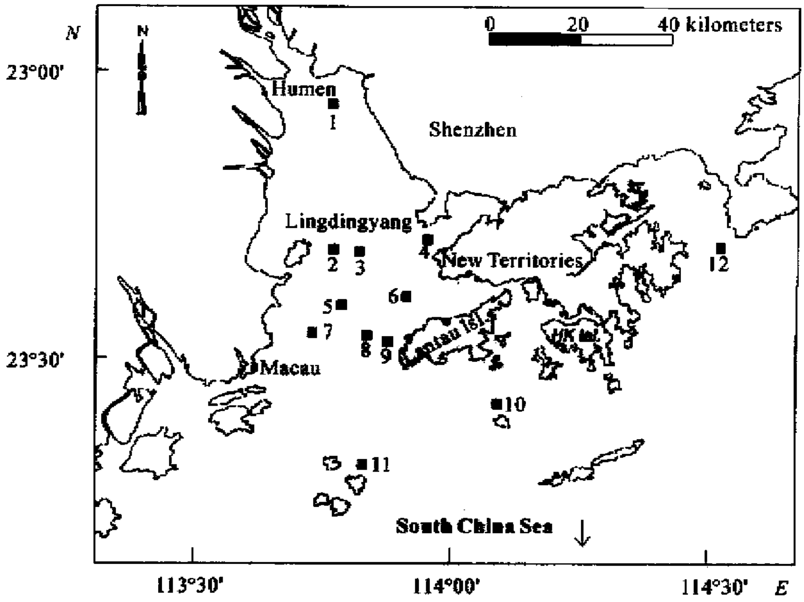

Fig.1 Location of sampling sites in the Zhujiang estuary

2. Sediment sampling and analysis

For this study of the sediment and hydrodynamic characteristic in this region, 12 sediment cores were collected in the Zhujiang estuary (Fig.1). Core samples (surface layer 0 – 45cm) taken with a multibarrel corer were divided into two centimeters sections and stored frozen (< 4℃) immediately after collection until laboratory analysis.

The samples from each core were dried at 100℃, ground in an agate mill to pass a 200 μm sieve and pressed into cakes for putting into a Simens SRS3000 type X-ray fluorescence spectrometer for analyzing elements Fe, Cu, Ti, Ni, Cr, Zn and V. Grain size was determined by a Malvern MAM5005 type laser particle analyzer.

3. Establishing baseline relationship

Two criteria were used to identify unriched site for defining baseline metal-iron reference element relationships. The first criterion was selection of sites distant from known sources of trace metal inputs. Based on vertical and horizontal distribution of the heavy metals, site 11 and 12 were chosen as unriched site. The second criterion was based on identification of outliers from two sites using regression analysis (Daskalakis et al., 1995; Pao et al., 1988; Wu et al., 1983). To meet the requirements of this criterion, a number of regressions between each heavy metal and iron were developed, then the residuals from the regression for normality were examined. We assessed normality using Kolmogorov-Smirnov test. If a normal distribution was not achieved, the values with residuals greater than two standard deviations were eliminated and the regression was recalculated. The testing for normality and selection of outliers based upon standardized residuals was iterated until a normal distribution was achieved.

After Kolmogorov-Smirnov test, baseline

relationship could be obtained between the trace metal of interest and iron. This relationship represented the prediction of naturally occurring heavy metal concentrations. In order to define whether a sample is contaminated or uncontaminated, a threshold that exceeded our expectation was developed. For the purposes of comparing individual samples to the base relationship, double standard deviations were chosen as our threshold for contamination (Pao et al., 1988).

RESULTS AND DISCUSSION

In past studies, aluminum or grain size were usually used as normalizer (Daskalakis et al., 1995; Din et al, 1992; Loring et al., 1990). This time, Fe_2O_3 was chosen instead of aluminum or grain size as reference element, because Fe_2O_3 covaries in proportion to the naturally occurring concentration of the metal in the sediments of the Zhujiang estuary. Comparison of the strength of the regression relationships among the three conservative tracers showed that Fe_2O_3 performed better than grain size or aluminum (Table 1). We can find that Fe_2O_3 had the highest regression coefficients for the six heavy metals. Moreover, Fe_2O_3 is insensitive to the inputs from anthropgenic sources, but grain size may be affected by municipal wastewater discharge. These municipal wastewater inputs not only change levels of pollutants, but also alter the proportions of fine-grain particulate.

Table 1 Comparison of reference element normalizers

Correlation coefficient (r^2)	Fe_2O_3	Al_2O_3	Clay	Number of samples
Fe_2O_3	–	0.962^{**}	0.510^{**}	59
Al_2O_3	0.962^{**}	–	0.665^{**}	59
Clay	0.510^{**}	0.665^{**}	–	59
TiO_2	0.954^{**}	0.875^{**}	0.346^{**}	59
V	0.807^{**}	0.674^{**}	0.013	59
Ni	0.945^{**}	0.951^{**}	0.635^{**}	59
Cu	0.694^{**}	0.601^{**}	0.114	59
Cr	0.943^{**}	0.889^{**}	0.391^{**}	59
Zn	0.971^{**}	0.910^{**}	0.470^{**}	59

** The correlation is significant at the 0.01 level (two-tailed test).

Base relationships using iron as a reference element were highly significant. The correlation between iron and six metals was significant at the 0.01 level (two-asterisks). Most variances in the distribution of metal concentrations could be explained by the covariance with iron. Regression coefficients exceeded 0.75 for TiO_2, Cr, V and Zn except Cu (0.6627) and Ni (0.5760) (Table 2).

Fig. 2 gives plots of the reference element baseline regressions, double standard deviation thresholds. The samples were obtained

Table 2 Regression results of metal-iron baseline relationships in unriched sediment of the Zhujiang estuary [a]

Fe_2O_3(%) versus	Sample number	Mean	r^2	Slope(m)	Intercept(b)	Standard deviation
TiO_2	35	0.6874	0.887	0.1233	0.0629	0.0330
V	35	90.5889	0.9101	25.626	−38.707	6.3393
Ni	35	22.8831	0.5760	6.1064	−7.9263	2.5025
Cu	35	24.5917	0.6629	10.331	−27.531	2.9944
Cr	35	62.7369	0.7866	21.233	−44.393	5.6496
Zn	35	88.5943	0.7743	20.953	−17.121	5.2191

[a] The correlation is significant at the 0.01 level (two-tailed test).

from the surface sediments (0 – 10 cm depth) of 12 stations. The samples between two dotted lines or under the lower dotted line are uncontaminated samples. Samples over the upper dotted line are contaminated samples. The Fig. 2 shows that enrichment degree of the six heavy metals were different. Cu, Ni, Zn were more enriched in almost all samples; V, Cr, TiO_2 were close to or lower than the background value. For Fe_2O_3 concentrations of 0% to 4.5%, the six metals in the samples were all enriched, which indicates that site 1 was seriously polluted by heavy metal.

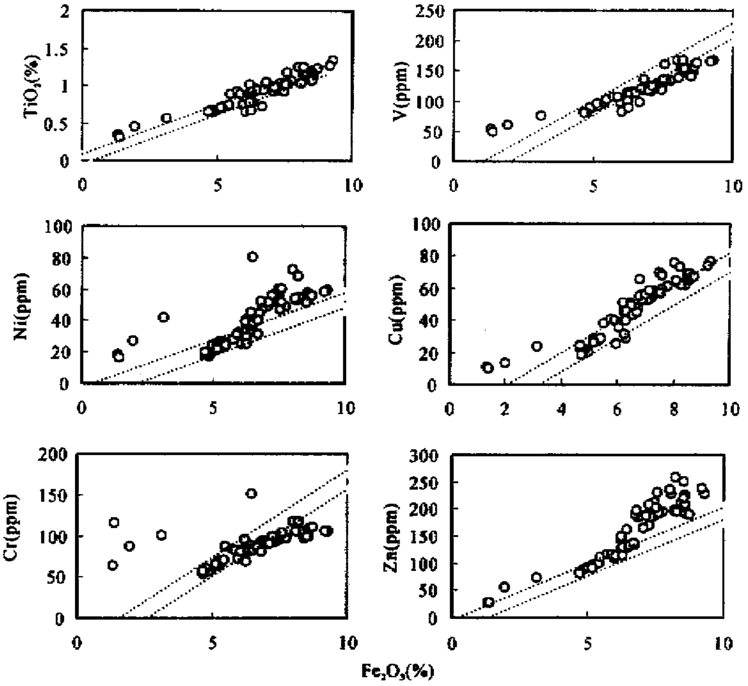

Fig. 2 Metal-Fe_2O_3 plots overlaid with reference element baseline relationships (Samples falling within the prediction interval between two dotted lines or under the lower dotted line were uncontaminated samples. The samples over the upper dotted line are considered anthropogenically enriched).

To obtain insight into the distribution of contaminated areas in the Zhujiang estuary, we used mean heavy metal concentration of surface sediments (0 – 10cm) to plot the heavy metal horizontal distribution. Data interpolation was made by Kriging method. Fig. 3 is the map of areas contaminated by the heavy metals. The contour levels and the filled color denote the gaps between observed concentration and predicted concentration in contaminated sediments. Fig. 3 shows that there are two zones that were seriously contaminated. One is nearby the Humen mouth. The pollution conditions of V, TiO_2, Ni, Cr, Cu except Zn are the worst in this region. The other is around the west coast of the Zhujiang estuary in which TiO_2, Ni and Cu are mainly enriched as well as in the mouth of Humen, into which Zhujiang River mainstream flows. The flow of freshwater into the estuary changes the physical, chemical and hydrological conditions sharply, and under the interaction between the freshwater and brine, large amounts of pollutants including heavy metals deposited rapidly and caused high heavy metal concentration in the surface sediments of this area. The enrichment of heavy metal in the west coast of the Zhujiang estuary is due to two reasons. On the one hand, some branches, for example Xinjing, of

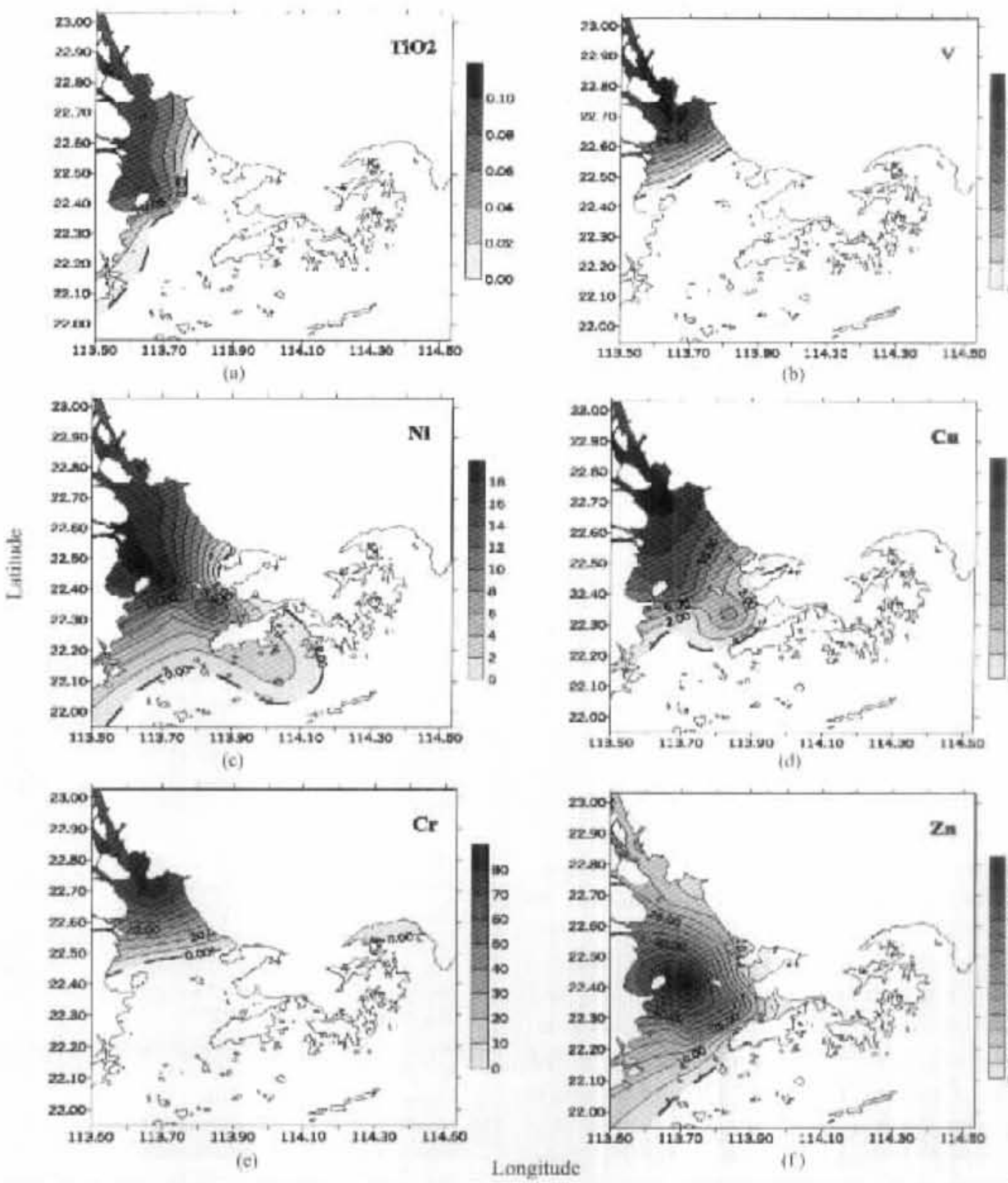

Fig. 3 **Didtributions of contaminated areas in the Zhujiang estuary. Enrichment was assessed using Fe_2O_3 as a reference element to determine background concentrations.**
（a）TiO_2；（b）V；（c）Ni；（d）Cu；（e）Cr；（f）Zn

the Zhujiang River enter the estuary's west coast. Previous work showed that these branches are pollutant sources causing heavy metal enrichment in the west coast of the Zhujiang estuary（Chen et al.，1991a； Li et al.，1981； Li et al.，2000； Ying et al.，1995）. On the other hand，under the influence of alongshore current，the flow of the Zhujiang River is directed to the southwest of the estuary throughout the year，except in part of summer（Chen et al.，1991b； Ying et al.，1995）. Therefore，the west coast of the estuary receives more terrestrial pollutants than the east coast. However，the heavy metal distribution in the Zhujiang estuary is not only controlled by geographical location and hydrological conditions, but also controlled to large extent by chemical characteristics. Some studies revealed that existing species, transfer form, and transfer ability of pollutants could strongly influence the heavy metal distribution in the estuary (Li et al., 1996; Li et al., 2001; Li et al., 1981; Li et al., 1989). Fig.3 showing that the elements Zn, Ni, Cu have a wider contaminating area than TiO_2, V and Cr in the estuary, indicates that Zn, Ni and Cu are to some extent more chemically active in the Zhujiang estuary, where Zn is mainly transformed into the dissolved phase, and so; disperse farther than the other elements (Li et al., 1981; Li et al., 1989). When Zn ions arrive the turbidity maximum zone of Lingdingyang (see Fig. 3), they are adsorbed by colloids and then deposit in the sediments. Therefore, the Zn pollution degree in sediments is highest near the turbidity maximum zone. The highest concentration of Zn in this area could disperse eastward and contaminate the east part of the estuary as a second pollution source.

CONCLUSIONS

Fe_2O_3 was used in this study as a conservative tracer to differentiate natural components from anthropogenic components of heavy metal sediment concentration in the Zhujiang estuary. Regression analysis indicated that Fe_2O_3 is more suitable than clay and Al_2O_3 as a reference element and a good predictor of naturally occurring concentrations of TiO_2, V, Ni, Cr, Zn, Cu. The final results showed that there are two zones seriously contaminated by heavy metal in the Zhujiang estuary. One is nearby the Humen mouth. The other is around the west coast of the Zhujiang estuary. The horizontal distribution of heavy metal indicated that Zn, Ni and Cu have wider contaminating areas than TiO_2, V and Cr in the estuary.

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