CONCENTRATION AND PARTITIONING OF PARTICULATE TRACE METALS IN THE CHANGJIANG (YANGTZE RIVER)

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Abstract. Suspended sediments from the lower Changjiang (Yangtze River) were sampled to determine concentrations of Cu, Cd, Pb, Ni, and Cr. The particulate trace element values in the Changjiang are higher than in the Huanghe (Yellow River), but lower than in the other large Chinese rivers (e.g. Pearl River) and polluted rivers. A general pattern of high element levels in the clay minerals and low element concentrations in coarse sediment fractions are observed in the Changjiang. Sequential extraction shows the predominance of metals in the residual fraction relative to labile fractions in the Changjiang, emphasizing the importance of natural weathering and erosion in the drainage basin on the transport of particulate metals. Elevated Enrichment Factors (EF: the ratio of element concentration in microsurface to that in subsurface layer minus 1.0) suggest a potential influence of atmospheric input on the concentrations of particulate metals in the river.

1. Introduction

Industrialization is often followed by environmental contamination, especially in developing countries. The annual waste water discharge in China has passed 35.0×10^9 t, with waste water treatment available for only about 5% of the total discharge (Huang and Zhao, 1987). Recent work indicates that surface water pollution is common in the primary tributaries of river systems, whereas more severe conditions have been observed in secondary tributaries (Huang and Zhao, 1987).

Rivers are the major pathway by which both the natural weathering products and pollutants reach the ocean, they carry seaward 90% of the worldwide dissolved and suspended solids (Presley *et al.*, 1980). The total water discharge and sediment load of Chinese rivers are estimated ca. 1.8×10^{12} m^3 yr^{-1} and 2.0×10^9 t yr^{-1}, respectively (Cheng and Zhao, 1984), accounting for 5% of the total water and 15% of the total suspended sediment globally. Despite the importance of water and sediment transport by the Chinese rivers to the West Pacific Ocean, the geochemistry of these river/estuary systems still remains poorly known. Recent studies at several large Chinese river estuaries (Lin *et al.*, 1982; Zheng *et al.*, 1982; Milliman *et al.*, 1984; Demaster *et al.*, 1985; Edmond *et al.*, 1985; Zhang, 1985; Elbaz-Poulichet *et al.*, 1987; Zhang, 1988; Zhang *et al.*, 1988) have begun to improve our knowledge base.

With a mean water discharge of 928.2×10^9 m^3 yr^{-1}, the Changjiang (Yangtze River) is the fourth largest fresh water source to the ocean (after the Amazon, Zaire and Orinoco). The annual sediment load of the Changjiang averages 0.5×10^9 t, with a mean suspended sediment concentration of 0.54 g L^{-1}. The lower part of the river is significantly influenced by the tidal dynamics. Previous studies have shown a tide affected zone of 200 to 250 km in the lower Changjiang, even during the high water discharge period (Chen and Shen, 1987). The tidal range averages 2.5 to 4.0 m, near the river mouth. Tidal dynamics have an important influence on water circulation and sediment transport in the Changjiang estuary (Shen *et al.*, 1986; Chen and Shen, 1987).

The present paper reports the distribution of particulate transition metals among different particle size fractions, their chemical forms, and microsurface behavior in the lower part of the Changjiang. This work was undertaken to obtain more information about the chemical speciation and particle size control of transition metal concentrations, as well as the potential atmospheric influence in the Changjiang.

2. Sample Collection and Methods

Monthly water discharge and suspended sediment concentration of the Changjiang during the sampling period (September-October, 1984) average 41.0×10^3 m^3 s^{-1} and 0.75 g L^{-1}, respectively, being higher than mean annual values. River water samples for this study were collected with precleaned polyethylene bottles in the lower part of the Changjiang (Figure 1). Subsurface water samples for particulate element concentration analysis were collected 0.5 m below the water surface, and filtered with acid cleaned Sartorius filters (0.45 μm). Particle size fractions were obtained by wet sieving with precleaned nylon screens, to separate the suspended sediment into the following size fractions: >155 μm, 155 to 70μm, 70 to 50 μm, and <50 μm. The suspended sediments smaller than 50 μm were further separated into <16 and <2 μm fractions, respectively, according to the 'Stokes' equation. Microsurface samples (150 ± 50 μm) were taken with a precleaned nylon screen (mesh 12) with plexiglass frame on the calm river surface. The method was described in detail elsewhere (Zhang and Huang, 1988).

TABLE I

Data for metals in Chinese GSD standard samples (GSD–4). For detailed information of Chinese GSD standards, see Xie and Yan (1985)

Element	GSD–4 μg g^{-1}	This study μg g^{-1}	$\sigma x/\bar{x}$ (n=11)	Detection limit μg g^{-1}
Cu	37.3±3.2	34.6	1.3%	0.01
Cd	0.19±0.03	0.20	0.6	0.0006
Ni	40±5	38.8	3.2	0.1
Pb	30.4±6.9	29.8	0.7	0.005

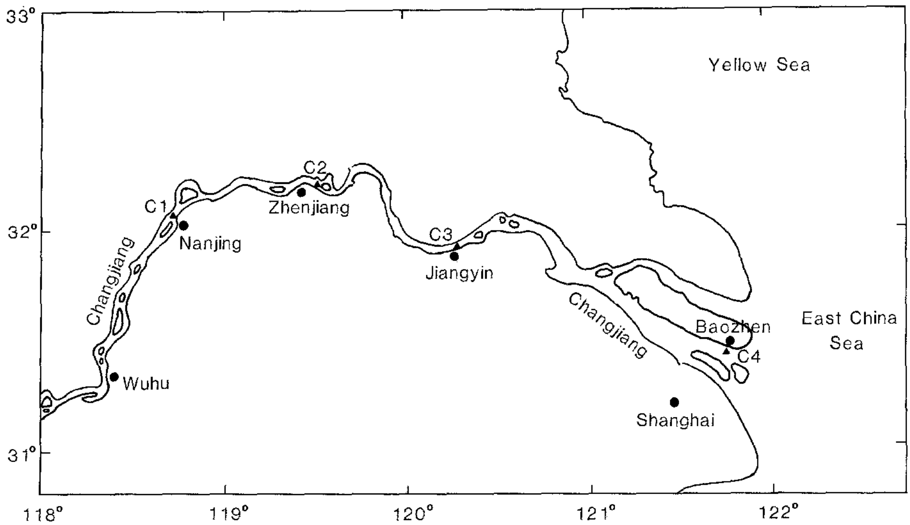


Fig. 1. Sample locations in the lower Changjiang. The cruise to the Changjiang was carried out in Autumn 1984.

In the laboratory the suspended sediment was digested with HNO_2–HF–$HClO_4$ in a closed Teflon system (Zhang *et al.*, 1988). The solution was analyzed using PE–370 GFAAS with deuterium background correction to determine the concentrations of Cu, Cd, Pb, Ni, and Cr. To estimate the quality of the analysis, we participated in inter-laboratory calibrations in China. Comparison between our data and those of the other marine laboratories shows satisfying results (Zhang, 1985). The precision and accuracy of this study were estimated through repeated analysis (n=11) of Chinese GSD standards (Table I). Reagent blanks were lower than the detection limit.

Several sequential extraction procedures have been proposed to study the speciation of the chemical elements in sediments (Chester and Hughes, 1967; Gibbs, 1977; Tessier *et al.*, 1979; Forstner *et al.*, 1981). However, it must be kept in mind that chemical forms of elements in the sediment may be very complicated, and that data from the sequential extraction experiments can only be operationally defined as a function depending on the intensity of the chemical reagents used and the treatment (e.g. pH, temperature, time, and ion strength, etc.) of each extraction process. With these caveats in mind, we used the extraction method of Tessier *et al.* (1979, 1980) in this study to sub-divide the particulate metals into five sub-fractions (Huang *et al.*, 1985) as follows:

(1) Exchangeable fraction (F1) – 15 mL CH_3COONa (1.0 M), pH=8.2;

(2) Carbonate fraction (F2) – 15 mL CH_3COON_a (1.0 M) + CH_3COOH, pH=5.0;

(3) Hydroxide fraction (F3) – 25 mL NH_2OHHCl (0.04 M, 25% V/V CH_3COOH, 98±2 °C;

(4) Organic matter fraction (F4) – 3mL HNO_3 (0.02 M) + 5 mL H_2O_2 (30%) 84±2 °C, two times; and

(5) Residual fraction (F5) – 6 mL HNO_3 + 3 mLHF + 2 mL $HClO_4$.

The quality of the sequential extraction experiments are estimated by the ratio of the sum of element levels in the five subfractions to the total element concentration, and are generally 90 to 110% (Zhang, 1985).

All equipment for the sample collection and laboratory experiments were pre-cleaned with methods reported by Huang (1983), as well as Zhang and Huang (1988). The mineral composition of the suspended sediments from the Changjiang was identified by X-ray diffraction (Zhang, 1985).

3. Results

3.1. Particulate Metal Concentrations

Particulate Cd and Ni in the lower Changjiang (Table II) show practically no differences between subsurface samples at these stations. In contrast, values for Cu, Pb, and Cr display a relatively high concentrations at Jiangyin and low concentratipons at Nanjing (Cu, Cr) or Baozhen (Pb), whereas the other stations show intermediate values. Table II shows little variation in element concentrations for subsurface samples over a distance of about 450 km along the Changjiang with a coefficient of variance ($\sigma x/\bar{x}$) of 2 to 15%. This probably reflects the natural fluctuations in element concentrations due to the difference of mineralogy and granulometry of the suspended sediments. Local anthropogenic contamination at sampling stations may affect the element concentrations, because the samples were taken close to industrial and dense population regions. As indicated in Table III, the Changjiang shows relatively high particulate metal concentrations compared with the Huanghe (Yellow River). The Qiantangjiang and Zhujiang (Pearl River) display even higher values for some metals than those found in the Changjiang (Table III). The high metal concentrations in the Qiantangjiang and Zhujiang may

TABLE II

Particulate transition metal concentrations ($\mu g\ g^{-1}$) in the lower part of the Changjiang. The sample locations are shown in Figure 1

Station	No.	Cu	Cd	Pb $\mu g\ g^{-1}$	Ni	Cr	Remark
Nanjing	C1	55.2	0.30	46.2	121.6	135.7	subsurface
		68.2	0.54	109.8	111.0	142.2	microsurface
Zhenjiang	C2	64.1	0.31	50.7	121.5	148.2	subsurface
Jiangyin	C3	68.6	0.35	61.9	125.1	172.6	subsurface
		76.7	0.48	119.0	121.7	174.6	microsurface
Baozhen	C4	61.7	0.32	41.6	127.7	141.6	subsurface
		103.0	0.44	76.5	142.0	163.9	microsurface

TABLE III

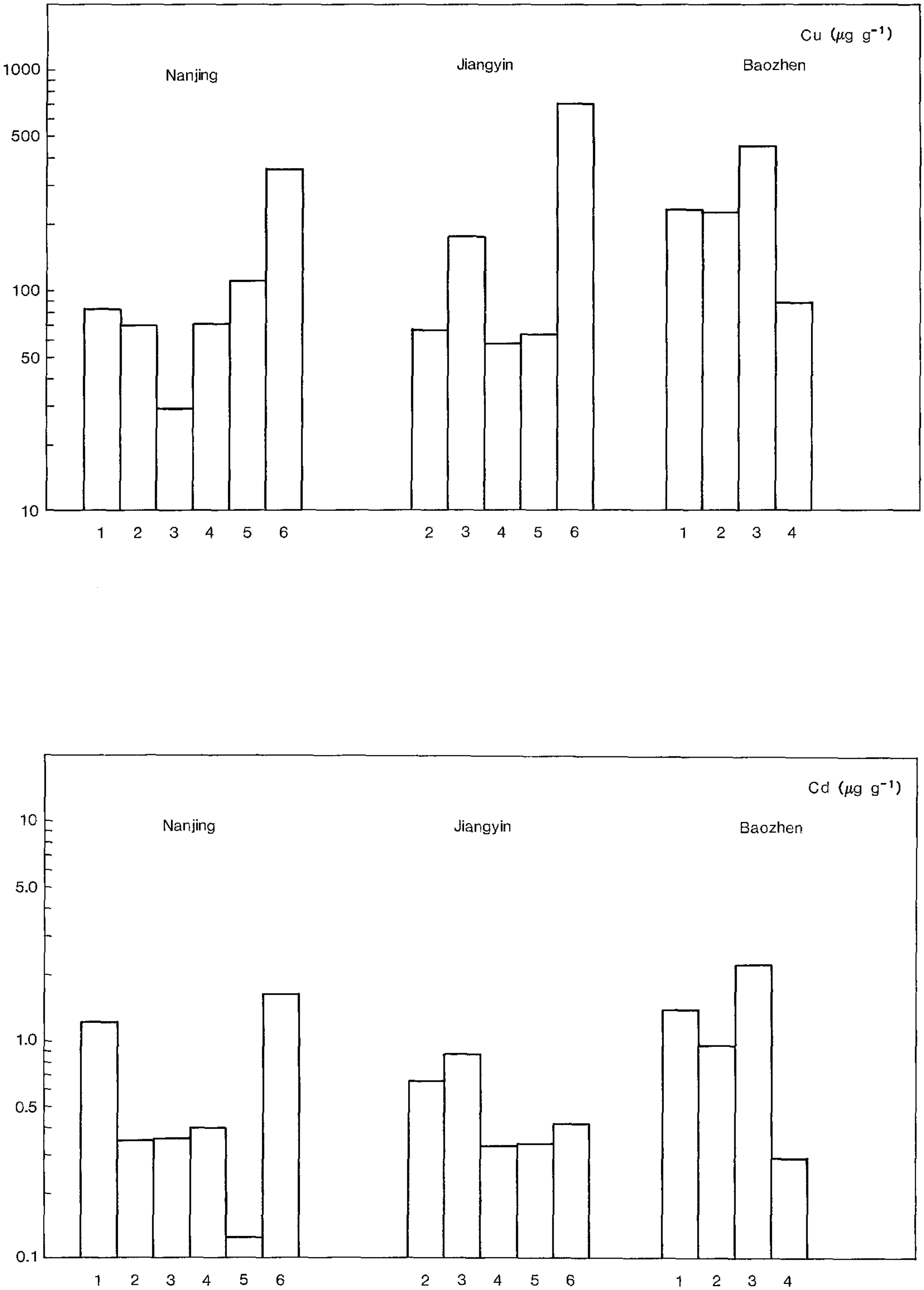
Comparison of particulate trace metal concentrations (μg g^{-1}) between Chinese rivers and the mean world river values. The element concentrations of the world soils are also shown here

Rivers	Cu	Cd	Pb μg g^{-1}	Ni	Cr	References
Changjiang	62.3	0.32	50.1	124.0	149.5	This study
Huanghe	30.1	0.20	34.1	42.6	75.8	Zhang, 1985
Qiantangjiang	89.3	0.30	76.0	92.6	161.8	Zhang and Huang, 1988
Zhujiang	42.6	1.58	63.3			Qu *et al.*, 1984
Haihe	89.0–436.1	0.94	77.5–292.1	51.9–>500		Zhang, 1985
Xiaoqinghe	10.5–35.7	0.03	5.7–15.4	9.1–23.4	68.8	Zhang, 1985
World mean	100	1.0	100	90	100	Martin and Gordeev, 1986
World soils	2–100	0.01–7	2–200	10–1000	5–3000	Aubert and Pinta, 1977; Bohn *et al.*, 1985

be in part due to the influence of anthropogenic activities (Li *et al.*, 1981; Zhang and Huang, 1988). Among the rivers in the Table III, much higher particulate metal levels are found in the Haihe, which passes Tianjin, the third largest city of China, and is considered to be seriously polluted (Zhang, 1985). Compared with results from the other large rivers of the world, the Changjiang has metal concentrations lower than or similar to those of the Amazon, Zaire, and Orinoco (Martin and Meybeck, 1979). All these rivers were considered to be less affected by anthropogenic activities than the European rivers, and the element concentrations in these rivers reflect mainly natural weathering characteristics over the drainage basin (Martin and Meybeck, 1979). An important difference (30 to 70%) is also found beween the particulate transition metal concentrations of the Changjiang and the mean world river values (Martin and Gordeev, 1986). The implication of this is that a simple comparison between the trace element levels of one individual river (e.g. Changjiang) and mean world values can give little or no information about what the river as a whole may do. The chemical composition of suspended sediment from one river is mainly controlled by the relative importance of local weathering/erosion and anthropogenic activities over the drainage basin. For the rivers with high turbidity and draining in poorly industrialized regions, the chemical composition of rock/soil and weathering of the drainage basin are of primary importance on their particulate trace element concentrations (Zhang, 1988). The X-ray diffraction data show following distribution of clay minerals: illite, for 60 to 65%; chlorite 15 to 20%; smectite, 10 to 15%; and kaolinite, 5 to 10%.

3.2. Particle size influence

As shown in Figure 2, most of the metals studied display a general pattern of higher concentrations in the clay mineral size fraction ($<=2$ μm), whereas coarse sediments (>2 μm) are characterized by relatively lower values. Similar observations



Cu (μg g⁻¹)
Nanjing
Jiangyin
Baozhen
1000
500
100
50
10
1 2 3 4 5 6
2 3 4 5 6
1 2 3 4
Cd (μg g⁻¹)
10
5.0
1.0
0.5
0.1

Fig. 2.

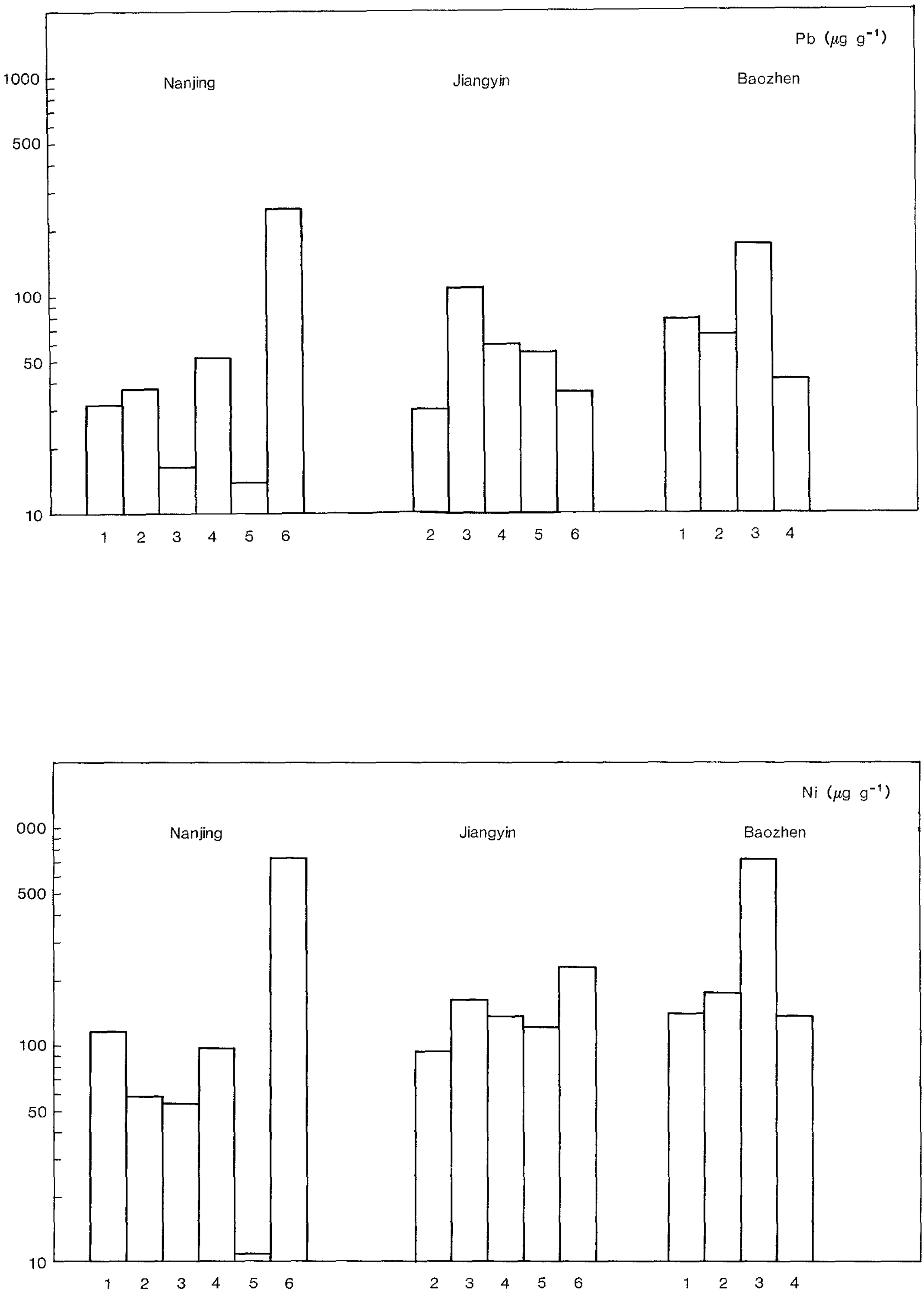

Pb (μg g⁻¹)
Nanjing
Jiangyin
Baozhen
1000
500
100
50
10
1 2 3 4 5 6
2 3 4 5 6
1 2 3 4
Ni (μg g⁻¹)
Nanjing
Jiangyin
Baozhen
000
500
100
50
10
1 2 3 4 5 6
2 3 4 5 6
1 2 3 4

Fig. 2.

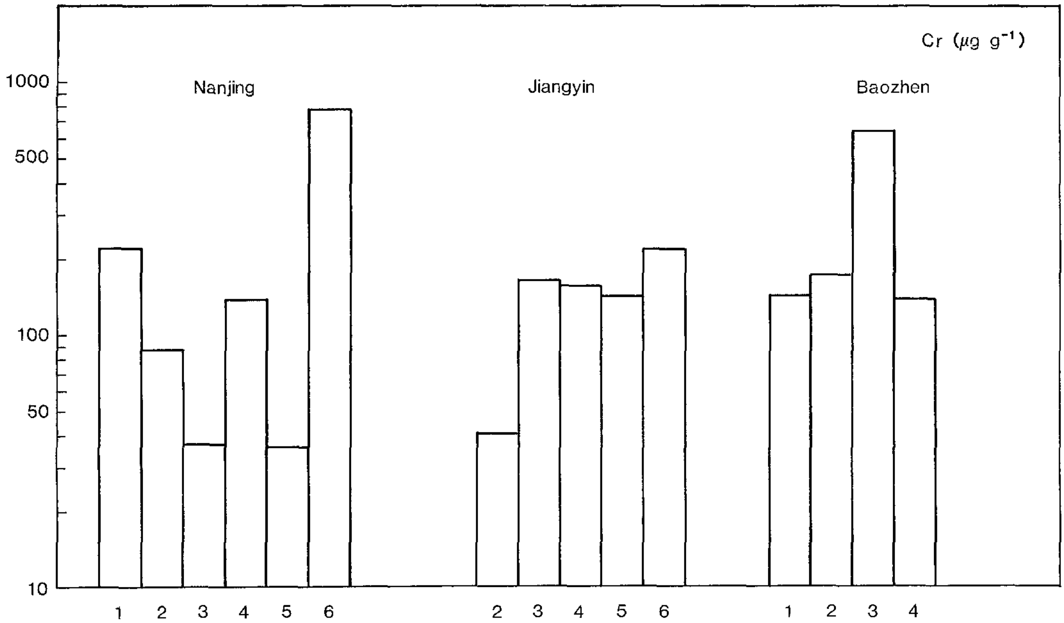


Fig. 2. Concentration of the particulate transition metals (μg g^{-1}) in different particle size fractions in the Changjiang. (1) >= 155 μm; (2) 155–70 μm; (3) 70–50 μm; (4) <50 μm; (5) <16 μm; (6) <2 μm.

have been made for other rivers (Gibbs, 1977; Brook and Moore, 1988). This reveals the enrichment of transition metals in the clay minerals from the Changjiang, which is probably a result of both element adsorption due to their high surface area to volume ratio and ion exchange in clay mineral lattice. Quartz, feldspars, and carbonate are important minerals in coarse sediments of the Changjiang (Yang and Milliman,1983; Zhang and Xie, 1984), and are relatively metal poor phases as compared to the heavy minerals (Gibbs, 1977; Windom *et al.*, 1989). However, certain particle size fractions (e.g. >155 μm, etc.) of coarse sediments (>2 μm) show high element concentrations during this cruise (Figure 2), presumably reflecting the contribution of heavy minerals in suspended sediment.

From Nanjing to Baozhen (river mouth), most of the metals show a decrease of element concentrations in the clay size fraction and a weak increase in the coarse particle size fractions (>2 μm) (Figure 2). Without granulometry and POC (particulate organic C) data, the reason of such a variation is still not clear. This is most likely related to the difference of particle size and mineral compositions of the suspended sediment in the sampling area, since previous studies emphasize that the tidal dynamics can affect 600 to 650 km of the river channel in land the river mouth and the suspended sediment regime in this region is controlled by the combination of river discharge and tidal dynamics (Shen *et al.*, 1985; Chen and Shen, 1987). Furthermore, the turbidity maximum zone in the estuary where the total suspended sediment concentration ranges from 0.1 to 1.0 g L^{-1} in surface and 1.0 to 10.0 g L^{-1} in near bottom layers, affect an area of 25 to 50 km in the river channel, and has a remarkable influence on the river mouth evolution.

3.3. Speciation of the Particulate Metals

Figure 3 shows the results of sequential extraction of the suspended sediments from the Changjiang. The most remarkable characteristic of the element distribution among different chemical forms is the predominance of crystalline phases (carbonate + silicate) which account for >70% of total particulate transition metals. In general, the elements in the exchangeable fraction are <5%; the carbonate fraction represents 1 to 15%, corresponding to an average carbonate concentration of about 5% in the suspended sediments (unpublished data). Hydroxides fraction is the most important among the labile fractions (F1 – F4), the elements in this fraction occupies 8 to 25%, as a result of high hydroxides content of soils in the South China (Gong, 1986). Organic matter fraction is <5 to 10% of the total particulate metal concentrations due to most likely low organic matter content as indicated by a mean POC value of 0.5 to 1.5% in the Changjiang (G. Cauwet, personal communication). The residual fraction is the most significant fraction with 60 to 65% for Pb and from 85 to 90% for Cr, the other elements show intermediate values. Such an element distribution pattern among different chemical forms of suspended sediment from the Changjiang is similar to the observations from the Amazon and Yukon Rivers (Gibbs, 1977), and to those of the Huanghe (Huang *et al.*, 1988),

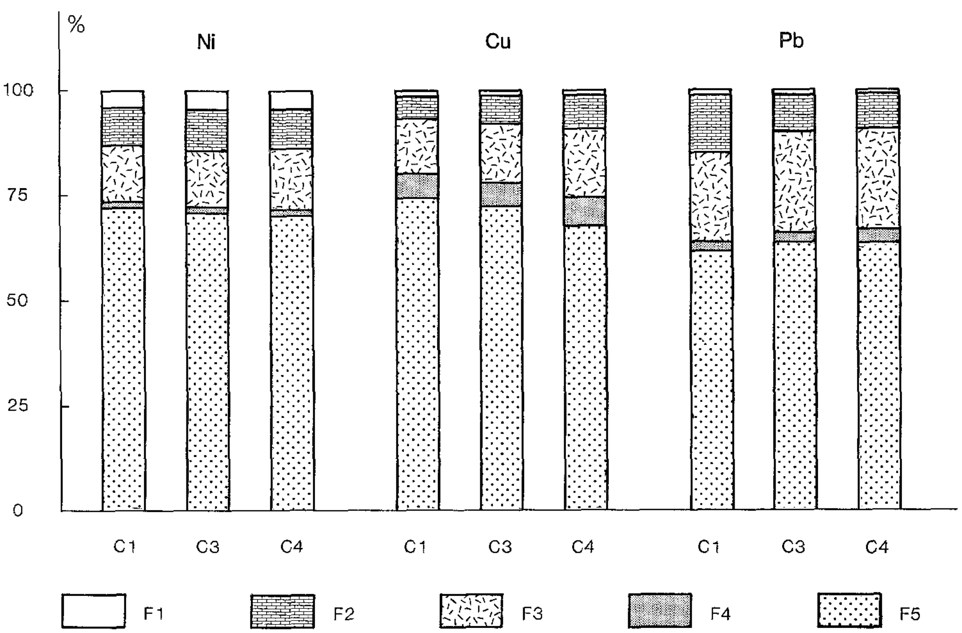


Fig. 3. Sequential extraction of suspended sediments in the Changjiang. (F1) exchangeable fraction; (F2) carbonate fraction; (F3) hydroxide fraction; (F4) organic matter fraction; (F5) residual fraction.

but shows much difference from the results from the polluted river/estuary systems such as the Rhine River (Hong and Forstner, 1984) and some other rivers in Europe (Salomons and Forstner, 1980, 1984; Schoer and Eggersgluess, 1982), in which the labile fractions are often more important than crystalline phases.

3.4. Microsurface enrichment

It is well known that atmospheric transport may be an important source of trace elements in the aquatic environment. Table IV shows the 'EF' value of particulate transition metals in the lower part of the Changjiang. The EF value in the Table IV is defined as the ratio of element concentration in microsurface over that in subsurface minus 1.0 (Table IV). Copper, Cd, and Pb display high EF values, indicating an enrichment of these elements in the microsurface as compared to subsurface samples. However, Ni and Cr generally show no enrichment in the microsurface layer for which the EF values range from −0.09 to 0.15. Relatively high EF values of Ni and Cr (>0.1) are only found at Baozhen (Table IV). Since the sampling stations in this study are close to industrial/residential centers and/or main channel of the Changjiang, the high EF values reveal the influence of temporal atmospheric pollution in this region. Similar conclusions have been made on the Qiantangjiang in the South China (Zhang and Huang, 1988). Indeed the atmospheric pollution in the Changjiang drainage basin has been reported by recent studies (Zhao and Sun, 1986; Huang and Zhao, 1987). The organic compounds of Cd and Pb are widely used as antiknock agents in liquid fuel. The combustion may serve as main aource of these elements in the atmosphere and the microsurface layer of the river.

4. Discussion

With an enormous water discharge and huge sediment load, the self-purification capacity of the Changjiang may be high. Waste discharge into the Changjiang will be rapidly diluted in the river and its estuary (Zhang, 1988). In this case, the particulate transition metal concentrations of the river reflect mainly the contribution of natural weathering and erosion products from the drainage basin. Previous studies indicated that most of the suspended sediment in the Changjiang is supplied from the upper

TABLE IV

Enrichment of particulate metals represented as 'EF' values in the microsurface layer of the Changjiang. EF = (element concentration in microsurface layer/element concentration in subsurface layer) − 1.0

Station	Cu	Cd	Pb	Ni	Cr
Nanjing	0.24	0.80	1.38	−0.09	0.05
Jiangyin	0.12	0.37	0.92	−0.03	0.01
Baozhen	0.69	0.38	0.84	0.11	0.15

reaches of the river and by the tributaries in the northern part of the drainage basin (Shi *et al.*, 1985; Shen *et al.*, 1986). These sediments are produced mainly in an orogenic zone of Mesozoic Era (Mz) – Cenozoic Era (Kz), and the chemical composition of the suspended sediments are controlled by the weathering and erosion of the rock formations (sedimentary rocks, granites, and metamorphic rocks) in this region. The complicated rock composition is much different from the sediment source of the other large Chinese rivers such as the Huanghe (loess) and the Zhujiang (granite + carbonate). The chemical compositions of rock/soil in the drainage basin are of primary importance in affecting the chemical composition of the suspended sediment in the river.

As mentioned above, the element distributions among different particle size fractions of the suspended sediments shows several differences among the sampling stations. This results most likely from the role of particle size/mineral phase on the metal concentrations of the Changjiang. The granulometry of the suspended sediments in the river suffers the influence of the hydrodynamics when the river flows from the upper reaches to the river mouth, and such a phenomenon is further complicated in the lower part of the Changjiang owing to the relatively strong tidal influence from the East China Sea. Besides saline water intrusion, the effect of the tidal dynamics on the lower Changjiang behaves mainly as the semidiurnal – diurnal variation of river water level and shoal formation in the study area. Due to the tidal intrusion the water current is slowed down in the lower part of the river course. The coarse sediments will preferentially deposit towards the bottom, and the population of fine particles in surface water increases as a result of both their relatively low sedimentation rate and the hydrographic condition strong enough to prolong their residence time in the water column. However, this general situation is often disturbed by the resuspension of bottom sediments which occurs as the result of either river bed erosion due to the change of the river dynamical regimes or the tidal/wave action in the estuary which induce an onshore sediment transport in the Changjiang estuary (Milliman *et al.*, 1985; Shen *et al.*, 1986). These hydrographic and dynamic processes may play an important role in affecting the particle size and mineral compositions, as well as the element concentrations of suspended sediments in the Changjiang.

The predominance of the crystalline phases over the other chemical forms reveals the importance of natural weathering processes on the transport of the particulate elements in the Changjiang. This is similar to the observations in some other large rivers of the world such as the Amazon River (Gibbs, 1977), and the large Chinese rivers, for example, the Zhujiang (Lin *et al.*, 1982) and the Huanghe (Huang *et al.*, 1988). All these rivers are characterized by abundant water discharge and/or high river suspended sediment concentration. The anthropogenic contamination to most of these rivers is considered to be not important as compared to some of the European rivers (Rhine, Gironde, Rhone, etc.) which drain the industrialized regions and suffer serious human being contamination (Elbaz-Poulichet *et al.*, 1984; Salomon and Forstner, 1980, 1984). In these polluted rivers, the total particulate metal concentrations increase and the relative contribution of the residual fraction decreases. It seems that the trace metal content of hydroxides fraction is particularly sensitive to anthropogenic perturbations (Salomons and Forstner, 1984). The same conclusions were also made for the Mississippi River (Presley *et al.*, 1980), as well as the Yamaska and St. François Rivers (Tessier *et al.*, 1980). Long term records show a mean suspended sediment concentration of 0.54 g L^{-1} at the Datong Hydrographic Station (625 km inland the river mouth), much higher suspended sediment concentrations such as 1 to 2 g L^{-1} are found in the upper reaches and some large tributaries of the Changjiang. This suggests an important physical weathering and erosion over the drainage basin of the Changjiang, corresponding to a mean annual erosion modulus of 500 to 550 t km^{-2} in the upper reaches of the river (above Yichang) and 250 to 300 t km^{-2} over the whole river drainage basin. The organic matter content as represented by POC (0.5 to 1.5%) is relatively low and plays an unimportant role in affecting particulate transition metals in the Changjiang. Rapid economic development and population growth with the lag of environment protection result in a common aquatic system pollution in China, and this is more serious in some affluents (Huangpujiang, Suzhouhe, etc.) draining through the large cities and dense population areas in the Changjiang drainage basin. This poses a potential threat to the water management and aquatic ecosystems of the Changjiang.

Without the atmospheric monitoring data, the danger of air pollution to aquatic system can not be judged. However our data on microsurface present a preliminary estimate of atmospheric transport of trace metals to the Changjiang: the high EF values observed at the stations in the lower Changjiang reflect most likely the impact of atmospheric inputs. Recent studies revealed that nationwide emission of pollutants into the atmosphere reached 4.2×10^9 t yr^{-1} of which 50% is in the form of dustfall (Huang and Zhao, 1987). Air pollution is common over the Changjiang drainage basin, especially in the middle and lower reaches of the river. An example is the acid rain which occurs mainly due to the SO_2 pollution. The frequency of the acid rain may account for 70% of total rainfall in the southewestern part of China (Huang and Zhao, 1987).

5. Conclusion

During a cruise to the lower Changjiang in Autumn 1984, higher particulate metal concentrations were found as compared with the Huanghe. A significant difference between the particulate transition metal concentrations of the Changjiang and the mean world river values is also observed.

The disequilibrium between the economical development and environment protection results in contamination of some primary and secondary tributaries of the Changjiang, but the pollutants may be largely diluted when they enter the Changjiang because of its enormous water discharge and sediment load. Sequential extraction experiment shows the predominance of crystaline phases on the transport of the particulate transition metals in the Changjiang, indicating the control of natural weathering and erosion processes on the level of particulate transition metals in large Chinese rivers. Most of the elements show higher concentrations in fine sediment fraction (<=2 μm) which is most likely due to the affinity of clay minerals with trace elements. In general, the coarse sediment fractions have relatively low transition metal concentrations, presumably this is related to the abundant metal poor minerals, such as quartz and feldspar in coarse sediments. The enrichment of transition metals in microsurface may serve as an index of the potential atmospheric transport to the aquatic systems.

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