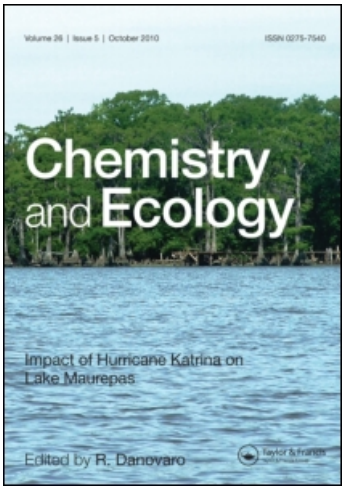

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SPECIES OF TRACE METALS, ORGANIC RESIDUES AND HUMIC SUBSTANCES IN SEDIMENTS FROM THE TAIWAN ERHJIN RIVER AND COASTAL AREAS

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Total organic carbon, humic substances, and the species of trace metals (including Cu, Zn, Pb, Cd, Cr, Mn and Fe) in six and seven phases, such as bioexchangeable (P1), skeletal (carbonates, P2), easily reducible (Fe and Mn oxides, P3), moderately reducible (crystalline Mn oxides, P4), organic matters with sulphides (P5), and detritus with minerals (P6) as well as organic with humic substances (PB4) and organic residues (PB6), were analyzed in sediments from the Taiwan Erhjin coastal (including river and estuarine) area, where places we found the copper pollution. Results indicate that higher percentages of P1 and P2 for copper, zinc, lead, cadmium and manganese in samples collected in March and September of 1990 were much higher than those in P3–P6. High percentages of chromium and iron in samples respectively collected in March and September of 1990 were found in P6. For the seven phase analysis, higher percentages of copper species in PB4 and PB6 as well as iron species in PB7 were observed. On the other hand, purified humic acid with the high contents of manganese and iron in humic acid as well as purified fulvic acids were generally found at the upstream stations; and low values at coastal stations. However, extremely high copper (as high as $1750\,\mu g\,g^{-1}$, dry weight in fulvic acid and $820\,\mu g\,g^{-1}$ in humic acid) and lead ($821\,\mu g\,g^{-1}$ in humic acid) concentrations with relatively high manganese and iron concentrations were observed in humic substances from the station near the copper recycling area. Comparing the results obtained from the Antarctic Ocean sediments with those from the Taiwan Erhjin Chi coastal sediments, the human impacts on the latter are evaluated.

Keywords: Trace metals; Trace metal species; Humic and fulvic acids; Total organic carbon; Taiwan Erhjin Chi coastal sediments

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During the past few decades, highly industrialization and urbanization have been taking place in Taiwan, accompanied by an increase in heavy metal pollution together with organic pollution in the coastal environment, especially near estuaries (Hung *et al.*, 1995; Hung, 1993; Lee and Fang, 1996a, 1996b). For instance, the high contents of cadmium (as high as 1,320 $\mu g\, g^{-1}$ with an average of $378 \pm 216\, \mu g\, g^{-1}$) and lead (as high as 12,700 $\mu g\, g^{-1}$ with an average of $3{,}150 \pm 3690\, \mu g\, g^{-1}$), discharged from industries, were found in the surface soils (0–10 cm) of agricultural environments (Hong *et al.* 1983). The extremely high concentrations of lead ($1420 \pm 709\, \mu g l^{-1}$) were usually observed in the industrial waste water, and the lead concentrations (with an average of $273 \pm 494\, \mu g l^{-1}$) in river water from down-stream sections were also high (Han *et al.*, 1992). The copper pollution causing green colouration of oysters (*Crassostrea gigas*) and mortalities were observed in both mariculture and wild oysters off the Erhjin Chi coast of Taiwan (Hung, 1988; Goldberg, 1993). The extremely high copper contents (4400 $\mu g\, g^{-1}$, dry weight) in oysters associated with high concentrations of particulate and nonlabile organic copper were found in water off the Erhjin Chi coastal area in January of 1989 (Hung and Han, 1992; Hung and Chuang, 1994; Han *et al.*, 1996).

Since Chester and Hughes (1967) first proposed a method for the separation of metal species from pelagic sediments by combination extraction, there have been several studies (Chester *et al.*, 1988; Aplin and Cronin, 1985; Forstner and Patchineelam, 1980) using this method. The species of copper and zinc in mud and sand, separated from the surface sediments from the Antarctic Ocean and the Taiwan Erhjin Chi coast have also been studied (Hung *et al.*, 1993). This paper is a continuation of studies on the distributions of sedimentary heavy metals (Cu, Zn, Pb, Cd, Cr, *etc.*) speciation with organic residues (as total organic carbon) and humic substances along the Taiwan Erhjin Chi river system: the riverine, estuarine and coastal environments. Comparing the results obtained from the Antarctic Ocean sediments with those from coastal sediments of Taiwan, the human impacts on the latter are evaluated.

METHODS

Sediment samples were collected by the dredging technique on board either the research vessel "Ocean Researcher 1" or fishing boats along

the Erhjin Chi coastal area (stations 3–12 and R8–R9 with depths ranging from 5 to 20 m) including the river (stations 1 and R1–R6) and estuary (stations 2 and R6) during the periods March 15–17 and September 20–22, 1990 (Fig. 1A); December 4–12, 1992, and

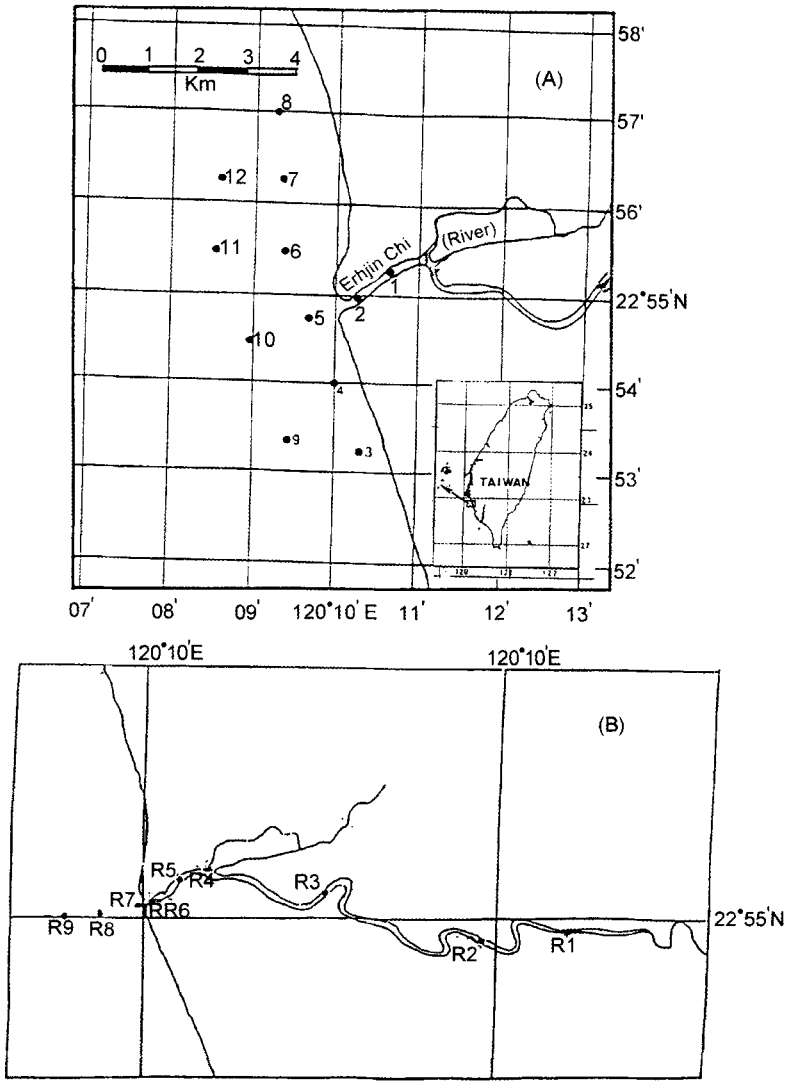

FIGURE 1 Sampling locations along the Taiwan Erhjin Chi coastal (including river and estuary) area (A: March 15–17 and September 20–22, 1990; B: December 4–12, 1992 and August 19–23, 1996).

September 4–6, 1997 (Fig. 1B). Immediately after collection, the mud (grain size $< 63\,\mu m$) and sand (grain size $> 63\,\mu m$) fractions in the sediments were separated by the wet sieving method (ASTM Standard No. 230), and then the total organic carbon (TOC), humic substances and heavy metals (such as copper, zinc, lead, cadmium, chromium, manganese and iron) as well as the species of these metals were analyzed. TOC was determined with a LECO Carbon Analyser and the humic substances (such as humic and fulvic acids) were extracted and isolated (Kuo *et al.*, 1993). The dried and isolated humic or fulvic acids were digested with a mixture of nitric and hydrofluoric acids (2 : 1, v/v), and then the total amount of trace metals were analyzed with a graphite atomic absorption spectrophotometer (Hitachi Z-8000). The species of heavy metals, such as exchangeable, skeletal (carbonates), easily reducible (Fe and Mn oxides), moderately reducible (crystalline Mn oxides), organic matter with sulphides, and detritus with minerals, were analyzed by a sequential leaching technique shown in Table IA (Hung *et al.*, 1993). Furthermore, the species of organic matter with sulphide was separated into the species

TABLE IA Scheme of classification of metal forms and species in sediments (Modified from Hung *et al.* 1993)

Phase	*Treatment*	*Association*	*Form/Species*
P1	Extract with 1 M ammonium acetate (pH = 7)	Exchangeable	Particulate, Labile
P2	After 1, extract with 1 M sodium acetate (pH = 5)	Skeletal phase (Carbonates)	Particulate, Non-labile
P3	After 2, extract with 1 M Sodium acetate + 0.25 M Hydroxylamine hydrochloride (pH = 5), overnight	Readily reducible (Fe and Mn oxides)	Particulate, Labile
P4	After 3, extract with 25% acetic acid + 0.25 M hydroxylamine hydrochloride at 75°C for 6 hours	Moderately Reducible (Crystalline Mn oxides)	Particulate, Non-labile
P5	After 4, extract with 5 mL 30% H_2O_2 + 3 mL 0.01 M HNO_3 at 85°C for 2 hours; extract with 3 mL 30% H_2O_2 + 2 mL 0.01 M HNO_3 at 85°C for 3 hours; then, extract with 1 M ammoni acetate (pH = 2) shake overnight	Organic matter with sulphides	Particulate, Non-labile
P6	After 5, digest with hydrofluoric acid and nitric acid	Detritus with minerals	Particulate, Non-labile

Total phases = Pt = P1 + P2 + P3 + P4 + P5 + P6; Inorganic phases = Pi = Pt − P5.

TABLE IB Scheme of classification of metal species in sediments (Modified from Hung *et al.*, 1995)

Phase	*Treatment*	*Association*
PB1	Extract with 1 M ammonium acetate (pH = 7)	Exchangeable
PB2	After B1, extract with 1 M sodium acetate (pH = 5)	Skeletal Phase (Carbonates)
PB3	After B2, extract with 1 M sodium acetate + 0.25 M hydroxylamine hydrochloride (pH = 5), overnight	Easily reducible (Fe and Mn oxides)
PB4	After B3, extract with 0.1 M sodium hydroxide + 0.1 M sodium pyrophasphate (1:1)	Organic with humic substances
PB5	After B-4, extract with 25% acetic acid + 0.25 M hydroxylamine hydrochloride at 75°C for 6 hours	Moderately reducible (Crystalline Mn oxides)
PB6	After B-5, extract with 5 mL 30% H_2O_2 + 3 mL 0.01 M HNO_3 at 85°C for 2 hours; extract with 3 mL 30% H_2O_2 + 2 mL 0.01 M HNO_3 at 85°C for 3 hours; then, extract with 1 M ammonium acetate (pH = 2) shake overnight	Organic residues with sulphides
PB7	After B6, digest with hydrofluoric acid and nitric acid	Detritus with minerals

of organic combined with humic substances and organic residues (Tab. IB, Hung *et al.*, 1995).

The analysis of trace metal contents in the Standard Reference Material samples such as bovine liver (NBS-SRM 1577), orchard leaves (NBS-SRM 1571), sediments and green oysters (*Crassostrea gigas*, prepared by this laboratory) were intercalibrated with Trace Metal Analytical Laboratory, Department of Chemistry, University of Idaho and Silver Valley Laboratory, Inc. (USEPA-core laboratory), Kellogy, Idaho. The results indicated that the performance for analysis of trace metals at this laboratory was satisfactory (Hung *et al.*, 1997).

RESULTS AND DISCUSSION

Contents of Mud, Trace Metals and Total Organic Carbon

Except stations 1 (river) and 8 (near the His-Su oyster mariculture area), the sediments collected from the Taiwan Erhjin Chi system in

March and September of 1990 (Tab. II) were mostly sand (grain size $> 63\,\mu m$; range from 90.09% to 99.81%). The mud ($< 63\,\mu m$) contents in the sediments from station 1 (51.29% in March and 90.21% in September of 1990) and station 8 (35.39% in March and 82.67% in September of 1990) varied with season due possibly to the slightly changed sampling locations.

Trace metals and TOC contents in mud and sand separated from the sediments vary with the characteristics of sediments (mud and sand), location and season. In principle, the greater the mud in sediments, the greater the concentrations of TOC and trace metals were observed. For instance, Tables IIA–IIB indicate the results observed in March, 1990 that higher mud contents (51.29%) gave the higher contents of TOC (1.603%) and trace metals (Cu, $757\,\mu g\,g^{-1}$; Zn, $878\,\mu g\,g^{-1}$; Pb, $237\,\mu g\,g^{-1}$; Cd, $2.65\,\mu g\,g^{-1}$) from station 1 compared with those values of low mud ($0.19 \sim 35.39\%$), TOC ($0.092 \sim 0.149\%$) and metals (Cu, $69.4 \sim 254\,\mu g\,g^{-1}$; Zn, $214 \sim 345\,\mu g\,g^{-1}$; Pb, $37.6 \sim 100\,\mu g\,g^{-1}$; and Cd, $0.20 \sim 0.48\,\mu g\,g^{-1}$) from stations 2–12 (estuarine and coastal areas). A similar trend was observed in samples collected in September of 1990 that high contents of copper ($417\,\mu g\,g^{-1}$), zinc ($526\,\mu g\,g^{-1}$), lead ($104\,\mu g\,g^{-1}$), and cadmium ($1.01\,\mu g\,g^{-1}$) with high mud (90.12%) were obtained at station 1 compared with those values at other Stations. Station 1 is the location of the copper recycling area since

TABLE IIA Concentrations of total organic carbon (TOC, %), trace metals ($\mu g\,g^{-1}$, dry weight) in mud separated from the sediments of Taiwan Erhjin Chi river system (including river and estuarine and coastal area)

	March 1990			*September* 1990	
St. No.	*Mud* (%)	*TOC/Mud*	*Cu/Mud*	*Mud* (%)	*Cu/Mud*
1	51.29	1.603	757	90.12	417
2	0.19	0.117	249	0.13	160
3	1.26	0.149	190	0.8	30.5
4	2.00	0.137	254	8.12	42.3
5	0.40	0.114	197	2.55	87.1
6	12.48	0.097	105	0.83	47.7
7	0.97	0.094	82.1	9.03	44.4
8	35.39	0.139	69.4	82.67	62.6
9	2.49	0.103	85.4	3.79	49.8
10	3.49	0.118	125	4.43	48.9
11	2.39	0.092	86.2	6.15	46.6
12	2.33	0.098	79.7	2.33	43.3
Ave.			138		60.0

TABLE IIA (Continued)

*Station**	*Zn/Mud*	*Pb/Mud*	*Cd/Mud*	*Cr/Mud*	*Fe/Mud*	*Mn/Mud*
			March 1990			
1	878	237	2.65	37.2	37000	361
2	345	37.6	0.33	63.3	15400	227
3	245	74.3	0.34	82.7	45200	704
5	280	100	0.48	80.4	42700	431
7	214	68.0	0.20	68.0	21200	654
10	236	60.5	0.32	65.9	17800	558
Ave.	366	96.3	0.72	66.3	29800	489
			September 1990			
1	526	104	1.01	58.5	39800	380
2	338	44.9	0.21	53.0	21700	590
3	183	28.1	0.74	48.4	28700	495
5	188	57.0	0.13	55.7	25100	401
7	170	38.5	0.09	59.7	36600	433
10	199	48.4	0.35	75.6	33800	522
Ave.	267	53.4	0.42	58.5	30900	470

* Location of stations: Taiwan Erhjin Chi river system: See Figure 1A.

1986 (Hung, 1988). Compared with stations 2–12, station 1 has lower contents of chromium (37.2 $\mu g\,g^{-1}$ in March and 58.5 $\mu g\,g^{-1}$ in September), manganese (361 $\mu g\,g^{-1}$ in March and 380 $\mu g\,g^{-1}$ in September) and iron (37000 $\mu g\,g^{-1}$ in March and 39800 $\mu g\,g^{-1}$ in September) which might be due to the geological variations.

TABLE IIB Concentrations of total organic carbon (TOC, %), trace metals ($\mu g\,g^{-1}$, dry weight) in sand separated from the sediments of Taiwan Erhjin Chi river system (including river and estuarine and coastal area)

	March 1990			*September* 1990	
St. No.	*Sand* (%)	*TOC/Sand*	*Cu/Sand*	*Sand* (%)	*Cu/Sand*
1	48.71	0.615	746	9.79	555
2	99.81		63.5	99.87	39.8
3	98.74	1.036	25.1	99.20	15.6
4	98.48	0.792	18.7	91.88	19.6
5	99.60	0.637	32.7	97.45	37.7
6	97.52	0.712	17.3	99.17	18.5
7	99.03	0.701	17.1	90.97	17.3
8	64.61	0.526	18.6	17.33	21.8
9	97.51		24.5	96.21	22.6
10	96.51	0.609	19.9	95.57	22.5
11	97.61	0.581	19.5	93.85	21.3
12	97.67	0.587	16.8	97.67	18.6
Ave.			24.9		23.2

TABLE IIB (Continued)

*Station**	*Zn/Sand*	*Pb/Sand*	*Cd/Sand*	*Cr/Sand*	*Fe/Sand*	*Mn/Sand*
			March 1990			
1	924	427	3.01	31.0	28600	220
2	106	32.9	0.28	30.3	36300	441
3	81.4	27.5	0.23	32.1	40300	538
5	85.9	27.1	0.17	32.8	37800	371
7	65.0	18.0	0.21	31.9	14100	285
10	75.6	24.3	0.38	34.7	16500	304
Ave.	223	92.7	0.72	32.1	28900	360
			September 1990			
1	686	206	1.50	85.9	23500	187
2	115	31.3	0.11	60.6	23800	445
3	79.9	24.2	0.15	33.2	22200	626
5	94.5	23.9	0.13	40.1	14800	196
7	73.9	24.2	0.14	47.4	25000	201
10	92.8	28.0	0.17	99.2	27000	222
Ave.	190	56.3	0.37	61.1	22700	313

Rainy season dominates the distributions of trace metals and TOC. The rainy season (mainly contributed by storm rainfall) usually begins from March/April and the dry season begins from September/October. For example, in 1990, the heavy rain began on 25 March and the dry season began in October. Stream flow in the dry season is much less than that in the rainy season. Shortage of water usually occurs from January through March. During the dry season, the river bed (mainly mud) absorbs organic pollutants (as TOC) and trace metals discharged freely from domestic and industrial sources without any treatment. Immediately after heavy rain, TOC and trace metals in the river sediments are released into the river water and then discharged to the estuarine and coastal environments. After heavy rain, TOC and trace metals continue to accumulate in the sediments as the input from pollution sources continues. Unfortunately, only the TOC data were available in March of 1990. However, higher average concentrations of trace metals in samples collected in March, shown in Table II, were usually much higher than those average concentrations of September of 1990. More evidence of the influence of precipitation was obtained (Tab. III) that extremely high copper ($932\,\mu g\,g^{-1}$), zinc ($10400\,\mu g\,g^{-1}$), lead ($417\,\mu g\,g^{-1}$), cadmium ($1370\,\mu g\,g^{-1}$), arsenic ($10.1\,\mu g\,g^{-1}$), chromium ($223\,\mu g\,g^{-1}$), Tin ($52.4\,\mu g\,g^{-1}$) and nickel ($82.9\,\mu g\,g^{-1}$) concentrations were in the bulk sediments from station

TABLE III Total heavy metal contents in sediments collected along the Erhjin Chi river system in August, 1996 (Unit: $\mu g\ g^{-1}$, dry weight)

*St. No.**	*Cu*	*Zn*	*Pb*	*Cd*	*As*	*Cr*	*Sn*	*Ni*
R1	37.9	56.8	8.25	nd	2.44	5.80	nd	44.0
R2	16.0	213	10.6	0.51	5.35	1.63	2.11	39.6
R3	92.9	482	12.0	0.22	6.77	9.24	3.11	11.5
R4	932	10400	417	1370	10.1	223	52.4	82.9
R5	98.9	173	27.8	2.79	6.83	111	9.61	26.2
R6	27.1	203	64.4	1.13	2.56	6.45	nd	73.5
R7	3.75	110	1.61	0.37	nd	5.37	nd	15.9
R8	0.93	93.4	nd	0.02	nd	0.83	nd	2.57

* Location of stations: Taiwan Erhjin Chi river system: See Figure 1B.
nd: $0.02\,\mu g\,g^{-1}$ for Cd; $0.45\,\mu g\,g^{-1}$ for As; and $0.10\,\mu g\,g^{-1}$ for Sn.

R4 collected in August of 1996 during the low precipitation of 94.3 to 307.4 mm with a total of 633.0 mm from June to August of 1996 (Fig. 2). Stations R4 (Fig. 1B) and 1 (Fig. 1) are located in the copper recycling area. When the precipitation increased (547.7 mm in June, 425.1 mm in July and 464.9 mm in August of 1997) with a total of 1437.7 mm from June to August 1997, except chromium and nickel, the trace metals such as copper ($132\,\mu g\,g^{-1}$), zinc ($169\,\mu g\,g^{-1}$), lead ($4.48\,\mu g\,g^{-1}$), cadmium ($3.50\,\mu g\,g^{-1}$), arsenic ($5.37\,\mu g\,g^{-1}$), and Tin ($2.99\,\mu g\,g^{-1}$) were found to decrease in September of 1997 compared with those values of August of 1996. Higher concentrations of chromium ($532\,\mu g\,g^{-1}$) and nickel ($174\,\mu g\,g^{-1}$) found at station R1 during the period of higher precipitation in June to August of 1997 might be due to illegal discharge of industrial effluents. Further investigation on this subject is needed.

Trace Metal Species and Complexing Capacity with Total Organic Carbon

Among six phases [bioexchangeable (P1), skeletal (P2), easily reducible (Fe and Mn oxides, P), moderately reducible (crystalline Mn oxides, P4), organic combined with sulphides (P5) and detritus with minerals (P6)] of trace metal species in the mud and sand separated from the sediments collected along the Erhjin Chi river system in March and September of 1990. P1 and P2 are important as they represent very loosely bound trace metals which may both regulate and influence biological metabolism and be toxic to aquatic life. The results in

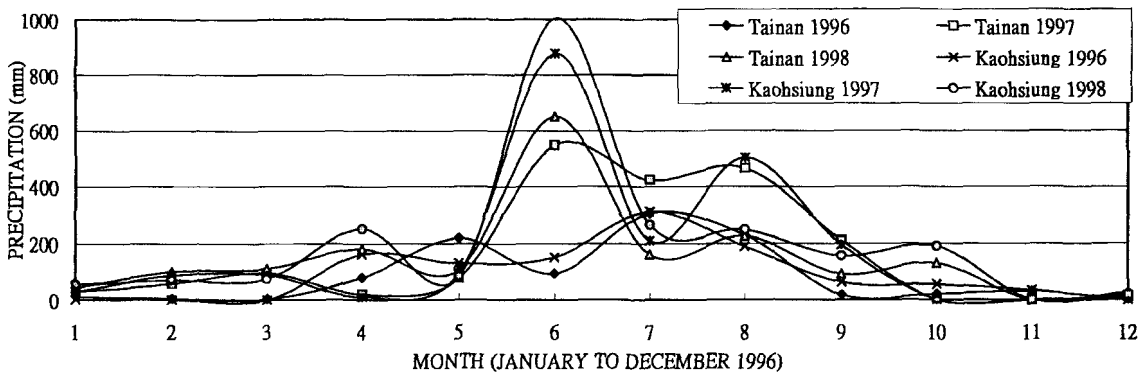

FIGURE 2 Seasonal variation of precipitation in Tainan and Kaohsiung near the Erhjin Chi river system from January, 1996 to December, 1998.

Figure 3 indicate that, except chromium and Iron, the average percentages of P1 and P2 for copper (34.1 ~ 35.3% in mud and 35.3 ~ 25.7% in sand), zinc (34.1 ~ 35.3% in mud and 41.0 ~ 31.3% in sand), lead (33.4 ~ 33.1% in mud and 24.2 ~ 24.5% in sand), Cd (57.1 ~ 61.1% in mud and 48.0 ~ 36.2% in sand), and manganese

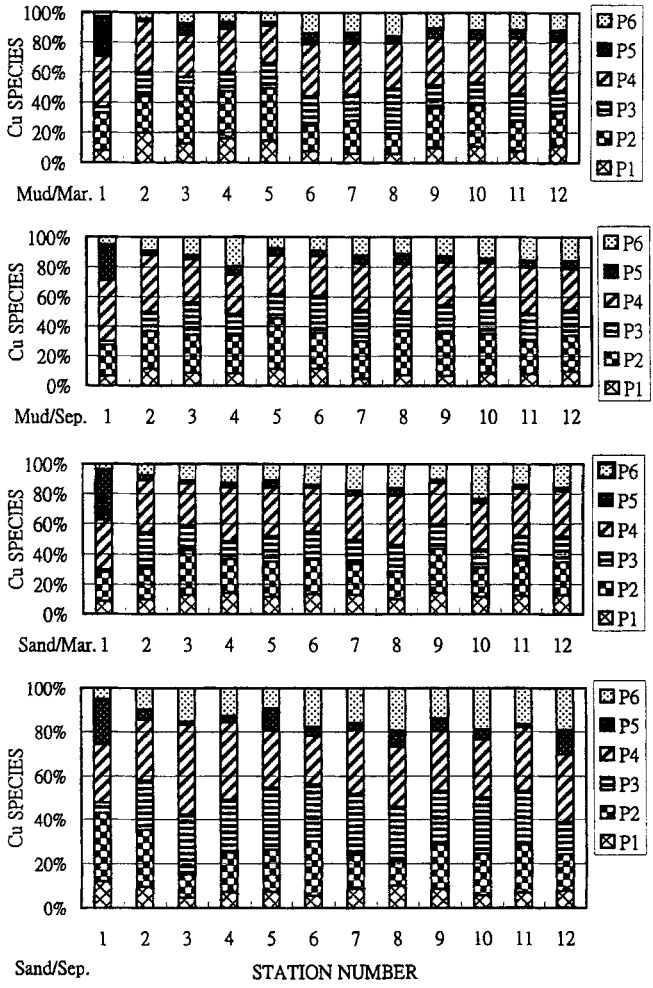

FIGURE 3 Trace metal species in mud (< 0.63 μm) and sand (> 0.63 μm) separated from samples along the Taiwan Erhjin Chi river system (River, estuary and coast) in March and September, 1990 (Location of stations as Fig. 1A).

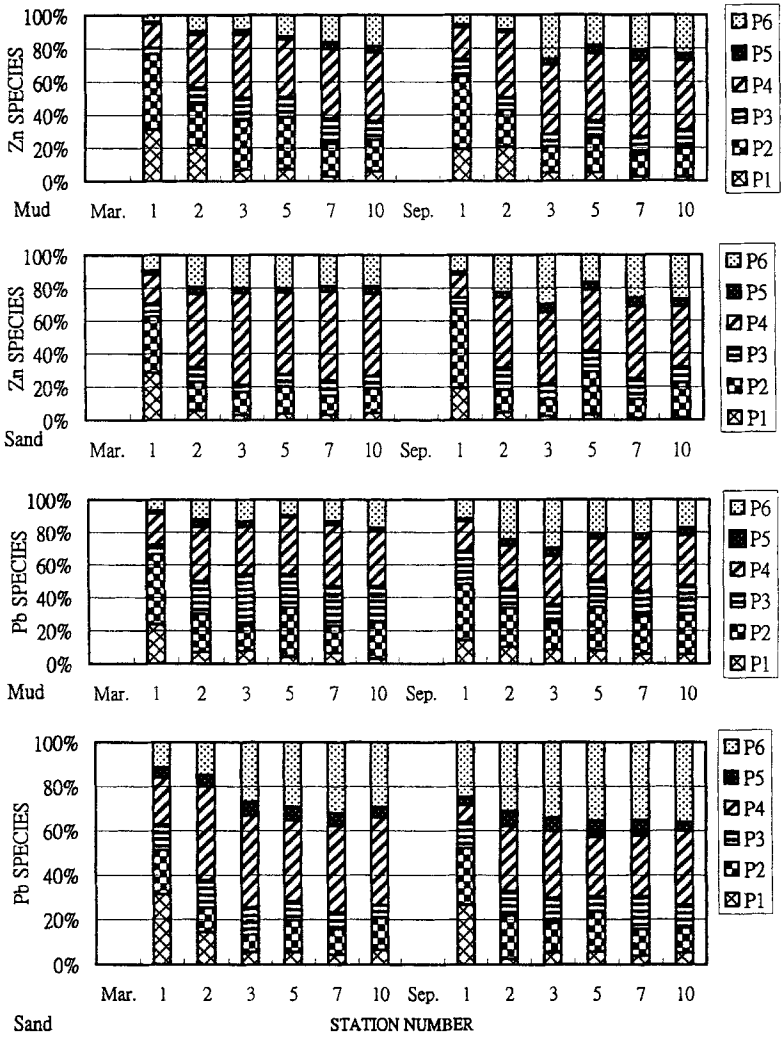

FIGURE 3 (Continued).

(53.5 ~ 54.6% in mud and 60.0 ~ 54.5% in sand) in March and September of 1990 were much higher than those of P3–P6. High percentages of chromium (44.8 ~ 61.8% in mud and 54.3 ~ 71.9% in sand) and iron (45.5 ~ 40.4% in mud and 49.6 ~ 49.0% in sand) in samples respectively collected in March and September of 1990 were in P6. It is interesting to note that, for the sediments collected

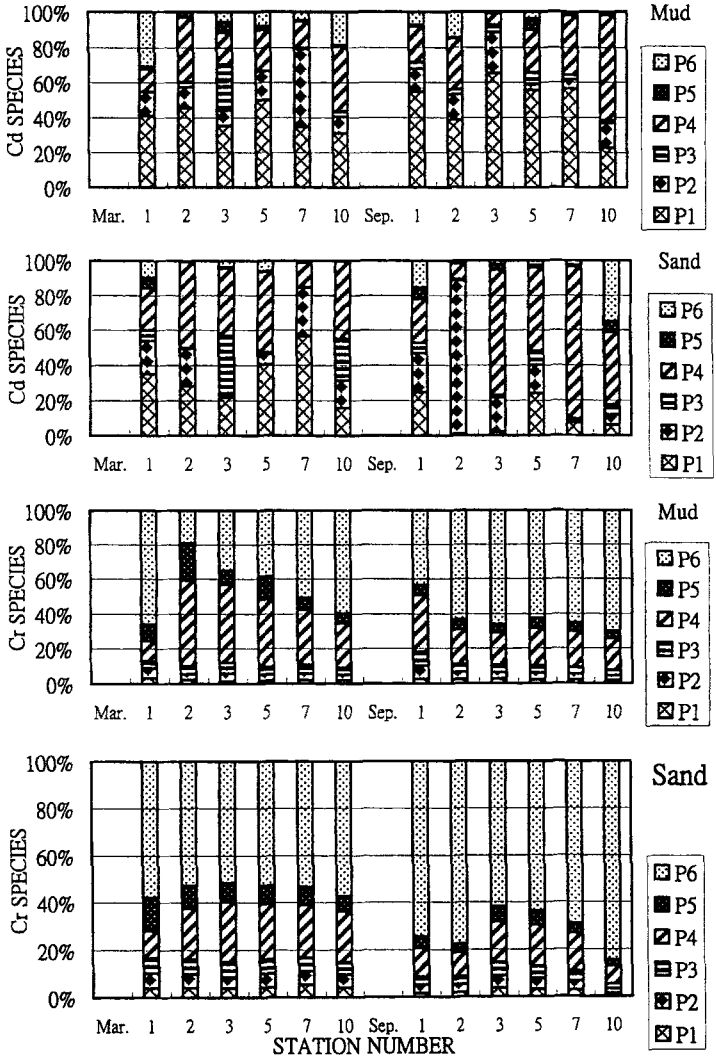

FIGURE 3 (Continued).

from the Antarctic Ocean (Hung *et al.*, 1993), much lower values of P1 and P2 for copper (5.65 ~ 16.8% in mud; 5.36 ~ 7.18% in sand) and zinc (3.35 ~ 10.7% in mud; 2.61 ~ 4.81% in sand) were observed. A comparison of those data might strongly indicate that the higher contents of copper and zinc in bioexchangeable and skeletal phases

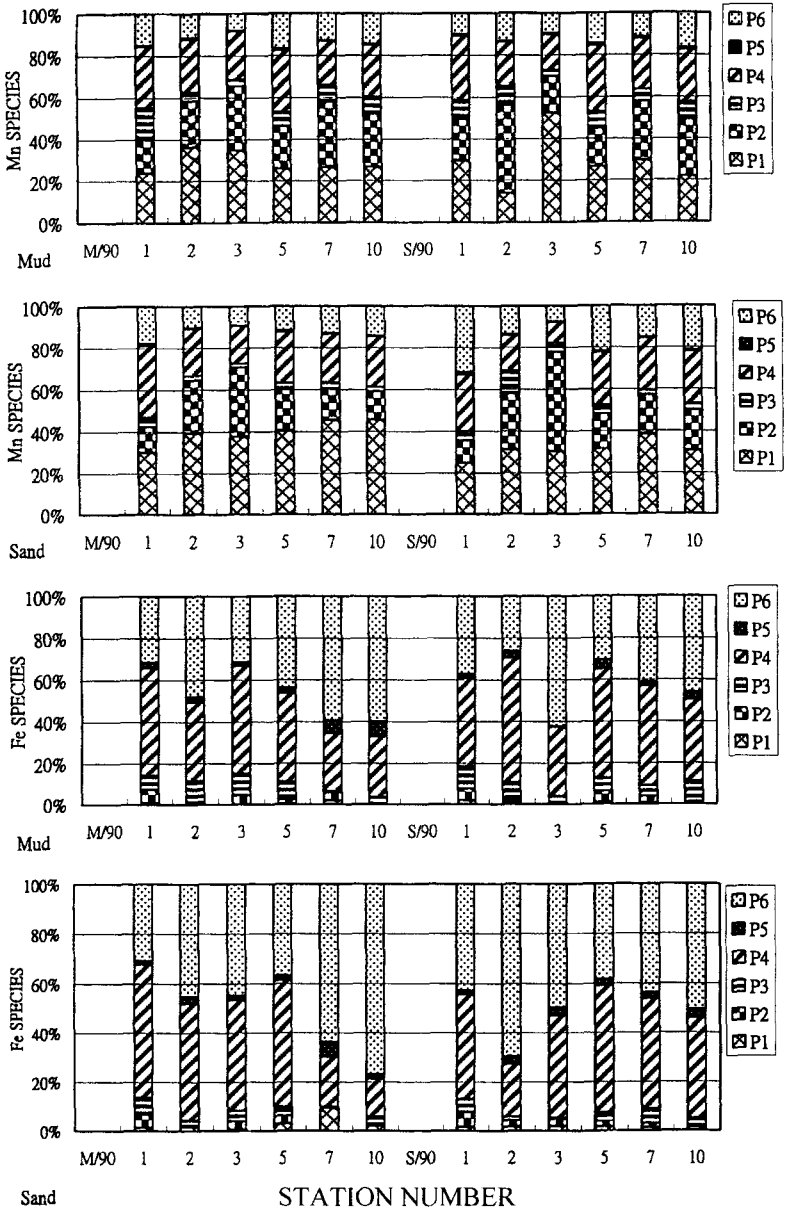

FIGURE 3 (Continued).

in the Taiwan Erhjin Chi riverine, estuarine and coastal sediments are associated with the problems arising from the inorganic and organic pollutants discharged from local families and industries. There is no doubt that many incidents of green discolouration and mortality of mariculture oysters (Hung, 1998), as well as mass killing of larval shrimps (Chen, 1981), have been observed along the southwestern coast of Taiwan.

The second high percentages of trace metals in mud and sand were the P4, moderately reducible (crystalline Mn oxides). Figure 3 shows the results that the species of trace metals in P4, such as copper (26.3 ~ 40.8% in mud; 21.8 ~ 40.9% in sand), zinc (14.5 ~ 41.7% in mud; 14.1 ~ 55.4% in sand), lead (18.1 ~ 35.1% in mud; 7.72 ~ 42.3% in sand), cadmium (6.79 ~ 59.7% in mud; 8.77 ~ 87.0% in sand), chromium (11.6 ~ 49.3% in mud; 7.73 ~ 25.4% in sand), manganese (17.1 ~ 31.4% in mud; 9.96 ~ 34.3% in sand) and iron (33.3 ~ 59.6% in mud; 15.5 ~ 54.1% in sand), vary with the characteristics of sediments (mud and sand). In general, the higher the sand content in sediments, the higher the percentages of P4 species.

The species of organic combined with sulphide (P5) might be related to the biogenic particulate matter. Along the Taiwan Erhjin Chi river system, the relatively low values of copper (1.80 ~ 26.3% in mud; 1.48 ~ 34.1% in sand), zinc (1.27 ~ 6.35% in mud; 1.85 ~ 5.47% in sand) and chromium (4.46 ~ 21.8% in mud; 2.37 ~ 14.1% in sand) compared with those of lead (1.38 ~ 4.90% in mud; 3.69 ~ 7.69% in sand), cadmium (0.14 ~ 6.35% in mud; 0.35 ~ 6.67% in sand), manganese (0.16 ~ 1.15% in mud; 0.21 ~ 1.23% in sand) and iron (0.45 ~ 7.32% in mud; 1.60 ~ 3.54% in sand) in P5 were obtained compared with those values obtained of mud and sand separated from the Antarctic Ocean sediments. The percentages of P5 for copper (24.8 ~ 32.6% in mud; 5.63 ~ 37.6% in sand) and zinc (2.37 ~ 8.05% in mud; 0.20 ~ 4.70% in sand) were relatively high in the Antarctic Ocean sediments from station VI (67°01.93'S and 73°01.65'E at a depth of 500 m) and station VII (68°00.2'S and 72°53.9'E at a depth of 620 m). Higher correlation coefficient (0.9992) between copper species in P5 and TOC was observed in mud compared with zinc (0.6348), lead (0.8701), cadmium (0.7899) and chromium (0.5946). In sand, the only high coefficient (0.8983) was found for chromium and TOC. This was in accordance with the results obtained by

Chester *et al.* (1988), who showed that in hemipelagic environments, the preservation of organic carbon leads to the storage of significant amounts of organically associated copper (P5) in the sediments, such as mud.

The inorganic species [Pi] can be obtained by subtracting with the species of organics combined with sulphide (P5) from total species (P1 to P6). The metal species complexing capacities of TOC, plot of the regression equations with the correlation coefficients (R^2) among TOC *versus* metal in organic species (P5) and inorganic species [Pi] in mud and sand separated from sediments, might be controlled by the characteristics of sediments (mud and sand) and the environmental conditions of trace metals and humic substances. For instance,

TABLE IV Metal complexing capacity, correlation coefficient (R^2) and significance (p) between total organic carbon with metal species in organic phase (P5) and inorganic phases (Pi) in mud ($< 63\,\mu m$) and sand ($> 63\,\mu m$) separated from the sediments of Taiwan Erhjin Chi river system in March, 1990

	Species	*Metal*	*Metal Phase = a POC + b*	R^2
Mud	P5	Cu	$Y = 129.0X - 7.816$	0.9992, $p < 0.01$
		Zn	$Y = 3.2878X - 6.8822$	0.6348, $p < 0.05$
		Pb	$Y = 1.8117X - 1.6022$	0.8701, $p < 0.01$
		Cd	$Y = 0.0216\,X - 0.0038$	0.7899, $p < 0.01$
		Cr	$Y = -1.0227X - 13.401$	0.5946,
		Mn	$Y = -0.21.324X - 4.1347$	0.4450
		Fe	$Y = -6861.3X - 1785.9$	0.1237
	Pi*	Cu	$Y = 390.10X - 109.94$	0.9465, $p < 0.01$
		Zn	$Y = 413.84X - 180.77$	0.9680, $p < 0.01$
		Pb	$Y = 109.12X - 46.606$	0.9244, $p < 0.01$
		Cd	$Y = 1.0337 - 0.1835$	0.9845, $p < 0.01$
		Cr	$Y = -3.5733X - 62.186$	0.8997, $p < 0.01$
		Mn	$Y = 2431.6X - 162.70$	0.0736
		Fe	$Y = 0.7526X - 5561.9$	0.9595, $p < 0.01$
Sand	P5	Cu	$Y = -1.2367X - 1.7783$	0.1981
		Zn	$Y = -3.3294X - 18.405$	0.4745
		Pb	$Y = -2.7806X - 14.329$	0.4623
		Cd	$Y = -0.0256X - 0.4286$	0.4286
		Cr	$Y = -0.146X - 3.020$	0.8983, $p < 0.01$
		Mn	$Y = -0.230X - 2.300$	0.3333
		Fe	$Y = -148 + 1199.5$	0.6796, $p < 0.05$
	Pi*	Cu	$Y = -676.88X - 655.37$	0.1404
		Zn	$Y = -6.18X - 85.28$	0.6325, $p < 0.05$
		Pb	$Y = -52.999X - 264.72$	0.4568
		Cd	$Y = -0.3418X - 1.8585$	0.4001
		Cr	$Y = 0.1044X - 11.633$	0.0966
		Mn	$Y = -51.055X - 498.1$	0.6531, $p < 0.05$
		Fe	$Y = -4951.1X - 29892$	0.6430, $p < 0.05$

* Pi: Inorganic phases = [Total phases – Organic phases] = Pt – P5 (Tab. IA).

Table IV also shows the results of the Erhjin Chi river system that higher correlation coefficients between TOC and species in inorganic phases for copper (0.9465), zinc (0.9680), lead (0.9244), cadmium (0.9845), and chromium (0.8997) in mud were observed. Relatively high coefficients for manganese (0.6531), iron (0.6430) and zinc (0.6325) were found in sand.

Trace Metals and Complexing Capacity with Humic Substances

For studying the possible competition of organic metal between humic substances (humic and fulvic acids) and organic residues, the sediments along the Erhjin Chi river system collected on December 4–10, 1992 were investigated. Figure 4A indicates that the contents of humic acid ($2.3 \sim 1.7\,\mu g\,g^{-1}$) and fulvic acid ($1.3 \sim 1.1\,\mu g\,g^{-1}$) in sediments collected from the upstream (R1 ~ R3) were higher than those ($1.1 \sim 0.6\,\mu g\,g^{-1}$ for humic acid and $0.06 \sim 1.0\,\mu g\,g^{-1}$ for fulvic acid) collected from down stream, estuarine and coastal stations (R4 ~ R9) along the Erhjin Chi (river) system. The correlation between the humic acid ($r = -0.9633$, $p < 0.01$) and fulvic acid ($r = -0.9335$, $p < 0.01$) in sediments along the up-stream to estuarine and coastal stations were significantly higher. The concentrations of copper, lead, manganese and iron in purified humic and fulvic acids isolated from sediments were also determined. The results shown in Figure 4B are that higher humic concentrations (range from $0.59 \sim 2.30\,mg\,g^{-1}$) with the high contents of manganese (range from $119 \sim 454\,\mu g\,g^{-1}$) and iron (range from $15200 \sim 114000\,\mu g\,g^{-1}$) in humic acid and fulvic acids ($0.64 \sim 1.20\,mg\,g^{-1}$) were generally found at R1, the upstream station, and low values at coastal stations. However, extremely high

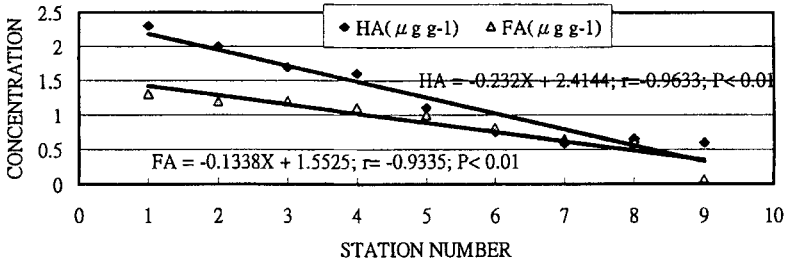

FIGURE 4A Contents of humic and fulvic acids isolated from the sediments collected from the Erhji river system in December, 1992 (Location of stations as Fig. 1B).

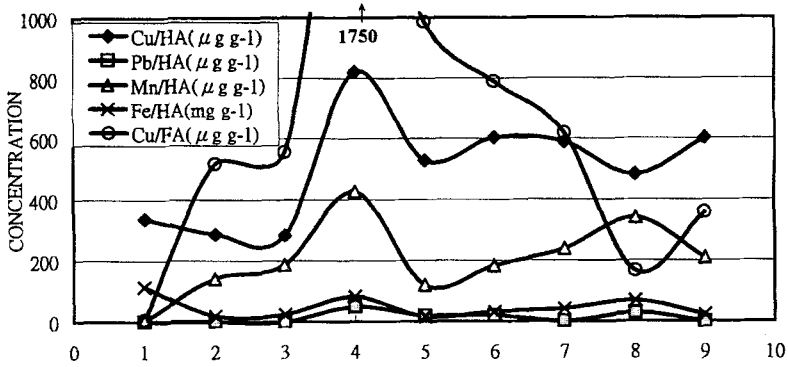

FIGURE 4B Concentrations of heavy metal (dry weight) in purified humic and fulvic acids isolated from the sediments collected from the Erhjin River system in December, 1992 (Location of stations as Fig. 1B).

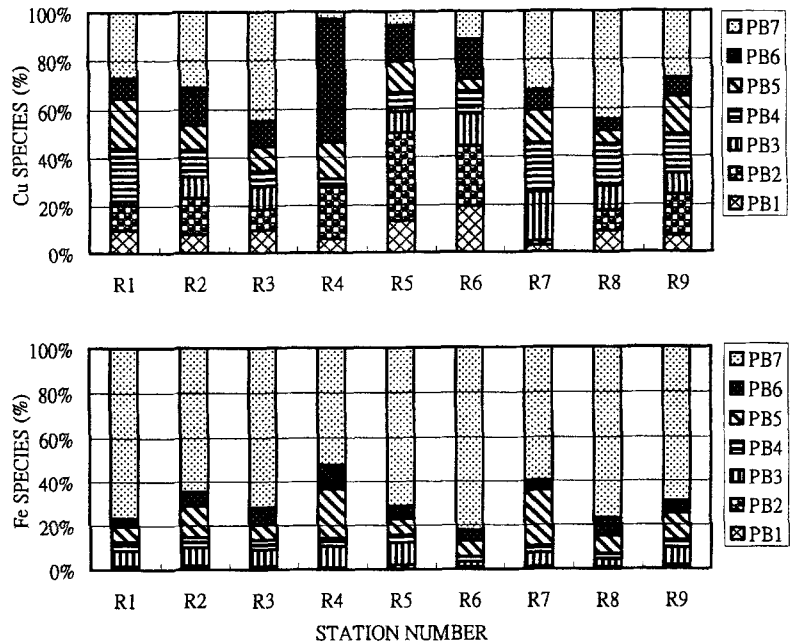

FIGURE 5 Copper and iron species collected in sediments along the Erhjin Chi river system in December, 1992 [Location of station number: R1–R3, Upstream; R4–R5, Downstream; R6, Estuary; R7–R9, Coastal (See Fig. 1B); PB1, Exchangeable; PB2, Skeletal phase (Carbonates); PB3, Easily reducible (Fe and Mn oxides); PB4, Organic with humic substances; PB5, Moderately reducible (Crystalline Mn oxides); PB6, Organic residues with sulphides; and PB7, Detritus with minerals].

concentrations of copper (range from $165 \sim 1750\,\mu g\,g^{-1}$, dry weight in fulvic acid; $282 \sim 820\,\mu g\,g^{-1}$ in humic acid) and lead (range from $282 \sim 821\,\mu g\,g^{-1}$ in humic acid) with relatively high concentrations of manganese ($426\,\mu g\,g^{-1}$) and iron ($82.3\,\mu g\,g^{-1}$) were observed in humic substances from station R4. The concentrations of lead, manganese and iron in fulvic acid were under the detection limits (Pb, $< 12\,\mu g\,g^{-1}$; Mn, $< 10\,\mu g\,g^{-1}$; and Fe, $< 0.7\,mg\,g^{-1}$).

Figure 5 shows that higher copper species in PB6 ($4.8 \sim 50.9\%$) and lower values in PB4 ($2.2 \sim 21.9\%$) were obtained among the seven phases of sequential analysis, such as exchangeable (PB1), skeletal (carbonate, PB2), easily reducible (Fe and Mn oxides, PB3), organic with humic substances (PB4), moderately reducible (crystalline Mn oxides, PB5), organic residues with sulphides, (PB6), and detritus with minerals (PB7), in sediments compared with those of iron species in P4 ($2.3 \sim 4.4\%$) and PB6 ($3.7 \sim 11.2\%$). For the iron species, extremely high species of PB7 ($52.5 \sim 82.4\%$) was observed.

Based on the results of complexing capacities of all metal species with TOC as well as organic detritus and humic substances in sediments from the Erhjin Chi river system, there is no doubt that many incidents of green discolouration and mortality of mariculture oysters (Hung, 1988), as well as mass killing of larval shrimps (Chen, 1981), have been observed along the southwestern coast of Taiwan.

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