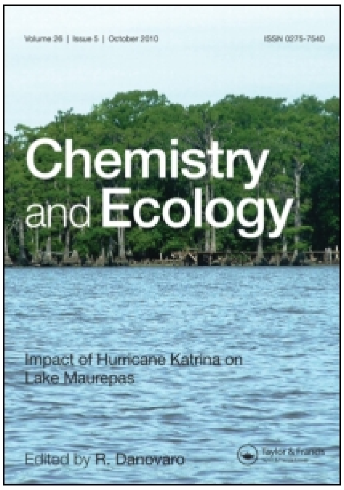

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Interactions Among the Copper Species and Forms in Sea Water/Sediments and Copper Bioaccumulation in Oysters

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INTERACTIONS AMONG THE COPPER SPECIES AND FORMS IN SEA WATER/SEDIMENTS AND COPPER BIOACCUMULATION IN OYSTERS

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Earlier papers indicated that the first incident of green discoloration in oysters (*Crassostrea gigas*) and the mass mortality observed in 1986 along the Taiwan Erhjin Chi coastal area were caused by the higher contents of total copper and copper species (mainly bioavailable and free ion) in sea water. The copper in sea water would be sorbed by suspended matter and transferred to sediments, and the copper in the sediments would also be desorbed to sea water. Processes of copper adsorption and desorption are the major factors influencing the contents of total copper and copper species in sea water and sediments. In this study, the Erhjin Chi sediments were mixed with sea water by a shaker technique. When the mixture was shaken for one hour, analogous to tidal mixing in estuaries, only copper desorption from sediments was observed. If the shaking time is increased for more than 3 hours, the copper released from the sediments was resorbed to the remaining solid phases. The higher the contents of mud (91.71%) and total copper (701 mg kg^{-1}) in sediments, the higher the copper desorption rate (1.86 ppm hr^{-1}) and copper adsorption rate (0.50 ppm hr^{-1}) were observed. In sediments containing lower mud (0.80%) and lower copper (43.5 mg kg^{-1}), the copper desorption and adsorption rates were 0.83 ppm hr^{-1} and 0.22 ppm hr^{-1}, respectively. The interactions among the total copper and copper species in sea water and sediments, chemical and ecological parameters, and copper bioaccumulation in oysters in the Erhjin Chi estuarine and coastal area are also discussed.

KEY WORDS: Copper species/forms, sea water/sediments, ecological parameters, copper bioaccumulation in oysters, Taiwan coastal area

INTRODUCTION

Some toxic and potentially toxic heavy metals are being released to the marine environment at an increasing rate. When heavy metals enter the coastal water, the majority are sorbed to suspended matter and transferred to sediments. The heavy metals in sediments could also be released, and the amount of released metals would exceed that from the decomposition of plankton (Aplin and Cronin, 1985). One of the most important processes of sea water and sediment interaction can be found in the river/sea mixing zone, i.e., the estuarine environment, and estuaries also display high levels of biological activity (Goldberg, 1978). In recent years many investigators (e.g. Bryan and Langston, 1992; Chagot *et al.*, 1990; Hung and Han, 1992; Hung and Tsai, 1992; Tessier and Campbell, 1987) reported that the species and forms of heavy metals play an important role in the marine ecosystem and their toxicity to organisms along the estuarine and coastal environments.

Along the Erhjin Chi estuarine and coastal (mariculture) area, the first incident of 'green oysters' (*Crassostrea gigas*) occurred in January 1986 and oyster mortality reports appeared three months later. The cause of green oysters was immediately identified as due to copper pollution (Hung, 1988). The copper bioaccumulation in oysters and the oyster mortality were found to be influenced by the copper species (complexed by inorganic and organic anions, such as labile and nonlabile, polar and nonpolar, free ions and bioavailable) and forms (particulate and dissolved), and the copper assimilative capacity (detoxifying) (Hung *et al.*, 1989a; 1989b; Hung and Han, 1990; Han and Hung, 1990a; 1990b). The relationships among the copper species in water, sediments and biomass along the Erhjin Chi estuarine and coastal area were also evaluated (Hung *et al.*, 1992). The purposes of this paper are to continue our study on interactions among the total copper and the copper species and forms in sea water and sediments, and to elucidate the processes of sorption of total copper and copper species from sediments in relation to such a biological system as the Erhjin Chi estuarine and coastal area.

MATERIALS AND METHODS

Water, sediment and bivalves (mainly oysters) samples were collected from the Erhjin Chi (river) and its estuary as well as the coastal (mariculture) area (Figure 1) during

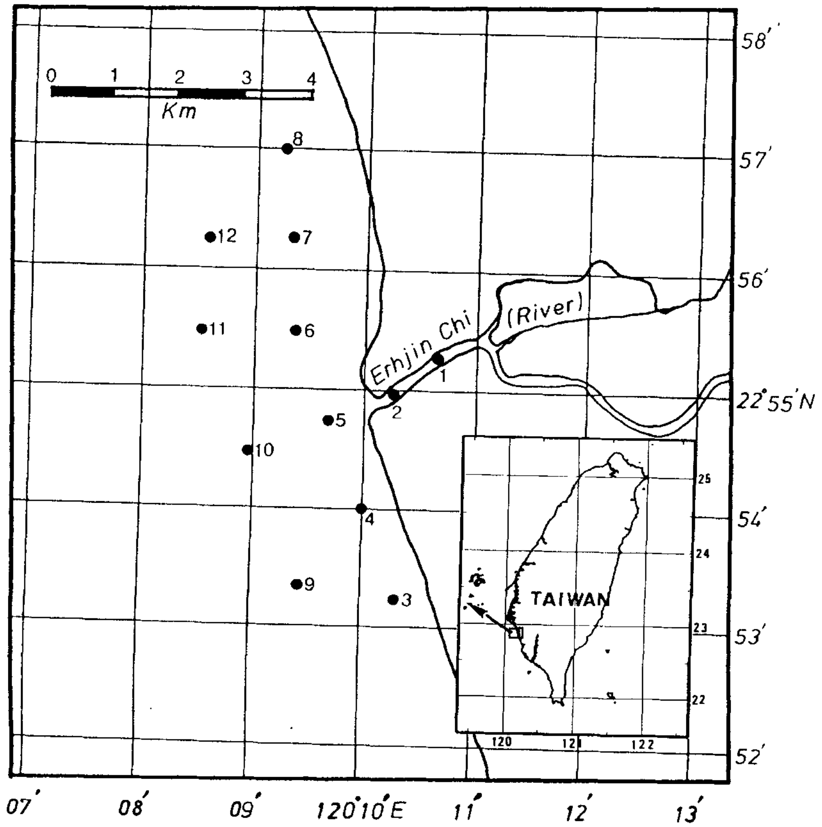

Figure 1 Sampling locations along the Taiwan Erhjin Chi coastal (including river and estuary) area.

the periods of March 12–14, October 4–6, 1991 and March 25, 1992. Water samples at different depths (0, 3, 10 and 20 metres) were collected with non–metallic Niskin bottles aboard fishing boats. Immediately after collection, water samples were analyzed for hydrographical, chemical and the following biomass parameters: temperature, salinity, pH, dissolved oxygen, nutrients, chlorophyll-a, particulate organic carbon, adenosine triphosphate, and primary productivity. Standard procedures for analysis, except the species and forms of copper, were employed (Hung and Tsai, 1992). The species and forms (dissolved and particulate, labile and nonlabile, polar and nonpolar, inorganic and organic, free ion) were analyzed by the procedure of Hung *et al.* (1989b) shown in Figure 2. Bottom sediments, collected by dredging, were separated into mud (grain size < 63 μm) and sand (grain size > 63 μm) fractions by wet sieving by the ASTM Standard Mesh (No. 230) separation method, and then extracted separately with 1M ammonium acetate (pH 7), 1M sodium acetate (pH 5), 1M sodium acetate and 0.25M hydroxylamine hydrochloride (pH 5), 0.25M hydroxylamine hydrochloride and 25% acetic acid and hydrogen peroxide in various proportions, and finally digested with a mixture of HF/HNO_3 solutions (Table 1). The copper species and forms obtained by each extraction-step were analyzed by both Differential Pulse Stripping Voltammetric (DPASV) and Graphite Atomic Absorption Spectrophotometric (GAA) methods. The standard deviations (0.17% and 0.86%) of these two methods for analysis of copper concentrations in sediments were satisfactory. The copper content in oysters was

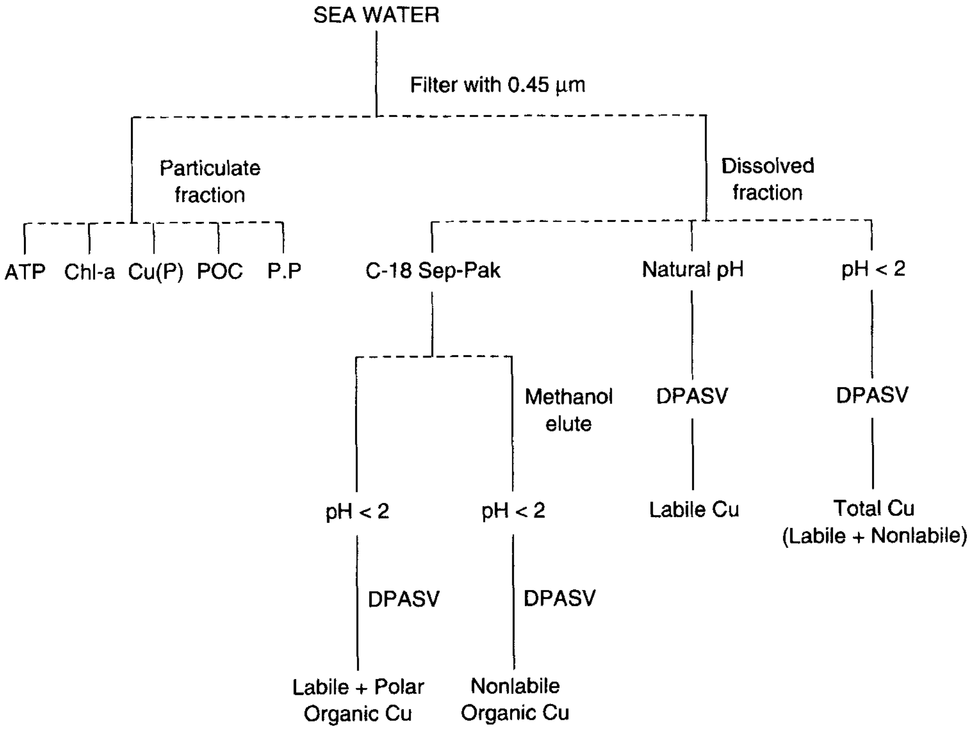

Figure 2 Scheme for the classification of copper forms and species in sea water. (Cu(P), Particulate Cu; POC, Particulate organic carbon; P.P., Primary productivity).

Table I Scheme of classification of copper forms and species in sediments

PHASE	TREATMENT METHOD*	ASSOCIATION
(1)	Extract with 1M ammonium acetate (pH = 7)	Exchangeable
(2)	After (1), extract with 1M sodium acetate (pH = 5)	Skeletal phase (carbonates)
(3)	After (2), extract with 1M sodium acetate + 0.25M hydroxylamine hydrochloride (pH = 5) overnight	Readily reducible (Fe & Mn oxides)
(4)	After (3), extract with 25% acetic acid + 0.25M hydroxylamine hydrochloride at 75°C for 6 hours	Moderately reducible (cryst. Mn oxides)
(5)	After (4), extract with 5ml 30% H_2O_2 + 3ml 0.01N HNO_3 at 85°C for 2 hours, then, extract with 3ml 30% H_2O_2 + 2ml 0.01N HNO_3 at 85°C for 3 hours, then, extract with 1N Ammonium acetate (pH = 2), shake overnight	Organic matter with sulphide
(6)	After (5), digest with hydrofluoric acid and nitric acid	Detritus with minerals

* After Hung and Meng (1992).

digested with a mixture of nitric acid and sulphuric acid (1:1, v/v) solution (Horwits, 1975), and then the supernatant was analyzed for copper by both DPASV and GAA methods. The analysis of copper contents in the standard reference samples [such as bovine liver (NBS-SRM-1577), orchard leaves (NBS-SRM-1571), green discoloured oysters (*Crassostrea gigas*) and sediments (the later two were prepared by this laboratory)] were calibrated internationally (Hung *et al.* 1989b). The standard deviation of copper analysis in sediments among these laboratories was < 6%.

INTERACTIONS OF TOTAL COPPER IN MIXTURE OF SEA WATER AND SEDIMENTS

Table II indicates that the estuarine and coastal sediments, except at Station 8 (near the Hsi-Su oyster mariculture area), were mostly sandy (from 93.11% to 99.79%). The mud contents of coastal sediments at Station 8 (27.31% in March, and 14.54% in October 1991) and of river sediments at Station 1 (92.36%, 93.53% and 91.71% in March, September 1991 and March 1992, respectively) varied with season, due possibly to the slightly changed sampling locations. The higher the mud content in sediments, the higher the concentrations of total copper and copper species and forms observed (except easily reducible copper, phase 3), similar to those results previously reported (Hung *et al.*, 1992).

For the study of interactions among the copper species and forms in sea water and sediments, the Erhjin Chi river sediments at Station 1 (total copper 408 $\mu g\ g^{-1}$) and the estuarine sediments at Station 2 (total copper 45.1 $\mu g\ g^{-1}$) were collected in March 1992. Each sediment sample (100.0 g, dry weight) was mixed with 2.0 litres of sea water by shaking for a suitable time, i.e., 1.0, 3.0, 5.0, 7.0, 24, 48, 96 and 120 hours. The sea water used for interaction experiments was collected from the eastern coast of Taiwan near Lanyu Island in March 1992. The concentrations of total copper

Table II Total concentration of copper (mg kg^{-1}) and the contents of sand and mud (%) in sediments collected from the Erhjin Chi coastal area

STATION	COPPER	SAND	MUD	STATION	COPPER	SAND	MUD
		March 12–14, 1991					
1	581	7.64	92.36	5	31.0	99.02	0.98
2	45.1	99.79	0.21	6	23.2	98.01	1.99
3	24.6	98.15	1.85	7	24.8	93.11	6.89
4	18.6	98.58	1.42	8	40.7	72.69	27.31
		October 4–6, 1991					
1	362	6.47	93.53	7	26.3	99.19	0.81
2	71.6	99.09	0.91	8	26.6	85.46	14.54
3	33.0	99.52	0.48	9	18.0	98.09	1.91
4	17.2	94.69	5.31	10	14.6	98.01	1.99
5	17.0	97.59	2.41	11	18.6	97.63	2.37
6	24.5	97.00	3.00	12	20.6	94.94	5.06
		March 25, 1992					
1	408	8.29	91.71	2	45.1	99.20	0.80

(2.40 μg l^{-1}) and the copper species in sea water were analyzed, and the results tabulated in Table III. After shaking the mixture for a suitable time, the supernatant (150 ml) was analyzed for total copper and copper species, and the results are also shown in Table III. In general, the higher the mud content, the higher the concentrations of total copper, mainly as particulate copper, were released from the sediments. For instance, when the sea water and sediments were mixed by shaking for one hour, probably analogous to tidal current mixing of sea water and sediments in the estuarine area, the concentration of total copper (94.8 μg l^{-1}) released from river sediments (mud content as high as 91.71%) was higher than that, 43.8 μg l^{-1}, in estuarine sediments (mud only 0.80%). When the mixture of sea water and river sediments was shaken for periods from 3 to 120 hours, the concentration of total copper decreased (Table III) from 94.8 μg l^{-1} to values ranging from 41.1 to 15.2 μg l^{-1}; a similar change was seen with estuarine sediments, decreasing from 43.8 μg l^{-1} to 20.2 to 10.2 μg l^{-1}.

If the experimental results are recalculated from the balance of total copper concentrations in both sea water and sediments during each mixing process, it is of interest to note that copper desorption from sediments to sea water was found only in the one-hour mixing process. When the mixture was shaken for more than 3 hours, the copper released from the sediments may be readsorbed to the remaining solid phases, i.e., the same sediments. A higher copper desorption rate (1.85 ppm hr^{-1}, Figure 3A) was found for both the higher mud and copper containing river sediments, and a lower desorption rate of 0.83 ppm hr^{-1} (Figure 3B) for the lower mud and copper containing estuarine sediments. If the term 'specific desorption rate' is defined as the copper desorption rate divided by the copper concentration in original mixed sediments, then the reasonable expectation is that the higher the sand content of sediments, the higher the specific desorption rate observed. For instance, a high value (1.8×10^{-2} hr^{-1}) of this specific rate was found in estuarine sediments (sand, 99.20%; Cu, 45.1 mg kg^{-1}, Table II) and a low value (4.5×10^{-3} hr^{-1}) was found in river sediments (sand, 8.29%; Cu, 408 mg kg^{-1}, Table II). When shaking the mixture for more than 3 hours, the initial copper sorption rate (0.50 ppm hr^{-1}, Figure 3A) in river sediments was higher than for one and three hour shaking periods, and then decreased to the equilibrium point (0.00 ppm hr^{-1}) after 24 hours shaking. For the estuarine sediments, the initial sorption rate was 0.22 ppm hr^{-1} (Figure 3B)

Table III The concentrations ($\mu g\ l^{-1}$) of total copper and copper species observed from the interaction of sea water and sediments*

SHAKING TIME	TOTAL COPPER	PARTICULATE COPPER		DISSOLVED COPPER					BIOAVAILABLE COPPER	
				TOTAL		LABILE	Cu++	NONLABILE		
(Hr)	(Conc)	(Conc)	(%)	(Conc)	(%)	(Conc)	(Conc)	(Conc)	(Conc)	(%)
Sea water collected from the eastern Taiwan in March 1992										
—	2.40	0.30	12.5	2.10	87.5	1.47	0.02	0.61	1.79	74.6
River Sediments (composed of mud 91.71%, sand 8.29% and copper 408 $\mu g\ g^{-1}$)										
1.0	94.8	79.7	84.0	15.2	16.0	7.58	0.13	7.45	87.4	92.1
3.0	41.1	27.9	68.0	13.2	32.0	6.55	0.11	6.50	34.6	84.2
5.0	38.5	26.0	67.7	12.4	32.3	6.14	0.10	6.16	32.3	84.0
7.0	32.7	22.4	68.5	10.3	31.5	4.91	0.08	5.29	27.4	83.8
24	15.9	5.38	33.8	10.5	66.2	4.69	0.08	5.76	10.2	63.8
48	14.9	4.76	31.9	10.2	68.1	4.08	0.07	6.03	8.91	59.6
96	15.1	4.75	31.5	10.4	68.5	4.11	0.07	6.17	8.93	59.1
120	15.2	4.46	29.3	10.8	70.7	4.17	0.07	6.53	8.70	57.1
Estuarine Sediments (Composed of mud 0.80%, sand 99.20% and copper 45.1 $\mu g\ g^{-1}$)										
1.0	43.8	18.0	41.0	25.9	59.0	16.3	0.28	9.24	34.6	78.9
3.0	20.2	6.00	29.7	14.2	70.3	8.79	0.15	5.29	14.9	73.9
5.0	13.9	2.72	19.6	11.1	80.4	6.94	0.12	4.08	9.78	70.6
7.0	11.2	1.21	10.8	10.0	89.2	5.50	0.09	4.44	6.80	60.5
24	11.2	1.30	11.7	9.86	88.3	5.07	0.08	4.71	6.45	57.8
48	10.3	1.04	10.1	9.28	89.9	5.00	0.08	4.20	6.12	59.3
96	10.2	0.94	9.2	9.24	90.8	5.03	0.08	4.13	6.05	59.4
120	10.2	0.93	9.1	9.31	90.9	4.95	0.08	4.28	5.96	58.2

* 100 g Erhjin Chi sediments (collected on March 25, 1992) and 2.0 l eastern sea water mixed by shaking for several hours, and then 150ml supernatant analyzed for total copper and copper species.

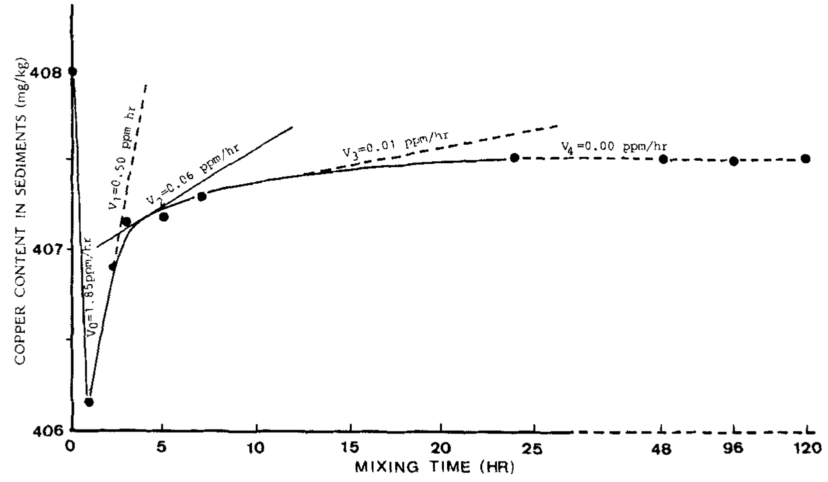

Figure 3A The process of copper desorption and adsorption during the mixing of sediments and sea water (For high mud-sediments, desorption rate, V_0, −1.85 ppm/hr; adsorption rate, V_i, 0.50–0.00 ppm/hr; equilibrium point, 24 hrs).

for the one to three hour shaking periods, and the equilibrium point (almost 0.00 ppm hr^{-1}) was reached in about 7 hours. Specific copper sorption rate (Cu sorption rate/Cu concentration in mixed sediment) applies to both desorption and adsorption. The high initial specific sorption rate (5.0×10^{-3} hr^{-1}) was found in more sandy estuarine sediments compared with that (1.2×10^{-3} hr^{-1}) in less sandy river sediments. The higher the sand content in sediments, the higher the copper specific desorption rate from sediments and the higher the copper specific sorption rate to the sediments were both observed. Therefore, to reach equilibrium, the more sandy estuarine sediments were subjected to only 7 hour shaking, but less sandy river sediments needed 24 hours.

INTERACTIONS OF COPPER SPECIES IN MIXTURE OF SEA WATER AND SEDIMENTS

For total copper desorption from sediments to sea water, the content of copper forms (particulate and dissolved) and copper species (labile and nonlabile, free ion and bioavailable) varied with the mud content of the sediments. For example, Table III also shows that when shaking the mixture of sea water and sediment for one hour, similar to tidal mixing in the estuary, a high percentage of particulate copper (84.0%) and a low percentage of dissolved copper (16.0%) was observed in the river sediments compared with that of sandy estuarine sediments. In the dissolved phase, high concentrations of free ion (0.28 $\mu g\ l^{-1}$ estimated on the basis of Hung *et al.* 1989b; Cu++/inorganic Cu = 0.017), labile (16.3 $\mu g\ l^{-1}$) and non-labile copper species (9.24 $\mu g\ l^{-1}$) were obtained for estuarine sediments, and relatively low concentrations of free ion (0.13 $\mu g\ l^{-1}$), labile (7.58 $\mu g\ l^{-1}$) and nonlabile copper species (7.45 $\mu g\ l^{-1}$) for river sediments. The content of bioavailable (sum of particulate and labile, 87.4 $\mu g\ l^{-1}$) copper released from the river sediments was higher than that of estuarine sediments, 34.6 $\mu g\ l^{-1}$. Fortunately, no oyster culture has been operating at river stations.

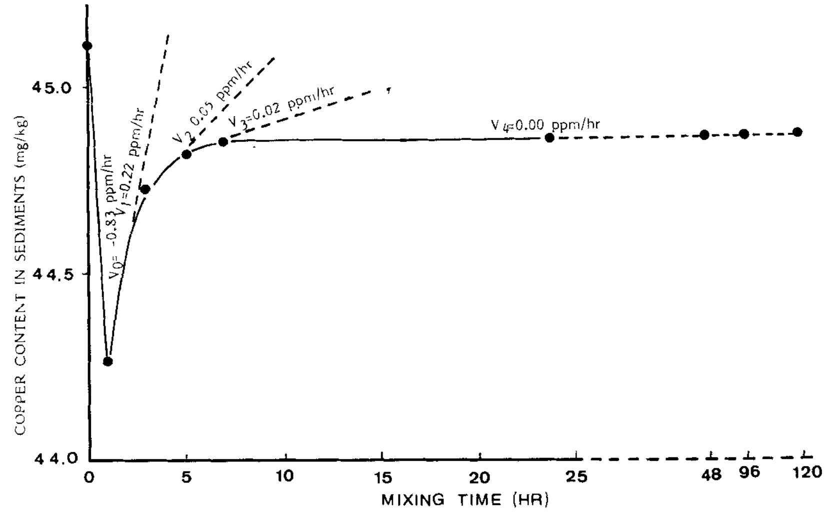

Figure 3B Continued (For high sand sediments, desorption rate, V_0, –0.83 ppm/hr; adsorption rate, V_i, 0.22–0.00 ppm/hr; equilibrium point, 7 hrs).

After mixing the sea water and sediments for more than three hours, the concentrations of all copper species decreased with increased shaking time. For example, Table III shows that when the mixture of sea water and river sediment was shaken for 3 to 120 hours the concentrations of particulate, dissolved, labile and nonlabile, free cupric ion and bioavailable copper decreased from 79.7 to 4.46 $\mu g\ l^{-1}$, 15.2 to 10.8 $\mu g\ l^{-1}$, 7.58 to 4.17 $\mu g\ l^{-1}$, 7.45 to 6.53 $\mu g\ l^{-1}$, 0.13 to 0.07 $\mu g\ l^{-1}$ and 87.4 to 8.70 $\mu g\ l^{-1}$, respectively; similar changes were seen with estuarine sediments, decreasing from 18.0 to 0.3 $\mu g\ l^{-1}$, 25.9 to 9.31 $\mu g\ l^{-1}$, 16.3 to 4.95 $\mu g\ l^{-1}$, 9.24 to 4.28 $\mu g\ l^{-1}$, 0.28 to 0.08 $\mu g\ l^{-1}$ and 34.6 to 5.96 $\mu g\ l^{-1}$, respectively. Although the percentages of dissolved copper increased from 16.0 to 70.7% for river samples and from 59.0 to 90.9% for estuarine samples when the mixing time increased from 3 to 120 hours, the percentages of free cupric ions from both river and estuarine sediments also decreased from 0.8% to 0.6% and from 1.1% to 0.9%, respectively. This might be the reason why green oysters were usually observed in the estuarine area rather than in the coastal area. For example, the extremely high copper concentrations of 2200 $\mu g\ g^{-1}$ and 4400 $\mu g\ g^{-1}$ (dry weight) in January 1986 and January 1989 were found in oysters from the estuarine area (Hung, 1988). Similar results were observed, for instance, in oysters (*Ostrea sandvicensis*) collected from the Honolulu Harbour in 1987 (NOAA, 1989) with a copper content of 2100 $\mu g\ g^{-1}$, dry weight. An early paper also indicated that a high value of copper (1527 $\mu g\ g^{-1}$, dry weight) was found in the Pacific oyster (*Crassostrea gigas*) grown in the Tamar River, Tasmania (Ayling, 1974). Roosenberg (1969) also found green oysters in Chesapeake Bay (estuary) around 1960s, attributed to copper discharged from the cooling water system of a power plant. In our experiment (Hung *et al.*, 1989b), the colour of oysters became green when the copper content was over 500 $\mu g\ g^{-1}$ (dry weight). The bioaccumulation of copper in oysters (26–81 ppm day^{-1}) has been found to be influenced by physical and chemical environmental parameters, particularly the concentrations of bioavailable copper (Hung and Tsai, 1992; Han and Hung 1990a). In this study, oysters cultured at Station 8 of the Erhjin Chi coastal area were collected on January

24 and March 25, 1992; high copper contents of 288 $\mu g\ g^{-1}$ (dry weight) in oysters were found in January compared with lower values in March (109 $\mu g\ g^{-1}$, dry weight). High concentrations of bioavailable copper (34.6 $\mu g\ l^{-1}$), free cupric ion (0.28 $\mu g\ l^{-1}$) and total copper (43.8 $\mu g\ l^{-1}$) were found in the estuarine water. These high total copper concentrations did not comply with EPA/China (Taipei) requirement of 20 $\mu g\ l^{-1}$ for both class A and class B ocean waters around Taiwan. With these high concentrations of bioavailable and free ion copper species in estuarine water, it is understandable why green oysters were usually found in January and the oyster mortality was found three months later (Hung, 1988; Han and Hung, 1990a) in the Erhjin Chi estuarine (mariculture) area. Unfortunately, we don't have recent data on copper content of oysters along the Erhjin Chi estuarine area because of the closing of oyster culture after 1986. The record of 4400 $\mu g/g$ copper in oysters in the Erhjin Chi estuarine area in January 1989 was through our oyster-culture experiments (Hung and Han, 1992). However, in this study we also collected oysters cultured at Luchukuo, about 40 kilometers north from Station 8 in January 24, 1992. The copper content of 162 $\mu g\ g^{-1}$ (dry weight) in these oysters was lower than those (288 $\mu g\ g^{-1}$, dry weight) collected from the Station 8 of Erhjin Chi coastal station.

CORRELATIONS AMONG COPPER SPECIES, CHEMICAL AND ECOLOGICAL PARAMETERS

Tables IV and V show that the biological, chemical and hydrographical parameters, including total copper and dissolved copper species, collected from the Erhjin Chi

Table IV Average values of biomass and chemical and biological parameters in bottom water along the Erhjin Chi coastal area*

Station	Temp.	Salinity	Oxygen Saturat.	Chl.-a	ATP	Primary Productivity	POC
		October 4, 1991					
1	30.2	3.141	30.6	0.96	641	0.94	1880
2	30.0	5.183	39.2	1.40	1740	1.07	2180
3	28.8	33.069	93.0	4.42	281	1.50	395
4	28.9	32.587	91.4	2.67	366	1.23	278
5	29.1	28.100	76.1	2.71	506	1.25	442
6	29.0	33.348	94.2	2.23	187	1.11	187
7	28.9	33.176	94.0	2.01	426	1.11	350
8	28.9	33.145	95.5	2.58	366	1.21	229
9	28.7	28.754	85.2	2.16	490	1.15	550
10	28.4	33.401	94.1	2.86	304	1.23	229
11	28.8	33.360	94.5	2.80	326	1.22	219
12	28.9	33.363	94.9	3.64	288	1.35	162
		March 25, 1992					
1	30.4	9.164	67.9	5.60	6870	1.56	4400
2	28.8	21.573	72.2	2.54	3860	1.19	2000
4	26.4	32.079	93.4	2.10	1470	1.11	222
5	26.2	34.090	87.3	2.98	2340	1.27	421
6	25.8	34.057	92.8	3.37	2800	1.33	80.8
10	25.6	34.146	88.7	0.61	731	0.63	157

* Units: Temperature, °C; Salinity, ‰; Oxygen saturation, %; Chlorophyll-a, $\mu g\ l^{-1}$; Adenosine triphosphate (ATP), ng l^{-1}; Primary productivity, $\mu g\ l^{-1} hr^{-1}$; Particulate organic carbon (POC), $\mu g\ l^{-1}$.

Table V Concentrations of copper species and forms ($\mu g\ l^{-1}$) in bottom water along the Erhjin Chi coastal area (Bioavailable = labile + particulate)

STATION	TOTAL	PARTI-CULATE	DISSOLVED IN WATER				BIOAVAILABLE FRACTION
			TOTAL	LABILE		NONLABILE	
				INORGANIC	FREE*		
	March 19–21, 1990						
2	7.07	1.06	6.00	4.88	0.08	1.10	5.94
3	6.90	0.69	6.21	5.11	0.09	1.00	5.80
4	11.2	1.45	9.70	4.52	0.08	5.10	5.97
5	6.82	0.63	6.19	3.34	0.06	2.80	3.97
6	8.71	1.93	6.78	4.03	0.07	2.70	5.96
7	11.0	0.66	10.3	4.81	0.08	5.40	5.47
8	5.36	0.31	5.05	4.00	0.07	1.00	4.31
9	7.82	0.39	7.43	6.30	0.11	1.00	6.69
10	10.2	0.75	9.48	2.87	0.05	6.60	3.62
11	8.55	1.03	7.52	4.78	0.08	2.70	5.81
12	10.9	1.25	9.46	2.44	0.04	7.20	3.69
	October 4–6, 1991						
1	84.8	52.5	32.3	nd	nd	32.3	52.5
2	57.4	20.9	36.5	6.97	0.12	29.5	27.9
3	13.4	8.99	4.41	1.95	0.03	2.46	10.9
4	22.5	5.60	16.9	3.08	0.05	13.8	8.68
5	10.6	2.85	7.75	4.70	0.08	3.05	7.55
6	6.32	0.84	5.48	2.73	0.05	2.75	3.75
7	7.58	1.69	5.89	1.86	0.03	4.03	3.55
8	9.14	2.88	6.26	1.46	0.02	4.80	4.34
9	10.6	5.02	5.58	2.87	0.05	2.71	7.89
10	16.9	6.30	10.6	1.83	0.03	8.77	8.13
11	7.86	2.10	5.76	1.41	0.02	4.35	3.51
12	9.85	3.11	6.74	5.82	0.10	0.92	8.93
Ave.2–12	15.7	5.48	10.2	3.15	0.05	7.02	8.63
Ave.2–8	18.1	6.25	11.9	3.25	0.08	8.63	9.50
Ave.9–12	11.3	4.13	7.17	2.98	0.05	4.19	7.12

* Calculated according to Hung *et al.* 1989b.
nd: < 1.0 $\mu g\ l^{-1}$.

river, estuarine and coastal area, varies with location and season, particularly with the onset of the rainy season. In southern Taiwan, the rainy season usually begins from March/April and the dry season begins in September/October (Hung *et al.*, 1992). Stream flow in the dry season is much less than in the rainy season, and the river-bed (mainly mud) absorbs heavy metals and organic pollutants discharged freely from domestic and industrial sources without any pretreatment. Immediately after heavy rain, pollutants in the river sediments are released to the river water and then flow to the estuarine and coastal areas. After heavy rain, pollutants continue to accumulate in the sediments as the input from pollution sources continues. Therefore, it was quite reasonable to find, see Table IV, that the values of salinity, oxygen saturation, chlorophyll-a, ATP, POC and primary productivity were generally low, especially at the river and estuarine stations, in October 1991 compared with values found in March 1992. Unfortunately, the total copper and copper species in water were not determined in March 1992. However, comparing the results obtained in March 1990 (Hung *et al.*, 1992) with those in October 1991 (Table V), the contents of total copper (6.32–84.8 $\mu g\ l^{-1}$), particulate (0.84–52.5 $\mu g\ l^{-1}$), dissolved (4.41–36.5

μg l^{-1})) and bioavailable copper (3.51–52.5 μg l^{-1}) were much higher, particularly at the river and estuarine stations, in October 1991. Lower values of total copper (5.36–11.2 μg l^{-1}), particulate (0.31–1.93 μg l^{-1}), dissolved (5.05–10.3 μg l^{-1}) and bioavailable copper (3.62–6.69 μg l^{-1}) (Table V) were obtained in the Erhjin Chi estuarine and coastal waters in March 1990.

The total copper and copper species, such as bioexchangeable (phase-1), skeletal (phase-2), easily reducible (Fe and Mn oxides, phase-3), moderately reducible (crystalline Mn oxides, phase-4), organic combined with sulphides (phase-5) and detritus with minerals (phase-6), in mud and sand separated from the Taiwan Erhjin Chi river and estuarine (including the coastal) sediments were analyzed. The results shown in Tables VI and VII indicate that the total copper and copper species contained in both mud- and sand- sediments varied with season and location, particularly at the onset of the rainy season. Extremely high concentrations of total copper in mud (580 mg kg^{-1} in March 1991, 363 mg kg^{-1} in October 1991, and 383 mg kg^{-1} in March 1992) and in sand (583 mg kg^{-1} in March 1991, 493 mg kg^{-1} in October 1991 and 701 mg kg^{-1} in March 1992) were found in the Erhjin Chi river sediments compared with those of total copper in estuarine and coastal sediments (mud, 79.4–151 mg kg^{-1} in March 1991, 27.7–209 mg kg^{-1} in October 1991, 246 mg kg^{-1} in March 1992; sand,

Table VI The concentration of total copper and copper species in mud separated from the Taiwan Erhjin Chi coastal sediments

STA.	TOTAL (mg kg^{-1})	PHASE-1 (%)	PHASE-2 (%)	PHASE-3 (%)	PHASE-4 (%)	PHASE-5 (%)	PHASE-6 (%)	PHASES-1+2 (%)
		Taiwan Erhjin Chi coastal sediments collected in March 1991						
1	580	3.40	14.3	0.86	37.1	39.1	5.11	17.7
2	151	11.5	18.7	9.28	48.0	3.73	8.77	30.1
3	119	8.53	29.1	6.94	35.6	10.4	9.46	37.5
4	132	11.2	27.5	11.9	38.2	4.96	6.27	38.6
5	122	11.1	28.1	11.9	36.0	6.05	6.82	39.1
6	87.5	9.05	25.5	13.2	37.3	5.02	9.89	34.6
7	79.4	10.0	27.7	13.4	32.3	5.82	10.7	37.7
8	88.8	9.6	29.9	14.2	31.5	3.92	11.0	39.4
Av.	108	10.1	26.6	11.5	37.0	5.69	8.98	36.7
		Taiwan Erhjin Chi coastal sediments collected in October 1991						
1	363	9.98	17.6	3.53	48.0	13.2	7.72	27.6
2	209	23.4	26.6	6.02	26.3	13.8	3.95	50.0
3	32.0	6.74	11.5	8.52	33.4	17.2	22.6	18.2
4	36.9	4.33	8.26	7.96	23.2	11.5	44.7	12.6
5	58.0	5.73	12.0	12.0	35.5	11.5	23.3	17.7
6	62.0	6.84	18.1	13.9	41.5	7.99	11.7	24.9
7	88.1	4.63	17.0	14.4	40.7	6.14	17.0	21.6
8	40.7	5.70	11.9	7.74	36.8	16.4	21.5	17.6
9	40.9	6.85	16.4	11.6	32.0	13.5	19.6	23.3
10	41.5	5.97	13.9	9.61	34.2	18.3	18.1	19.9
11	40.0	8.00	14.7	11.0	38.2	15.5	12.5	22.7
12	27.7	8.09	13.3	9.50	30.5	13.3	25.3	21.4
Av.	46.8	6.29	13.7	10.6	34.6	13.0	21.6	20.0
		Taiwan Erhjin Chi coastal sediments collected in March 1992						
1	383	16.3	24.9	2.20	35.4	16.1	5.26	41.1
2	246	8.96	26.0	14.7	24.6	18.6	7.20	34.9

Av.: Average values at estuarine and coastal stations.

Table VII Concentration of total copper and copper species in sand separated from the Taiwan Erhjin Chi coastal sediments

STAT.	TOTAL (mg kg^{-1})	PHASE-1 (%)	PHASE-2 (%)	PHASE-3 (%)	PHASE-4 (%)	PHASE-5 (%)	PHASE-6 (%)	PHASES-1+2 (%)
		Taiwan Erhjin Chi coastal sediments collected in March 1991						
1	583	4.31	13.2	0.79	33.7	42.2	5.82	17.5
2	44.9	12.5	19.1	23.1	37.6	2.94	4.77	31.7
3	22.8	14.0	27.7	15.1	28.6	2.02	12.5	41.7
4	17.0	14.5	20.9	12.4	35.1	2.23	14.9	35.4
5	30.1	11.4	23.0	17.6	34.2	4.12	9.56	34.4
6	21.8	9.66	20.7	18.6	36.1	3.43	11.5	30.4
7	20.7	11.1	19.6	18.9	33.9	3.95	12.4	30.7
8	22.7	11.4	23.3	18.9	28.8	3.31	14.2	34.8
Av.	25.7	11.9	22.0	17.8	33.5	3.14	11.4	34.2
		Taiwan Erhjin Chi coastal sediments collected in October 1991						
1	493	5.04	14.1	1.17	28.6	43.9	7.21	19.1
2	70.3	10.6	19.8	8.36	46.22	4.75	10.3	30.4
3	33.0	2.42	5.09	41.5	13.0	5.24	32.7	7.51
4	16.1	4.48	9.83	9.83	33.2	10.0	32.7	14.3
5	16.0	4.49	10.5	9.18	32.5	7.49	35.9	15.0
6	23.3	5.48	15.8	10.8	32.3	8.87	25.8	21.3
7	25.8	10.2	13.4	9.76	30.2	10.3	26.1	23.6
8	24.2	5.95	13.5	10.0	36.3	9.50	24.8	19.5
9	17.6	6.83	10.8	8.37	23.7	10.5	39.9	17.6
10	14.9	6.98	10.6	8.46	27.1	11.6	35.3	17.6
11	18.1	6.18	9.28	7.56	20.1	12.7	44.2	15.5
12	20.3	6.71	9.32	20.7	21.8	13.1	28.4	16.0
Av.	20.9	5.97	10.8	13.6	27.0	9.82	32.6	15.0
		Taiwan Erhjin Chi coastal sediments collected in March 1992						
1	701	5.27	10.2	0.47	32.5	45.4	6.16	15.5
2	43.5	5.86	16.4	11.2	29.0	13.9	23.7	22.2

Av.: Average values at estuarine and coastal stations.

17.0–44.9 mg kg^{-1} in March 1991, 14.9–70.3 mg kg^{-1} in October 1991, 43.5 mg kg^{-1} in March 1992).

For total copper, much higher percentages of the species in phase-4 (crystalline Mn oxides species, 23.1–59.6% in mud and 43.2–82.0% in sand) with lower percentages of phase-1 and phase-2 (bioexchangeable and skeletal species, 5.65–16.8% in mud and 5.36–7.18% in sand)) were found in Antarctic ocean sediments compared with those found in the Erhjin Chi area (phase-4, 24.6–48.0% in mud and 13.0–46.2% in sand; phase-1 and phase-2, 12.6–50.0% in mud and 15.0–41.7% in sand). Some explanation of these phenomena have been discussed (Hung *et al.*, 1989b). There is no doubt that the higher contents of copper- bioexchangeable and skeletal species in the Erhjin Chi area are correlated with problems arising from the inorganic (high concentration of total copper) and organic (low values of oxygen solubility) pollutants discharged from domestic and industrial sources. Furthermore, correlations between the total copper and copper species in sediments and bottom waters, and biological, chemical and hydrographical parameters (Table VIII) along the Erhjin Chi area were also found. These high concentrations of copper in bioexchangeable and skeletal phases will influence the biological activities in the marine ecosystem, including the incidence of green discoloration and mortality of cultured oysters (Hung, 1988) as well as the mass killing of larval shrimps (Chen, 1981) observed along the southwestern coast of Taiwan.

Table VIII Correlation coefficients among the copper species and forms in bottom water and mud- and sand- sediments, and chemical and biological parameters in October 1991 in the Erhjin Chi area.

	T/W	P/W	D/W	L/W	N/W	B/W	SAL	TEMP	pH	DO	POC	ATP	T/S	1/S	2/S	3/S	4/S	5/S	6/S
T/W	1												0.8546	0.8656	0.8789	0.2191	0.9021	0.5062	0.0385
P/W	0.9059	1											0.8754	0.8121	0.8186	0.4503	0.8369	0.4562	0.2827
D/W	0.9824	0.8765	1										0.8011	0.8570	0.8737	0.0694	0.8988	0.5125	0.1105
L/W	0.6464	0.5707	0.6616	1									0.5593	0.6054	0.6128	0.0936	0.6244	0.3969	0.1952
N/W	0.9690	0.8658	0.9855	0.5246	1								0.7829	0.8359	0.8532	0.0575	0.8790	0.4920	0.0813
B/W	0.9552	0.9767	0.8982	0.7392	0.8523	1							0.8705	0.8302	0.3876	0.3947	0.8557	0.4818	0.1788
SAL	0.9464	0.9031	0.9278	0.6840	0.8985	0.9262	1						0.9392	0.9589	0.9722	0.2177	0.9777	0.6517	0.1072
TEMP	0.7510	0.6547	0.7737	0.6716	0.7263	0.7191	0.8324	1					0.8245	07830	0.8349	0.2590	0.8577	0.5353	0.0689
pH	0.9583	0.9031	0.9464	0.7032	0.9152	0.9314	0.9934	0.8620	1				0.9325	0.9473	0.9626	0.2262	0.9746	0.6179	0.0857
DO	0.9286	0.8875	0.9096	0.7197	0.8697	0.9231	0.9832	0.8359	0.9839	1			0.9013	0.9167	0.9358	0.2004	0.9464	0.5373	0.1102
POC	0.9485	0.9204	0.9027	0.5684	0.9166	0.9090	0.9807	0.7934	0.9777	0.9515	1		0.9513	0.9597	0.9613	0.2771	0.9652	0.6517	0.1788
ATP	0.9165	0.8929	0.8875	0.6779	0.8541	0.9161	0.9697	0.8637	0.9636	0.9292	0.9515	1	0.9515	0.9417	0.9484	0.3196	0.9601	0.7174	0.1359
T/M	0.8504	0.7757	0.8554	0.5929	0.8369	0.7969	0.9479	0.8168	0.9461	0.9356	0.9508	0.8941							
1/M	0.9317	0.8850	0.9160	0.6692	0.8883	0.9073	0.9979	0.8228	0.9878	0.9769	0.9808	0.9625							
2/M	0.8786	0.8192	0.8730	0.6194	0.8509	0.8398	0.9723	0.8041	0.9626	0.9501	0.9687	0.9237							
3/M	0.4204	0.3197	0.4616	0.3189	0.4519	0.3487	0.5885	0.5593	0.5929	0.5965	0.6193	0.4987							
4/M	0.6710	0.5883	0.6893	0.4505	0.6805	0.6047	0.8222	0.7419	0.8164	0.8095	0.8399	0.7614							
5/M	0.9330	0.9002	0.9088	0.6068	0.8944	0.9028	0.9883	0.7869	0.9719	0.9697	0.9759	0.9545							
6/M	0.0321	0.1132	0.1183	0.0434	0.1245	0.0811	0.0000	0.1441	0.0139	0.0156	0.0431	0.1196							

T/W, Total Cu in water; P/W, Particulate Cu in water; D/W, Dissolved Cu in water; L/W, Labile Cu in Water; N/W, Nonlabile Cu in water; B/W, Bioavailable Cu in water; SAL, Salinity; TEMP, Temperature; DO, Dissolved oxygen; POC, Particulate organic carbon; ATP, Adenosine triphosphate; T/M, Total Cu in mud; 1/M to 6/M, Phase-1 to Phase-6 Cu in Mud; T/S, Total Cu in sand; 1/S to 6/S, Phase-1 to Phase-6 Cu in sand.

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