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THE RELATIONSHIP BETWEEN ADSORPTION OF HEAVY METAL AND ORGANIC MATTER IN RIVER SEDIMENTS

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Sediment samples of eight sites in two rivers located in northern Taiwan, the Tao-Chen River and the Lau-Che River, were collected to investigate the influences of organic matter on adsorbabilities of heavy metals in dry and wet periods. A batch scale adsorption study was conducted to examine the adsorbabilities of heavy metals of sediments. In the less polluted river (Tao-Chen River), pH, organic matter, cation exchange capacity (CEC), and heavy metals of sediments were independent of the changes of the flow of the river. In contrast, they would be related to those of the more polluted river (Lau-Che River). Metal concentrations and CEC in sediments were positively correlated with organic matter content. On the other hand, there was significantly positive correlation between the adsorbabilities of heavy metals of sediments and organic matter content. The adsorbabilities of sediments to heavy metals increased in the order Zn < Pb < Cu < Cr. The amount of adsorbed Cr in sediments was much greater than that of the other metals, and Zn was adsorbed much less than others. ©1998 Elsevier Science Ltd

INTRODUCTION

Most rivers in Taiwan are the receiving water bodies of domestic, industrial, and agricultural wastewaters. Resulting from high industrialization and discharge of domestic wastewater, the concentrations of heavy metals in rivers are increasing. Adsorption to suspended particulate matter and precipitation processes rapidly transfer contaminates from surface waters to bottom sediments (Förstner and Wittmann 1981). The major mechanism of accumulation of heavy metals in sediments generates the existence of five binding forms: 1) adsorptive and exchangeable, 2) bound to carbonates, 3) bound to organic matter and sulfides, 4) bound to Fe and Mn oxides, and 5) residual metals (Modak et al. 1992; Pardo et al. 1990; Salomons and Förstner 1980; Tessier et al. 1979). In the five binding forms of heavy metals in sediment, Zn appeared in the fractions of organic matter and sulfides, and Fe and Mn oxides. Cu was mainly found in fractions of organic matter and sulfides, and residuals. Most Pb was found in the residual fraction (Pardo et al. 1990).

In natural waters, there is a strong affinity between metals and organic matter (Förstner and Wittmann 1981). Dissolved and particulate organic matters in the water column act as scavengers for metals, and the scavenged metals may then be incorporated into bottom sediments. These organometallic complexes follow the Irwing-William series: Hg > Cu > Pb > Zn > Cd > Fe (Coquery and Welbourn 1995). On the other hand, adsorption is thought to be an important process in the transfer course of heavy metals in the river, but the mechanism of their interactions is not well known. Rose (1989) found that the valence of heavy metal would affect the adsorbabilities of the sediment to heavy metals; the greater the valence of the heavy metal, the greater adsorbability of the sediment. Therefore, adsorptive properties of sediments can provide

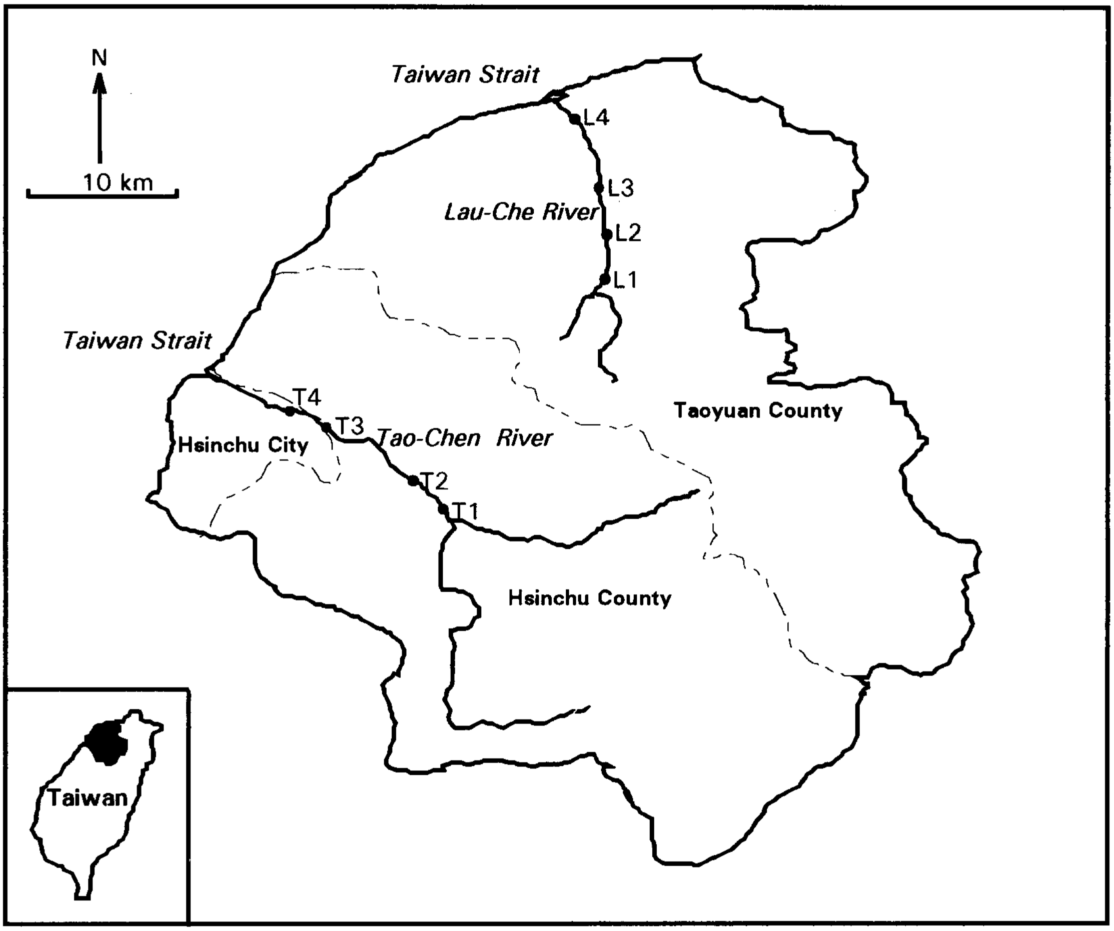

Fig. 1. Map of study area and sampling sites.

valuable information relating to the tolerance of the river to the added heavy metal loadings (Jain and Ram 1997).

Because of the abilities of accumulation, toxicity, and stabilization, heavy metals in sediments have been considered to be a pollution index of a territory. Concentrations of metals within bottom sediments can consequently be 1-3 orders of magnitude greater than in the overlying surface water (Bubb and Lester 1994). However, the transport of heavy metals in rivers is reversible. The accumulated heavy metals may be remobilized from sediments by natural processes and man-made changes in external parameters such as pH changes due to acid rain and complexing agents (Salomons et al. 1987). Sediment existing in the bottom of a river may cause various effects on the water quality, so it is important to understand the interaction between sediments and pollutants in the river.

At the same time, different compositions of the sediments also result in different reactions with pollutants in the river. In the present study, sediment samples of two rivers polluted in different degrees, the Lau-Che River and the Tao-Chen River, located in northern Taiwan, were collected to examine the influences of organic matter on adsorbabilities of heavy metals in dry and wet periods. The correlations of heavy metals with some physico-chemical properties of sediments, such as cation exchange capacity (CEC) and organic matter, were also investigated in this work.

MATERIALS AND METHODS

Sampling and sampling sites

The Lau-Che River (Fig. 1), which flows through two industrial parks in Taoyuan County, Taiwan, is a secondary river having a basin area of about 82 km^2. It has been seriously polluted by municipal and industrial effluents, whose daily discharges are 44 870 and 89 335 m^3/d, respectively. Sediment samples (top 5 cm) were collected from the center of the river channel at four sites, in which sites L1 and L4 were downstream of the industrial parks, through October 1993 to April 1994 (in dry (Nov 1993 and Feb 1994) and wet (Apr 1994) periods).

The Tao-Chen River (Fig. 1), flowing through Hsinchu County and draining an area of about 566 km^2, is 1 of the 21 primary rivers in Taiwan. The Tao-Chen River has been proclaimed to be a water-source, water-quality, and water-quantity conservation district for the uses of drinking water and irrigation water since 1983. The daily discharges of municipal and industrial effluents into the river were 75 460 and 3024 m^3/d. It is a less polluted river. Hence, four sites were also sampled at the same time as in the Lau-Che River.

Analysis of the sediments

All gravel and litter were removed from the sediment sample. The sample was natural dried at room temperature and screened with a 20 mesh (0.84 mm) sieve. The sediment samples were analyzed for pH value (LaBauve et al. 1988), organic matter (volatile solids) (APHA 1992), and the CEC (USEPA 1990). The "available" content of heavy metals in the sediment was examined by a 0.1 N HCl extraction method (Banat et al. 1974). The concentrations of Pb, Cu, Zn, and Cr were analyzed by a flame atomic absorption spectrometer (Hitachi, Model Z-8100). The minimum detection limits for Pb, Cu, Zn, and Cr were found to be 24, 6, 15, and 3 μg/L, respectively.

Adsorption experiment

A batch adsorption test was conducted to examine the adsorbabilities of heavy metals of sediments. Experiments were carried out as follows: a sediment sample (0.05 g) was placed in a 100-mL plastic flask. Various concentrations (5, 10, 15, 20, 30, and 40 mg/L) of 50 mL of heavy metals (Pb, Cu, Zn, and Cr, respectively) were added to a flask containing a 0.05 g sediment sample and the pH was controlled at 6.0-6.5. The flask was vibrated at a temperature of 20°C with a speed of 150 rpm in a horizontal shaker. The clear supernatant was collected in the flask after 4 h of shaking. The clear supernatant was filtered with a 0.45 μm membrane and stored in the plastic bottles. Then, the bottles were refrigerated in 4°C for further heavy metal analysis.

RESULTS AND DISCUSSION

Properties of sediment

The pH, content of organic matter, CEC, and "available" amount of heavy metals of the dried sediment in this research are shown in Table 1. Organic matter content in sediments of the Tao-Che River ranged from 19 to 50 mg/g, pH of sediments ranged from 7.1 to 8.1, and CEC ranged from 6 to 10 meq/100 g. Metal concentrations in sediments ranged from 2 to 10 μg/g for Cu, 5 to 28 μg/g for Zn, 0.7 to 20 μg/g for Pb, and 0.1 to 3 μg/g for Cr. Generally speaking, there were little variations in pH, organic matter, CEC, and heavy metals in the sediment of the Tao-Chen River, the less polluted river, between dry and wet periods. The results reveal that the properties of sediments in the less polluted river (Tao-Chen River) were independent of the changes of the flow of the river.

Organic matter contents in sediments of the Lau-Che River ranged from 14 to 626 mg/g, pH of sediments ranged from 4.0 to 7.6, and CEC ranged from 4 to 69 meq/100 g. Metal concentrations in sediments ranged from 0.2 to 278 μg/g for Cu, 2 to 26 μg/g for Zn, 0.6 to 250 μg/g for Pb, and 3 to 164 μg/g for Cr. Compared to the Tao-Chen River, pH, organic matter, CEC, and heavy metals in the sediment of the Lau-Che River, the more polluted river, varied obviously between dry and wet periods. Simultaneously, the contents of heavy metals in sediments in sites L1 and L4 downstream of the industrial parks were greater than others. It appeared to relate specifically to the anthropogenic discharge of metal laden effluents from the industrial parks. Due to higher flow of the river in the wet period, the organic matters and fine sediment particles were scoured from the bottom sediment. Thus, the pH and contents of heavy metals in the sediments of the Lau-Che River in the wet period were less than those in the dry period.

The relationship between organic matter and heavy metals

Metal concentrations in the sediments were positively correlated with organic matter contents for all metals, as shown in Table 2. Correlation coefficients were high for Zn and Cr with CEC (Fig. 2). Organic matter and clay colloid contribute to the CEC of the sediment. Adsorbability of the heavy metal of the sediment increased with increasing CEC. Accordingly, organic matters are the important scavengers for metals in river sediments.

Adsorbabilities of heavy metals

Figures 3 and 4 were the adsorbabilities of heavy metals of sediments of the Tao-Chen River and the Lau-Che River with initial concentrations of heavy

Table 1. The properties of sediments of the Lau-Che River and the Tao-Chen River.

Date	River	Site	pH	Organic matter (mg/g)	CEC (meq/100 g)	Cu (μg/g)	Zn (μg/g)	Pb (μg/g)	Cr (μg/g)
1993/11*	Tao-Chen	T1	8.1	26.0	-	3.3	5.3	ND	ND
		T2	7.6	49.6	-	1.5	14.9	ND	ND
		T3	7.5	18.7	-	10.1	14.2	10.0	ND
		T4	7.6	25.1	-	8.3	21.6	10.1	ND
	Lau-Che	L1	6.8	14.0	-	106.0	2.0	160.0	5.4
		L2	6.9	125.0	-	278.0	ND	250.1	32.1
		L3	7.6	22.0	-	60.0	14.1	110.0	2.6
		L4	4.5	626.0	-	201.5	25.5	20.2	163.5
1994/2*	Tao-Chen	T1	7.8	26.7	8.2	6.3	17.0	10.1	0.8
		T2	7.6	28.0	9.4	12.6	21.3	20.0	2.9
		T3	7.4	21.5	6.1	5.4	10.2	4.2	0.1
		T4	7.4	24.3	7.5	5.9	28.2	8.8	1.0
	Lau-Che	L1	6.9	151.6	21.2	89.8	ND	649.8	203.6
		L2	5.9	111.1	7.7	208.6	ND	392.4	91.7
		L3	7.1	499.7	68.8	2.1	24.7	0.6	ND
		L4	-	-	-	-	-	-	-
1994/4**	Tao-Chen	T1	7.6	23.9	6.7	2.8	10.4	4.0	ND
		T2	7.5	37.6	9.7	5.7	15.7	6.8	ND
		T3	7.4	20.7	7.2	3.1	7.3	2.5	ND
		T4	7.1	22.5	8.0	2.1	10.0	0.7	ND
	Lau-Che	L1	5.9	17.0	4.5	237.4	1.9	159.8	4.4
		L2	5.3	151.3	16.7	195.2	ND	169.8	30.1
		L3	6.9	41.3	63.2	0.2	2.9	ND	ND
		L4	4.0	48.3	8.5	27.3	14.5	27.3	4.8

* in dry period; ** in wet period; ND: not detectable.

Table 2. The relationship between organic matter (OM) and CEC, heavy metals in the sediment.

River	CEC/Metal	Linear regression	Correlation coefficient (r)
Tao-Chen	CEC	CEC = 1.88(OM) + 3.05	0.84
	Cu	Cu = 2.63(OM) - 0.24	0.25
	Zn	Zn = 17.35(OM) - 27.83	0.61
	Pb	Pb = 2.84(OM) + 0.64	0.30
	Cr	Cr = 3.42(OM) - 7.40	0.82
Lau-Che	CEC	CEC = 1.45(OM) - 1.62	0.99
	Cu	Cu = 0.83(OM) + 154.61	0.28
	Zn	Zn = 0.33(OM) + 6.78	0.86
	Pb	Pb = 17.99(OM) + 77.75	0.54
	Cr	Cr = 2.60(OM) + 20.86	0.64

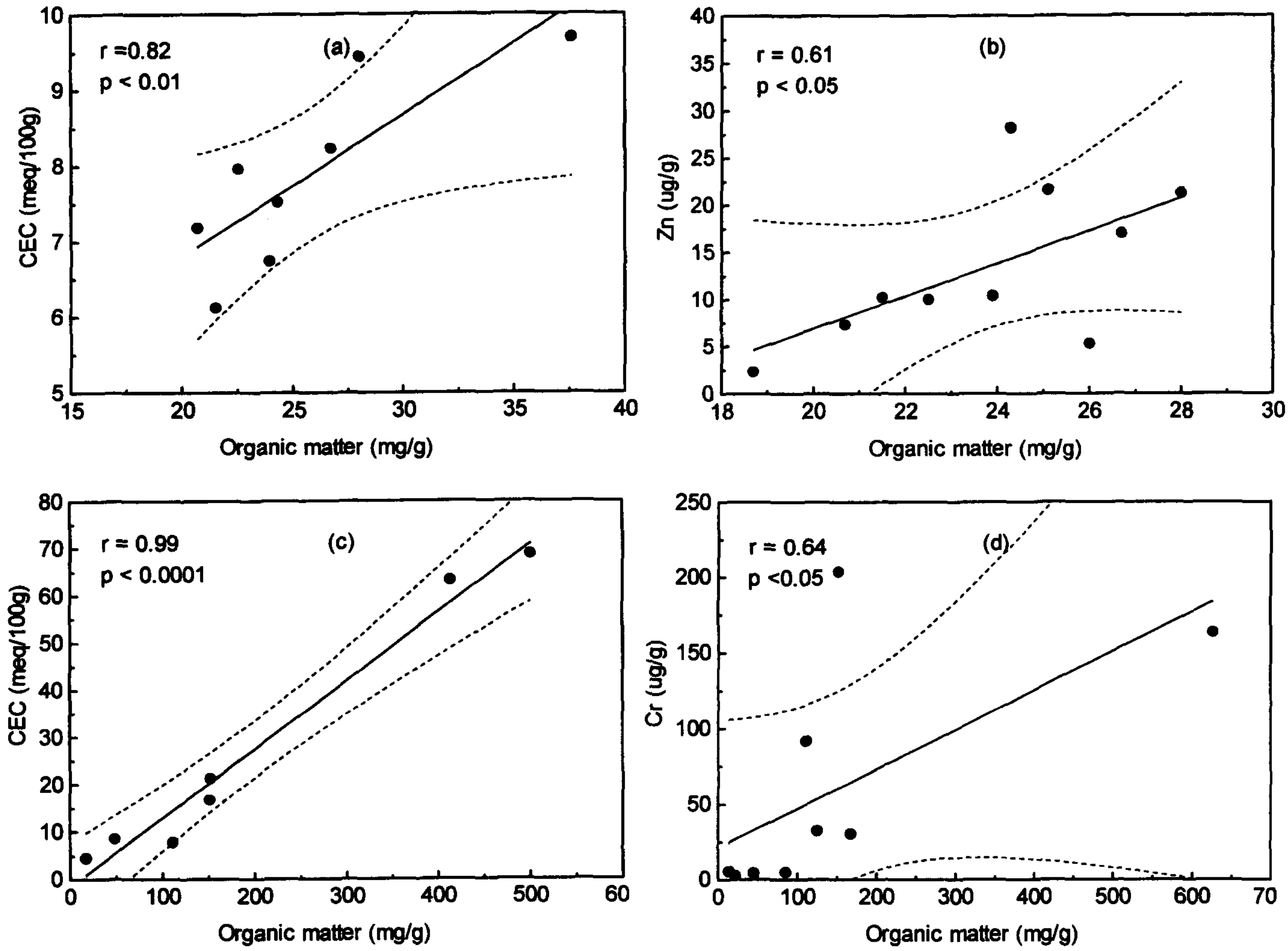

Fig. 2. Relationship between metal concentration, CEC, and organic matter content in sediments (dotted lines are the prediction interval at the 95% confidence level): (a) CEC of Tao-Chen River, (b) Zn of Tao-Chen River, (c) CEC of Lau-Che River, and (d) Cr of Lau-Che River.

metals of 30 mg/L. For both rivers, the adsorbabilities (meq of adsorbed metals/100 g of sediment) of heavy metals of sediments in the dry period were greater than those in the wet period, since organic matter contents of sediments were higher in the dry period. The adsorbabilities of sediments to heavy metals increased in the order Zn < Pb < Cu < Cr. This result agreed with the conclusion of Rose (1989) and the Irwing-William series (Coquery and Welbourn 1995). Based on the adsorption data, plots were prepared between the heavy metals adsorbed by per milligram of organic matter versus initial concentration of heavy metal (Fig. 5). This figure indicates that the total metal adsorbed by per milligram increases with increasing initial concentration of heavy metal. This is obvious because more efficient use of the adsorptive capacities of the adsorbent is expected due to a greater driving force by a higher concentration gradient pressure (Jain and Ram 1997).

The relationship between the adsorbability of heavy metal and organic matter

There was significant positive correlation between adsorbabilities of heavy metals of sediments and organic matter contents for all metals in dry and wet periods, as listed in Table 3. Correlation coefficients were high for Cu, Pb, and Cr. The adsorbabilities of heavy metals of sediments increased with increasing organic matter contents. Therefore, the organic matter content in the sediment can be used as a simple index for assessing the degree of pollution of the sediment.

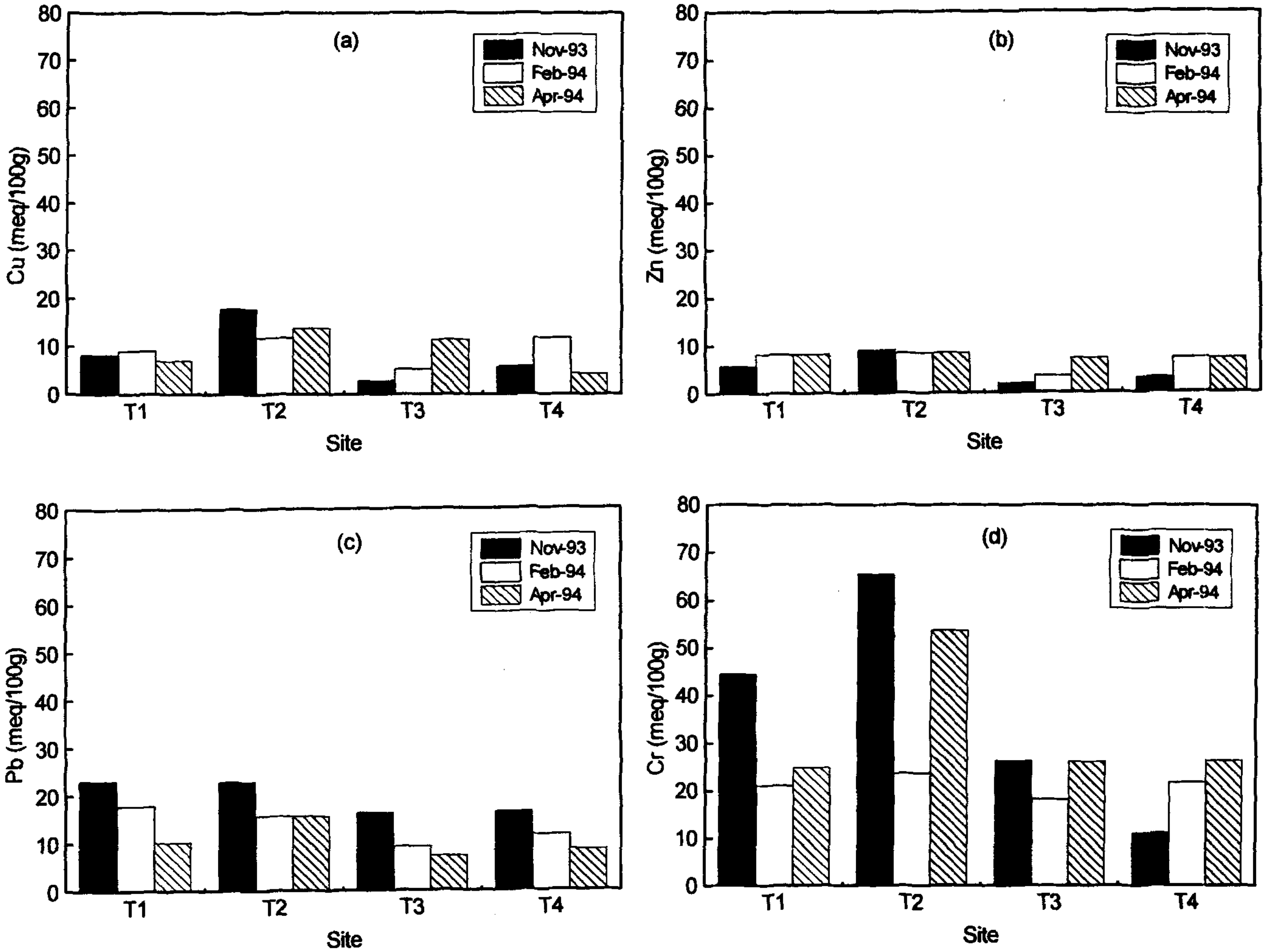

Fig. 3. Adsorbability of heavy metals in the sediment of the Tao-Chen River in dry and wet periods (Ç= 30 mg/L): (a) Cu, (b) Zn, (c) Pb, and (d) Cr.

Table 3. The relationship between OM and the adsorbability of heavy metal of the sediment.

River	Metal	Linear regression (dry period)*	Correlation coefficient (r)	Linear regression (wet period)**	Correlation coefficient (r)
Tao-Chen	Cu	(x/m) = 1.23(OM) - 0.71[a]	0.87	(x/m) = 1.08(OM) + 0.34	0.70
	Zn	(x/m) = 0.63(OM) + 0.26	0.69	(x/m) = 0.50(OM) + 1.05	0.73
	Pb	(x/m) = 2.95(OM) + 8.26	0.60	(x/m) = 4.76(OM) - 1.54	0.89
	Cr	(x/m) = 3.24(OM) - 3.84	0.81	(x/m) = 2.88(OM) - 2.18	0.89
Lau-Che	Cu	(x/m) = 0.19(OM) + 2.70	0.74	(x/m) = 0.19(OM) + 2.18	0.95
	Zn	(x/m) = 0.08(OM) + 0.81	0.88	(x/m) = 0.10(OM) + 0.75	0.82
	Pb	-	-	(x/m) = 0.38(OM) + 7.06	0.95
	Cr	(x/m) = 0.15(OM) + 3.86	0.80	(x/m) = 0.21(OM) + 3.88	0.82

* dry period-1993/11 and 1994/2; ** wet period-1994/4; a: (x/m) = the amount adsorbed per unit weight of sediment, mg/g.

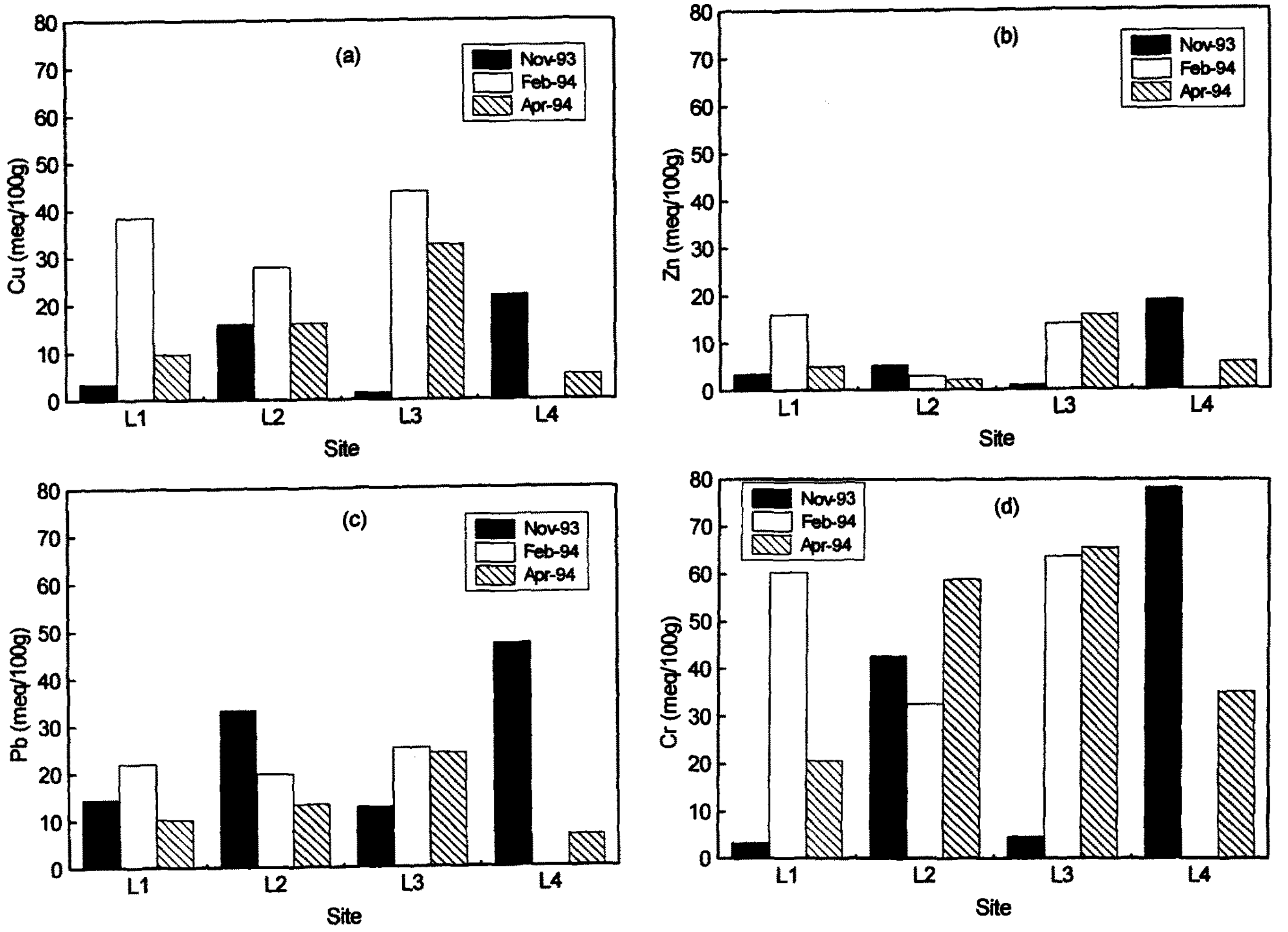

Fig. 4. Adsorbability of heavy metals in the sediment of the Lau-Che River in dry and wet periods $C_0 = 30$ mg/L): (a) Cu, (b) Zn, (c) Pb, and (d) Cr.

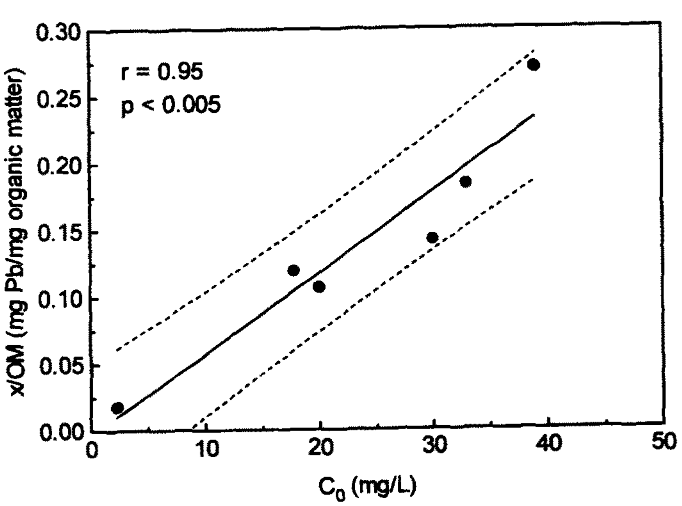

Fig. 5. Relationship between Pb adsorbed by per unit of weight of organic matter and initial concentration of Pb for site L2 (dotted lines are the prediction interval at the 95% confidence level).

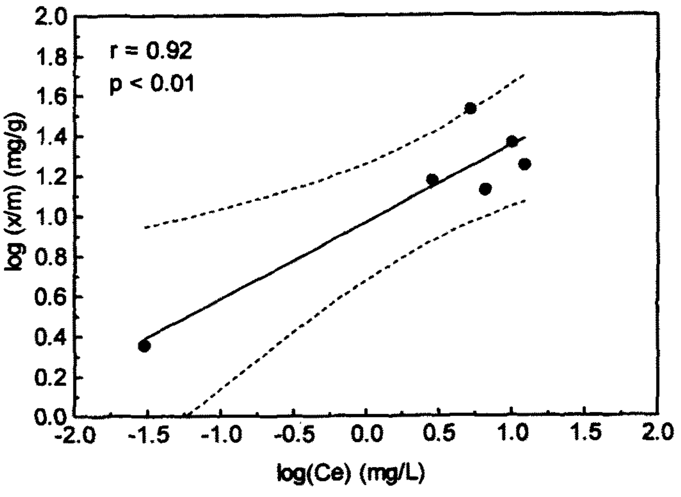

Fig. 6. Graphical representation of Freundlich isotherm for Pb in the sediment of the Lau-Che River (site L2) (dotted lines are the prediction interval at the 95% confidence level).

Table 4. Freudlich parameters for the adsorption of heavy metals of the sediment of site L2 in the Lau-Che River.

Metal	Date	K	1/n	Correlation coefficient (r)
Pb	Nov-93	9.30	0.38	0.92
	Feb-94	9.27	0.25	0.90
	Apr-94	7.13	0.61	0.69
Cu	Nov-93	6.20	0.13	0.39
	Feb-94	4.74	0.17	0.90
	Apr-94	4.08	0.08	0.34
Zn	Nov-93	3.62	0.42	0.55
	Feb-94	0.26	1.35	0.82
	Apr-94	1.96	0.60	0.74
Cr	Nov-93	3.81	0.14	0.91
	Feb-94	4.04	0.17	0.87
	Apr-94	4.00	0.18	0.62

The adsorption data of the heavy metals by sediments of site L2 in the Lau-Che River were analyzed with the linear form of the Freundlich isotherm as shown in Eq. 1:

$$\log(x/m) = \log K + \frac{1}{n}\log C_e \qquad (1)$$

where,
x/m is the amount adsorbed (mg/g);
C_e is the equilibrium concentration of the adsorbate ions (mg/L); and
K and *n* are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.
The Freundlich parameters, *log K* and *1/n*, can be obtained by plotting *log x/m* vs. *log* C_e, with *1/n* being the slope and *log K* being the intercept of the line (Fig. 6). This reflects the satisfaction of the Freundlich isotherm model for the adsorption of heavy metals. The Freundlich parameters for the adsorption of heavy metal ions are displayed in Table 4. Garcia-Miragaya and Page (1977) assumed that the coefficient, K, is a good index of the relative retention affinity of metals and soils. In Table 4, the retention affinity of the sediment of site L2 for heavy metals decreased in the order: Pb > Cu > Cr > Zn.

CONCLUSIONS

Adsorption of heavy metals on the sediment of a river contributes a considerable part of assimilative capacity to the heavy metal pollution. Hence, the organic matter content in the sediment plays an important role in the adsorption of heavy metals. Generally, the organic matter content in the sediment can be used as a simple pollution index of the sediment. There were significant positive correlations between metal concentrations, CEC in sediments, and organic matter content. The presence of high contents of organic matter in the sediment is shown to increase the adsorbabilities of heavy metals of sediments. In addition, the adsorptive capacity of the organic matter would increase with the initial concentration of heavy metal.

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