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螯合劑 CDTA 對河川底泥各鍵結型態重金屬釋出之研究

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ABSTRACT

Ell-Ren river enriched with heavy metals is the heavily polluted river of Taiwan. Batch tests were conducted to realize the remobilization effects of CDTA (cyclo-hexane-1,2-diaminetetraacetic acid; $C_{14}H_{22}O_8N_2$) on seven metals included Zn, Cd, Co, Cr, Cu, Ni and Pb from five sediment binding fractions (exchangeable, bound to carbonates, bound to manganese (Mn) oxides, bound to iron (Fe) oxides and bound to organic matters). The modified sequential extraction procedure (SEP) was used for the analyses of metal contents in five sediment binding fractions. The amounts of heavy metals remobilized by 10mM CDTA from dredged sediment at neutral pH were as follows : Zn (44.0 mg/Kg, 47% of potentially remobilizable content (PRC)) > Cu (36.0 mg/Kg, 68% of PRC) > Pb (25.0 mg/Kg, 75% of PRC) >Ni (5.2 mg/Kg, 34% of PRC) > Co (1.1mg/Kg, 18% of PRC) > Cd (0.2mg/Kg, 18% of PRC) > Cr (0.0mg/Kg, 0%). The remobilized amounts of Zn, Co, Cu, Ni, and Pb increased with increasing CDTA dose at neutral pH and were mainly transferred from "bound to carbonates" fraction. Under addition of 5mM CDTA, the remobilized amounts of Co, Cr and Ni increased with decreasing pH and were mainly transferred from both "bound to carbonates" and "bound to organic matters" fractions, but the remobilized amounts of Zn, Cu and Pb were significantly higher at neutral pH than at acidic or alkaline condition and were transferred from "bound to carbonates, Mn oxides and Fe oxides" fractions for Zn, "bound to carbonates and organic matters" fractions for Cu and "bound to carbonates, Fe oxides and organic matters" fractions for Pb, respectively. The remobilized Cd was mainly transferred from both "exchangeable" and "bound to carbonates" fractions.

KEYWORDS

Heavy metals; remobilization; sediment; CDTA; sequential extraction procedure.

INTRODUCTION

Heavy metals contained in water body are often strongly retained at sediment matrix by the physical-chemical processes (e.g. sedimentation, preciptation, adsorption, absorption, etc.). The particular behaviour of heavy metals in the environment is determined by their specific physicochemical forms rather than by their total concentration. The distributions and concentrations of heavy metals in the sediments of rivers or lakes have been studied by many investigations (Hiromitsu *et al*..,1986; Fuller *et al*.., 1990; Juan *et al*., 1994) and intended to understand the particular environmental behaviours of metals which present in a variety of fractionated forms. Some chemical speciation methods included SEP have been developed and applied for the heavy metal analysis in soils and sediments. Some sediments surveyed by SEP showed that the heavy metals in sediment bound to various geochemical phases (Modak *et al.,* 1992; Boughriet *et al.,* 1992; Surija *et al.,* 1995). Types of metals associated in sediments can be fractionated as follows : exchangeable, bound to carbonates, bound to Mn oxides, bound to Fe oxides and bound to organic matters fractions (Gibbs *et al.,* 1973; Tessier *et al.,* 1979). The partitioning equilibrium of metals between sediment matrix and solution had shown to be influenced by some environmental factors: pH, redox potential, salinity, chelating agents, temperature, etc. (Tessier *et al.,* 1989; Forstner, 1989; Lietz *et al.,* 1989; Calmano *et al.,* 1993; Warren *et al.,* 1994). One technique for remediating heavy metal contaminated sediments was to wash dredged sediment with chelating agent. Several chelating agents considered for the remobilization of heavy metals from contaminated soils included ethylenediaminetetraacetic acid (EDTA) (Peter and Shem, 1992), nitrilotriacetic acid (NTA) (Elliott *et al.,* 1989), citrate acid (Francis *et al.,* 1992), s-carboxymethylcysteine (SCMC) (Hong *et al.,* 1995) and diethylenediaminepentaacetic acid (DTPA) (Sommers and Lindsay, 1979). Hong (1995) stated that if the chelating agents were useful, the metal-ligand complex must be strong enough to overcome competition from soil surface adsorption and surface precipitation.The pH of extraction solution and concentraction of chelating agents were adjusted effectively in order to removing a wide range of heavy metals from sediment (Calmono *et al.,* 1993).

Various chelating agents have been used for the remediation of contaminated soils or sediments to release heavy metals from matrix , but few researches (Yu *et al.,* 1996, 1997) studied that from which binding fraction of soils or sediments, the heavy metals were extracted by chelating agents (EDTA, DTPA and EGTA). Ell-Ren river, located at the south of Taiwan, has been heavily polluted with heavy metals by several industrial and agricultural pollution sources.The objective of this paper is to elucidate the variations of heavy metals (Cu, Zn, Ni, Pb, Co, Cr and Cd) contents in five sediment fractions as affected by both CDTA and pH. In addition, a further interest is that whether both the largest remediation ability of CDTA on heavy metals from sediments and the stability constants of metal-CDTA complexes varied with pH value and species of metals or not.

MATERIALS AND METHODS

Sediment properties

The sediments were taken from the estuary of Ell-Ren river, near the Taiwan strait, by using a Ekman-Birge bottom sampler. The sediments were passed through a 2 mm sieve and air-dried at room temperature. The water content were 42.3 % before air -dried and 0.4 % after air-dried at 105 ˚C. The organic matter content was 1.2 % measured with Walkley and Black method. The sediment pH was 7.4 determined by a glass electrode with air-dried sediment to water ratio of 1: 1. The sediment was digested with microwave digestion method after adding 1ml hydrogen perchloride, 20 ml concentrated nitric acid and 1ml hydrogen peroxides. Then, the digester was analyzed by flame atomic absorption spectrophotometer (FAAS) (AA908, GBC, Australia). The total amounts of heavy metals in sediment were Fe (38238mg/Kg), Mn (191.6mg/Kg), Cu (64.63mg/Kg), Zn (196.6mg/Kg), Pb (51.45mg/Kg), Ni (46.67mg/Kg) and Cd (1.28mg/Kg).

Remobilization process

Two different remobilization processes were performed to study the effects of CDTA and pH on the remobilization of Ni, Pb, Zn, Co, Cu, Cr and Cd from sediment under equilibrium condition. Firstly, the dose of CDTA ranged from 0.1 to 10 mM under pH 7.4. Secondly, under the dose of 5 mM CDTA, the pH of sediment solutions were adjusted by 1% nitric acid or 1N sodium hydroxide, and the equilibrium pH of sediment solutions were 1.7, 4.6, 6.6, 6.9, 7.4, 9.4,10.8 and 12.6. Each 50 ml centrifuge tube contained 3g air-dried sediment, 30ml distrilled water, 5 mM total carbonate concentration by using sodium bicarbonate, and constant ionic strength by using 0.5 M sodium perchlorate. The sample solutions were agitated by a shaker with 180 rpm at room temperature (22-25 ˚C) for 48 hours. The final equilibrium pH of sample solutions were analyzed by glass electrode. The supernatants were obtained from centrifugation of sample solution at 9500 rpm (CF-15D, Hitach, Japan) for 10 minutes, filtered through 0.45 μm membrane, acidified with concentrated nitric acid to pH 2, and then analyzed by FAAS.

Sequential extraction procedure

The sediments obtained by centrifugation from remobilization process were extracted by modified SEP (Tessier *et al.,* 1979; Nelson *et al.,* 1982) to determine the trace metals content in five binding forms. During the extractions, a centrifuge was operated at 9500 rpm for 10 minutes to separate the extracts from sample solution. The process of SEP was shown as follows:

(a) exchangeable phase: the sediment from remobilization process was extracted at room temperature for 30 minutes with 20 ml ammonium acetate solution (1M, pH 7.0) and agitated continuously;

(b) bound to carbonates phase: the residue from (a) was extracted at room temperature for 5 hours with 20 ml sodium acetate solution (1M, pH 5.0 adjusted by acetic acid) and agitated continuously;

(c) bound to Mn oxides phase: the residue from (b) was extracted at room temperature for 30 minutes with 20 ml hydroxylamine hydrochloride solution (0.1M, dissolved in 0.1N nitric acid) and agitated continuously;

(d) bound to Fe oxides phase: the residue from (c) was extracted with 20 ml hydroxylamine hydrochloride solution (0.04 M, dissolved in 25 % (v/v) acetic acid) at 96 °C for 6 hours with occasional agitation;

(e) bound to organic matters phase: the residue from (d) was extracted with 5 ml of 0.1N nitric acid and 10ml of 30% hydrogen peroxides solution at 85 °C for 5 hours with occasional agitation; when the sample cooled, 15 ml of ammonium acetate solution (3.2 M, 20 % (v/v) nitric acid) was added to sample solution and agitated continuously for 30 minutes.

The total amounts of heavy metals including associated to five sediment fractions and remobilized were defined as potentially remobilizable content (PRC).

RESULTS AND DISCUSSION

Dose effect of chelating agent

Figures 1a-g show the dose effects of CDTA on the remobilization of metals from five sediment fractions at neutral pH (7.4). The remobilized amounts of heavy metals (Cu, Ni, Zn, Cd, Co and Pb) from sediment increased with the increasing dose of CDTA, except Cr. When increasing the CDTA dose, the increased amount of remobilized metals were mainly transferred from the "bound to carbonates" fraction, but some of the remobilized Cu was transferred from the "bound to organic matters" fraction. CDTA had a very high remobilization ability on Cd and could remobilize 95 % of the PRC of metals from sediment when its dosage was up to 10 mM. The remobilization abilities of CDTA on other metals were 75 % (Pb), 68 % (Cu), 47 % (Zn), 34 % (Ni) and 18 % (Co).

By using 10 mM CDTA, the amounts of remobilized metals from sediment were as follows: Zn (44 mg/Kg), Cu (36 mg/Kg), Pb (25 mg/Kg), Ni (5.2 mg/Kg), Co (1.1 mg/Kg) and Cd (0.2 mg/Kg).

Effect of pH

Under the influence of both pH and 5 mM CDTA, the amounts of remobilized heavy metals from sediment varied with pH value and species of heavy metals. Figure 2 showes that the lower the pH of sample solution existed, the higher the amounts of remobilized metals extracted by effect of CDTA combined pH or pH effect alone, except Pb and Cd. The largest amount of remobilized Pb and Cd occurred at pH 6.9 and 9.4, respectively. The effective pH ranges were wide for the remobilization of each heavy metals from sediment by 5mM CDTA and appeared as follows: Zn (pH ≤ 12.6), Co (pH ≤ 12.6), Cu (pH ≤ 12.6), Ni (pH ≤ 12.6), Pb (pH ≤ 12.6), Cd (pH ≤ 12.6) and Cr (pH < 4.6). In Figure 2, there are two curves in each subgraph. One stand for the amount of heavy metals remobilized by 5mM CDTA and hydrogen ions, the other stand for the amount of metals remobilized by hrdrogen ions only. At some pH value,the difference of altitude between two curves in Y coordinate expressed the remobilization ability of CDTA. The larger the difference existed, the higher the remobilization ability for the extraction of metals happened at this pH. The best remobilization ability of CDTA for heavy metals occurred at pH 9.4 (Cd), pH 6.9 (Zn, Cu, Ni and Pb), pH 6.6 (Co) and pH 1.7 (Cr). However, the largest amounts of remobilized metals affected by combined action of CDTA and pH occurred at pH 1.7 for Zn, Co, Cu, Cr and Ni (shown in Fig.2). The metals remobilized by CDTA occurred when the stability constants of metal-CDTA complexes were strong enough to overcome competitions from soil surface adsorption, surface precipitation and chemical binding force with geochemical forms (carbonates, Mn oxides, Fe oxides and organic matters). So, the largest stability constants of metal-CDTA complexes might occur consistently with the pH, at which the best remobilization ability of CDTA happened. The results suggested that CDTA had good, valid and economic efficiency for the remediation of heavy metal polluted sediment if the pH of dredged sediment was at neutral condition.

Transformation of metals by CDTA combined pH from sediment fractions

The variations of heavy metals contents in each binding fractions were determined by SEP to evaluate the behaviours of competitions between chelating agent (CDTA) and binding sites of sediment fractions. Table 1 showes the distribution of heavy metal contents in raw sediment fractions. Figures 3a-g show the

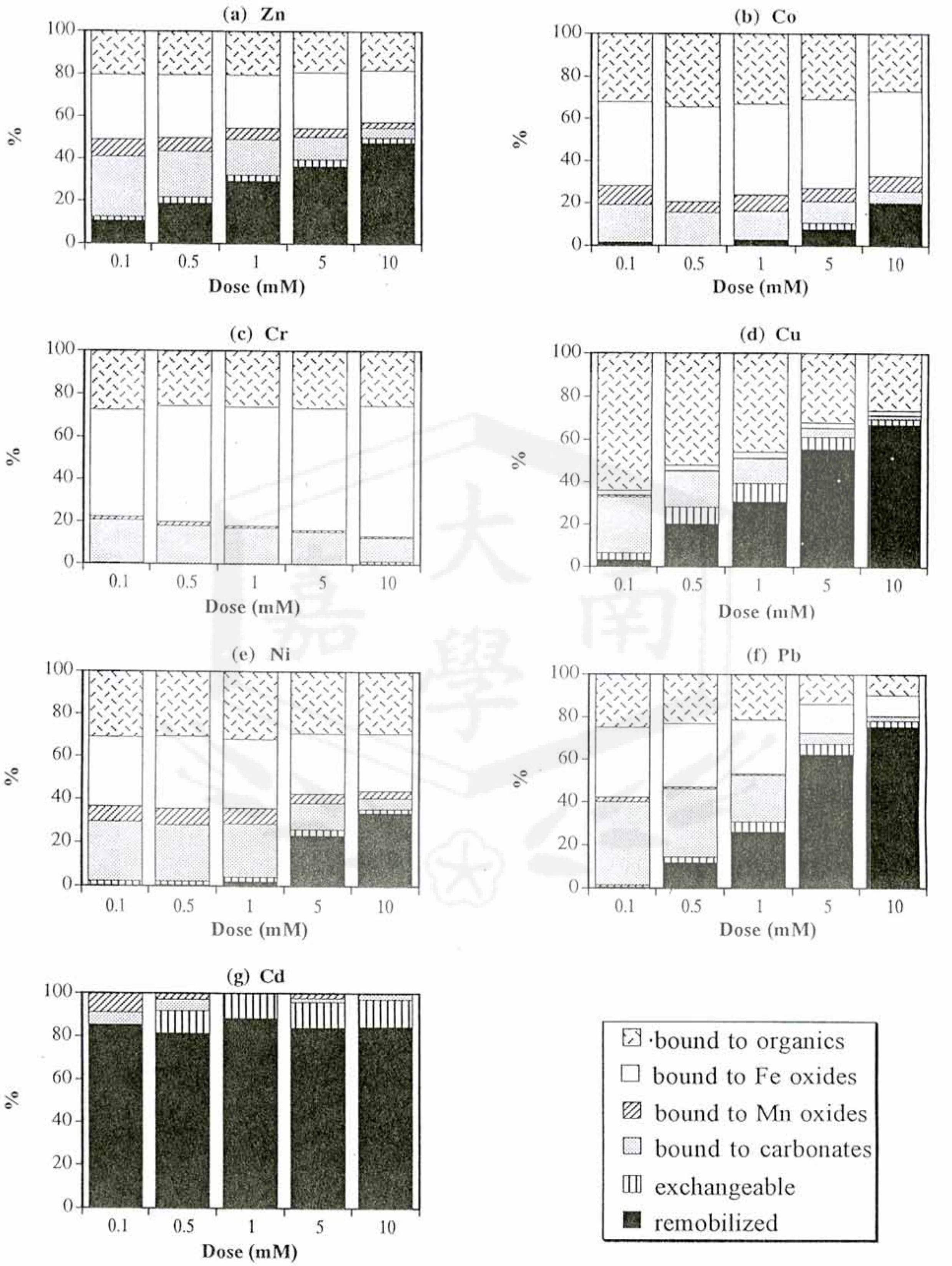

Figure 1 Dose effects of chelating agent (CDTA) on the remobilization of heavy metals from sediment (sediment solution: pH 7.4; 5 mM $NaHCO_3$; 0.5 M $NaClO_4$).

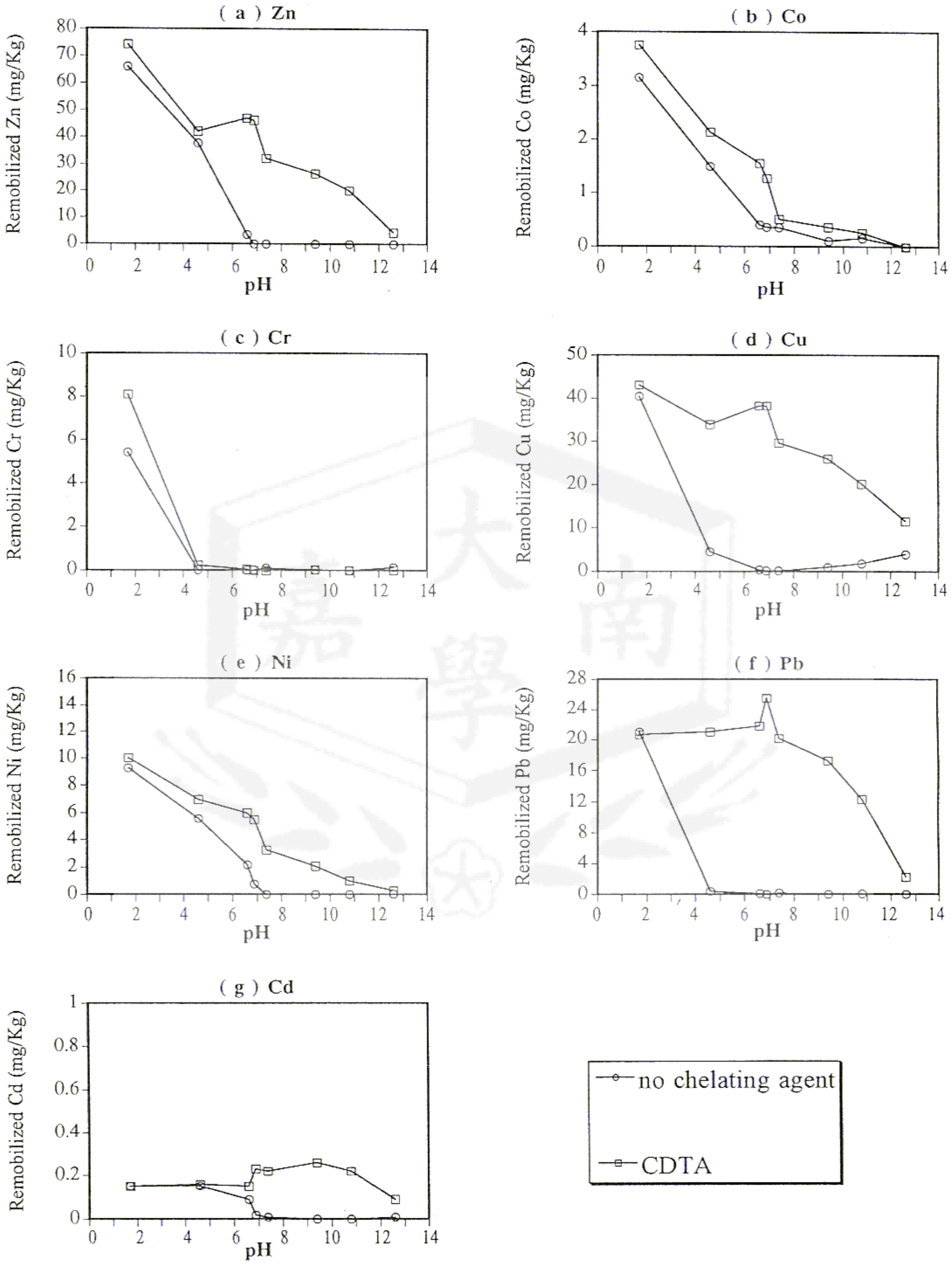

Figure 2 The efficiency comparison of remobilizing heavy metals from sediment between affected by pH alone and affected by pH combined 5mM CDTA. (sediment solution : 5 mM $NaHCO_3$; 0.5 M $NaClO_4$).

remobilization abilities of 5 mM CDTA on metals from each binding fractions within pH range from 1.7 to 12.6. The remobilized Cr extracted only by hydrogen ions was mainly transferred from "bound to carbonates" fraction near the neutral pH and mainly extracted from "bound to organic matters" fraction at extremely acidic or alkaline condition. Listed in Table 1, showes that the raw distribution of Cr in sediment fraction mainly bound to "Fe oxides", "organic matters" and "carbonates" fractions, but the remobilized metals by CDTA were not transferred from "Fe oxides" fraction (Fig. 3a). This phenomena may be resulted that the stability constant of Cr-CDTA was smaller than Cr-Fe oxides, but larger than Cr-carbonates, Cr-organic matters and Cr-Mn oxides. Among the complexes of metal-sediment fractions, the larger the percentage of metals transferred by CDTA from metal-sediment fraction occurred, the smaller the stability constant of metal-sediment fraction existed. At neutral pH solution, the Cr-carbonates was more unstable than other complexes of Cr with sediment fractions.

Table 1 Heavy metals distribution of Ell-Ren river sediment in five sediment binding fractions (unit: %)

Heavy metals	Bound to organics	Bound to Fe oxides	Bound to Mn oxides	Bound to carbonates	Exchangeable
Zn	32.9	17.0	9.5	38.8	1.7
Cd	26.3	0.0	7.9	26.3	39.4
Co	36.1	40.5	7.3	15.2	0.8
Cr	23.1	56.4	1.3	19.0	0.0
Cu	65.8	2.7	0.4	27.9	3.0
Ni	31.3	32.1	6.3	27.4	2.8
Pb	25.0	32.5	0.8	39.6	2.0

About 50-70 % of the remobilized Zn and Pb were transferred from the "bound to carbonates" fraction at the pH range of 1.7 up to 12.6. When increasing the pH of CDTA remobilizing solution, the amounts of remobilized Zn and Pb gradually increased, which were transferred from "bound to carbonates" fraction as well as the amounts of remobilized Zn and Pb gradually decreased, which were transferred from "bound to Fe oxides" fraction. From Table1, the remobilizable Zn and Pb distributed primarily at "carbonates", "Fe-oxides" and "organic matters" fractions, but the remobilized Zn and Pb mainly transferred from "bound to carbonates fraction" (Fig. 3b-c). So, the binding abilities of both Zn-carbonates and Pb-carbonates were smaller than complexes of Zn and Pb with other sediment fractions.

About 50-75 % of remobilized Ni was mainly transferred from "bound to carbonates" fraction from pH 1.7 to 12.6 (Fig. 3d). The remobilized Cu was only transferred from two binding fractions from pH 1.7 to 12.6 and kept in constant ratio. About 75% of the remobilized Cu was transferred from "bound to organic matters" fraction and 25% of the remobilized Cu was transferred from the "bound to carbonates" fraction. In this case, however, the amount of transferred Cu by CDTA was consistent with the distribution of Cu in raw sediment fractions (Fig. 3e). The primary sources of remobilized Co were "bound to carbonates", "bound to Mn oxides" and "bound to organic matters" fractions. The relative percentage of Co transferred from different binding fractions varied with pH of solution. The remobilized Cd was transferred from both "exchangeable" and "bound to carbonates" fractions at acidic condition and from "exchangeable", "bound to carbonates" and "bound to organic matters" fractions at alkaline condition.

CONCLUSIONS

By the application of CDTA for the remobilization of heavy metals from dredged sediments at different pH, the results can be concluded in the following:

(1) By the effect of chelating agent (CDTA), the lower the pH and the higher the dose of CDTA, the larger amount of remobilized metals can be transferred from sediment.

(2) When the sediment was remobilized by CDTA, the largest stability constants of metal-CDTA complexes occurred consistently with the pH, at which the best remobilization ability of CDTA happened. The largest remobilization amount of metals enhanced by CDTA varied with pH and species of metals, and were shown as follows: Cu, Zn, Ni and Pb at pH 6.9, Cd at pH 9.4, Co at pH 6.6 and Cr at pH 1.7.

(3) The metals remobilized by CDTA did not significantly correlate with their main binding fractions of raw sediment, but strongly associated with the species and binding forms of metals.

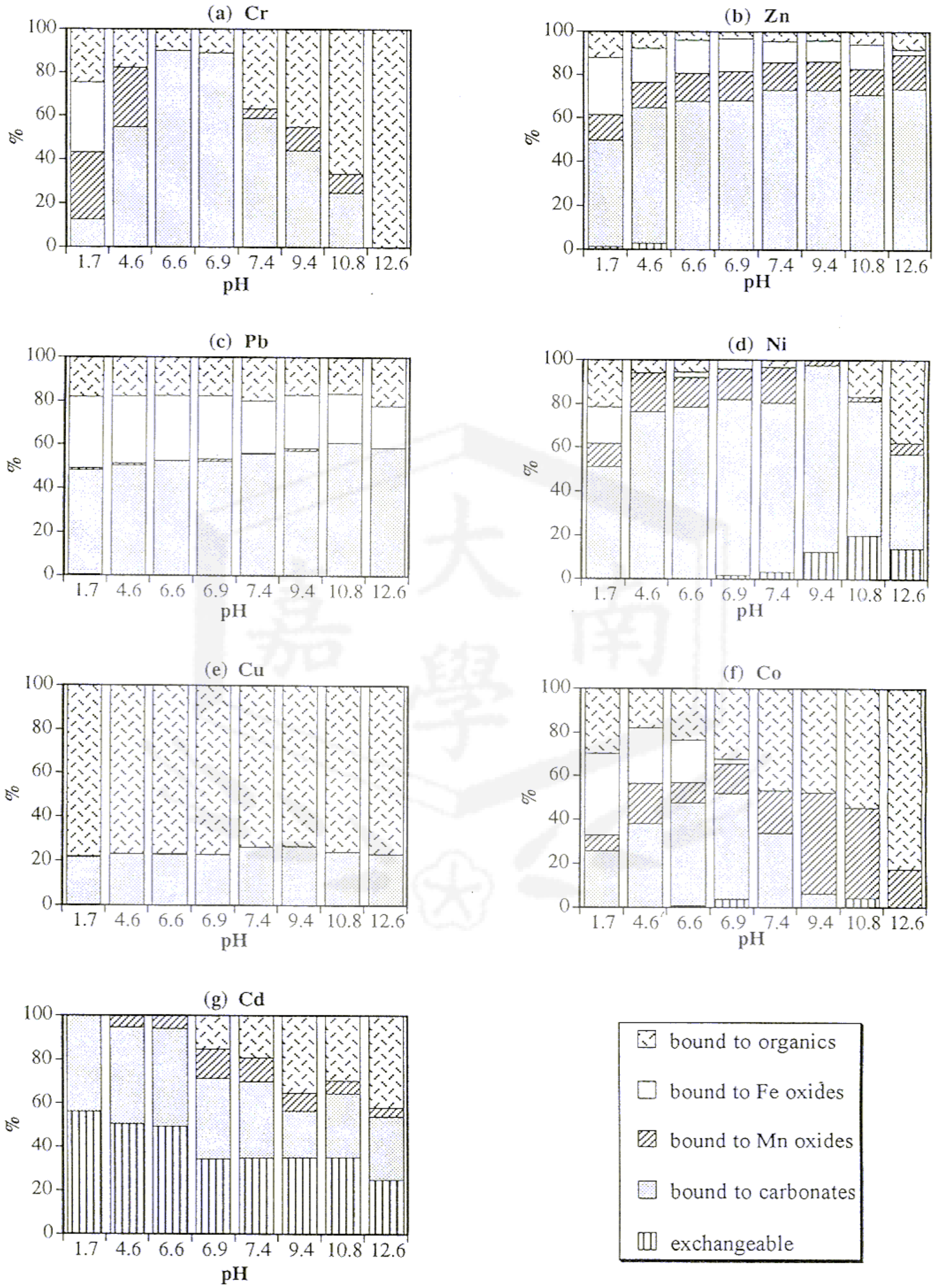

Figure 3 The percentage distribution of remobilized heavy metals by 5mM CDTA from five sediment fractions at different pH. (sediment solution : 5 mM $NaHCO_3$; 0.5 M $NaClO_4$).

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