

## EFFECT OF SALINITY ON HEAVY METALS MIGRATION AMONG DISSOLVED AND SOLID PHASES IN ESTUARY SEDIMENT

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### ABSTRACT

With the laboratory control, first aim of this study was to assess the effects of salinity on heavy metal partition coefficient ( $K_s^{Me}$ ,  $K_{DOM}^{Me}$ ) between free metal ions (Copper and Lead), dissolved metal-organic matter complex in aqueous phase and metals in sediment particles. The definition of  $K_s^{Me}$  means the ratio of metals in kaolite (g/g) versus metal ion in aqueous phase (g/mL). The definition of  $K_{DOM}^{Me}$  means the ratio of metal complex in dissolved organic matter (g/g) versus metal ion in aqueous phase (g/mL). The results shown that the increase of salinity in aqueous phase will induce the increase of heavy metal ions concentration (Cu, Pb) in aqueous phase and the decrease of partition coefficient ( $K_s^{Me}$ ,  $K_{DOM}^{Me}$ ) of Cu and Pb. The second aim of this study was to realize that salinity may affect the distribution of heavy metal between aqueous phase and five binding phases in sediment particles (including exchangeable (F1), bound to carbonates (F2), bound to Fe-Mn oxides (F3), bound to organic matters (F4) and residual (F5) fractions). When sediment was mixed with water in different salinity, Cu was remobilized primarily from exchangeable phase, secondary from iron-manganese oxides phase. Pb was remobilized primarily from exchangeable phase, secondary from iron-manganese oxides and organic matters phases. The definition of  $k_{F1}^{DSP}$ ;  $k_{F2}^{DSP}$ ;  $k_{F3}^{DSP}$ ;  $k_{F4}^{DSP}$ ;  $k_{F5}^{DSP}$  and  $k^{DSP}$  mean the ratios of metal (g/g) in five different binding phases and sum of metals in five phases of sediment particles versus metal ions in aqueous phase (g/mL). Salinity affects the partition coefficient ( $k_D^{DSP}$ ) of heavy metals between ion phase and five speciations of metals in sediment particle. The increase of salinity induces significantly the decrease of  $k_D^{DSP}$ . The lower  $k_D^{DSP}$  means the easy release of heavy metals from solids to the aqueous phase.

**Keywords: Dissolved Organic Matter, Heavy Metal, Partition Coefficient, Salinity.**

### INTRODUCTION

The effects of salinity on the partition coefficient of heavy metals between free metals ion, suspended particulate and sediment particles are due to the complicated interaction of physical, chemical and biological activities in the estuarine. This partition coefficient will be valuable to predict the distribution of heavy metals and to construct a water quality model in the estuary system (Lores et al., 1998; Chiffolleau et al., 1999). The river water has received a large load of domestic and industrial wastewater, especially metal-finishing, electroplating and metal-recycling wastewaters. The heavy metal will be adsorbed and absorbed into suspended particulate and different size of particles in sediment when it is transported through the river channel by water. The partition distribution of heavy metals between aqueous and five binding fractions in sediment particles will be affected by the variation of salinity when flowing down the river channel in estuary. If the increase of salinity can induce the remobilization of heavy metals in exchangeable and carbonates fractions, the metal toxicology in aqueous environment will increase (Rainbow, P.S., 1997a, b). In this study, the sediment from seriously heavy metals polluted ell-ren River was selected to research the partition distribution of metals among free metal ions, dissolved organic matter-metal complex, and solid phases and to realize the influence of organic matter concentration on trace metal distribution in different salinity environment.

### MATERIALS AND METHODS

#### Isotherm experiments

Equilibrium batch sorption isotherms were used to characterize the sorption coefficients of metals to a solid substrate (kaolinite clay) with tannic acid as dissolved organic matters (DOM) in aqueous phase. The sorption isotherm experiment finished in a centrifuge tube with 30 ml solution containing 1.5g kaolinite clay with average particle diameter of 1.5  $\mu$ m as solid phase, tannic acid as DOM and free heavy metal ion. In these experiments, free metal ions and tannic acid in aqueous, and clay particles phases are allowed to equilibrate each other for 7-day in continuous agitation. This technique used to obtain the sorption isotherms are operated in batch with different salinity and DOM concentration. Solutions with different salinity ranging from 0 to 35 ppt were prepared using an artificial seawater described by Hsieh et al. (1985). After stable experiment, the supernatant was removed from the centrifuge tube after 10000 rpm centrifugation for 10 minutes. The metal in solid phase was extracted by aqua-regia acid. The partition coefficient for free heavy metals ions in aqueous phase onto kaolinite clay,  $K_s^{Me}$  was obtained.

#### Dialysis technique

A dialysis technique was used to obtain the partition coefficient for free heavy metals ions onto DOM,  $K_{DOM}^{Me}$ . A 25 ml supernatant from isotherm experiment was filled into the dialysis bag containing heavy metal ions and tannic acid as DOM. The dialysis bag was put into a polyethylene bottle filled with 250 ml of distilled water. In these experiments, free metal ions in aqueous are allowed to equilibrate across the 5000 MWCO dialysis membrane (Aldrich Chemical Co.) with the DOM-metal complex. This procedure eliminated the difficulty of separating the free metals ions and the dissolved

DOM-metals complex. A series of long term experiments performed over 20 days showed that a 7-day equilibrium time was sufficient to reach stable isotherm experiment.

#### ***Separation of sediment into different particle sizes***

The separation of sediment into sizes of 210-125  $\mu$ m, 125-65  $\mu$ m, and <65  $\mu$ m was finished with the polyethylene or nylon mesh by the flush force of river water. The sediment collected at <65  $\mu$ m range was further separated into three smaller particle size ranges of 65-34  $\mu$ m, 34-16  $\mu$ m, and 16  $\mu$ m with modified elutriator apparatus (Follmer et al., 1973; Muller et al., 1977). All the size ranges of sediment particle were dried with oven at 60  $^{\circ}$ C.

#### ***Metal distribution between aqueous phase and five binding fractions***

To realize the effects of salinity on partition coefficient of heavy metals between free metal ions and five binding fractions in sediment particles, seriously polluted sediment was in equilibrium with different salinity of water solution. After stable experiment, the supernatant was removed from the centrifuge tube after 10000rpm centrifugation for 10 minutes. The metals in five binding fractions were extracted with sequential extraction procedure. The partition coefficients for free heavy metals ions onto five binding fractions,  $k_{F1}^{DSP}$ ;  $k_{F2}^{DSP}$ ;  $k_{F3}^{DSP}$ ;  $k_{F4}^{DSP}$  and  $k_{F5}^{DSP}$ , were obtained.

#### **Sequential extraction procedure**

A modified five-step sequential extraction procedure (SEP) (Tessier et al., 1979) was used to extract heavy metals contained in the different size ranges of sediment particles and thus five speciation phases of heavy metals (exchangeable, bound to carbonates, bound to Fe-Mn-oxides, bound to OM, and residual) could be determined in what amounts. After the first extraction (extraction of exchangeable metal), the sediment was washed by shaking with deionized water for 1 minute, and centrifuged, prior to each subsequent extraction.

#### **Chemical Analyses**

Geochemical components in different sizes of sediment were determined using the approximate gravimetric method (Allison and Moodie, 1965), for carbonates, the Walkley-Black method (Walkley, 1934), for OM, results of which were converted to a percentage (Sims, 1991), and the acid hydroxylamine method (Wang, 1987), for Mn-oxides and Fe-oxides. Fe and Mn in hydroxylamine solution were analyzed by atomic absorption spectrometer and expressed in mg/kg of MnO and % of Fe<sub>2</sub>O<sub>3</sub>, respectively. Heavy metals were measured using a flame atomic absorption spectrometer or atomic absorption spectrometer (GBC, 908AA, Australia), equipped with a graphite furnace (GBC, GF3000) and an auto-sampler (GBC, PAL-3000).

## **RESULTS AND DISCUSSIONS**

#### **Geochemical components of sediment particles**

The geochemical components of sediment particle were affected by the size distribution fractions. The larger the particle sizes were, the smaller the organic matter contents existed. However, the lowest concentration of Iron oxides and manganese oxides was found at 125~65  $\mu$ m of particles, and the largest concentration existed at the smallest size range of particle (<16  $\mu$ m). The variation of carbonate content did not have positive or negative correlation with the sizes of particle. The lowest concentration (2.17%) of carbonates was found at particle range of 125~65  $\mu$ m.

**Table 1. Characteristics of sediment in the Ell-rin River**

	CaCO <sub>3</sub>	OM	Iron oxides	Manganese oxides
Sediment size range	%	%	%	mg/Kg
Raw sediment	3.01	0.64	0.50	463.3
>210 $\mu$ m	3.65	0.37	0.48	594.6
210~125 $\mu$ m	2.76	0.26	0.40	314.7
125~65 $\mu$ m	2.17	0.26	0.40	291.7
65~34 $\mu$ m	3.33	1.40	0.55	766.0
16~34 $\mu$ m	3.45	1.96	0.68	968.9
<16 $\mu$ m	2.74	2.25	0.67	957.8

#### ***Effects of salinity on metal remobilization from different particle sizes***

From Table 2 and 3, the increase of salinity (0-35) can cause the remobilization of heavy metals (Cu and Pb) from all particle sizes partitioning (210-125, 125-65, 65-34, 34-16, and <16  $\mu$ m). It indicated that the formation of chloride will help the remobilization of metals from solid phase. The associations of particle sizes and metals remobilization did not correlate linearly in fixed salinity. The lowest degree of remobilization was found at <16  $\mu$ m particle size fraction, next the 125-65  $\mu$ m. It means that the distribution of binding fractions in particle size partitioning was different.

**Table 2. The effect of salinity on the remobilization of Cu from different range of particles in sediment (mg/kg)**

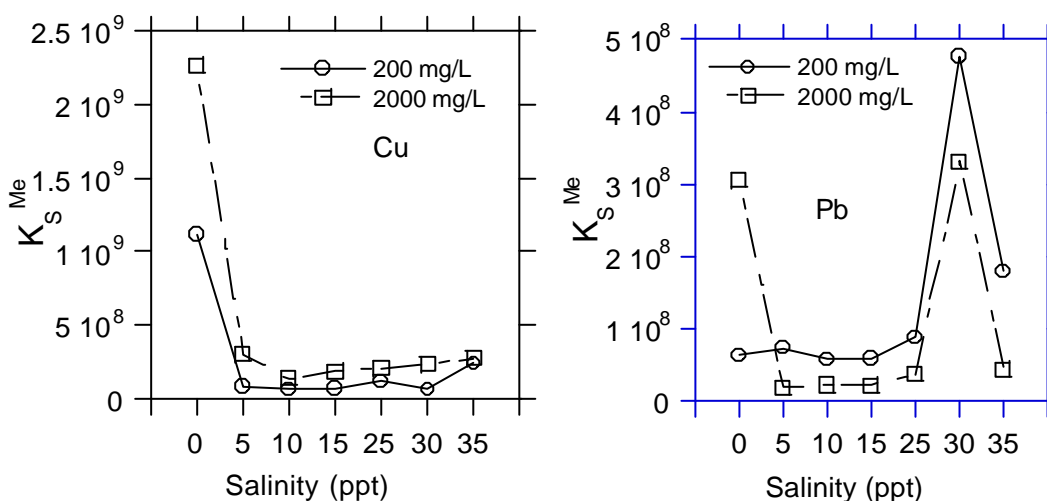
Particle size range	Salinity(ppt)							
( $\mu\text{m}$ )	0.00	5.00	10.00	15.00	20.00	25.00	30.00	35.00
Raw sediment	0.35	0.47	0.37	0.41	0.46	0.59	0.81	0.91
>210	0.69	0.84	0.88	0.94	1.16	1.22	1.32	1.46
210~125	0.52	0.58	0.54	0.98	1.28	1.44	1.53	1.98
125~65	0.23	0.24	0.25	0.61	0.54	0.16	1.69	0.57
65~34	0.14	0.67	0.71	1.45	1.30	0.44	1.16	0.99
16~34	0.03	0.54	0.49	0.63	0.59	0.30	1.50	0.92
<16	0.10	0.18	0.14	0.65	0.29	0.33	0.86	1.29

**Table 3. The effect of salinity on the remobilization of Pb from different size range of sediment particles (mg/kg)**

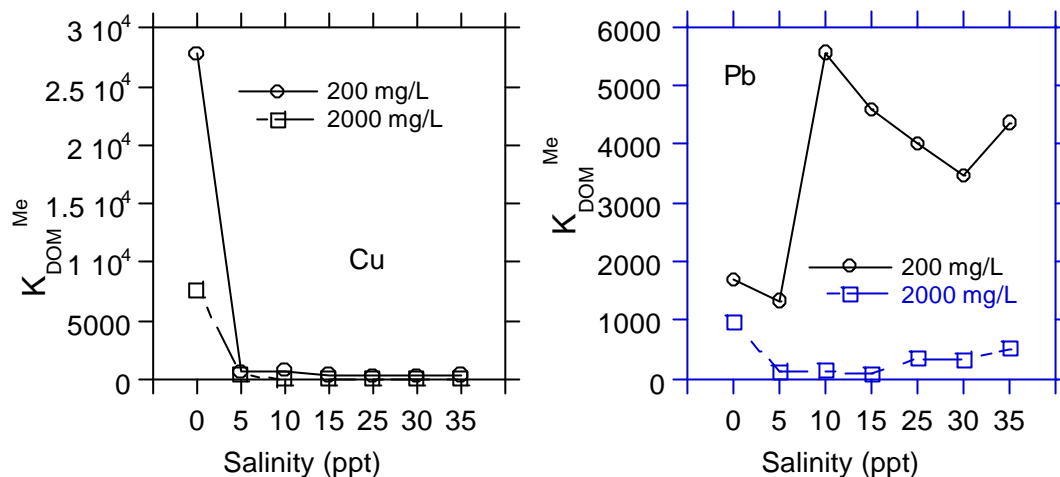
Particle size	Salinity ppt							
$\mu\text{m}$	0	5	10	15	20	25	30	35
Raw Sediment	0.07	0.35	0.57	0.87	0.89	1.29	1.58	2.04
>210	0.01	0.48	0.54	0.60	0.93	2.39	1.51	1.67
210~125	0.38	0.62	0.59	0.59	0.87	1.55	1.67	2.33
125~65	0.13	0.58	0.67	0.94	1.38	1.62	1.74	2.27
65~34	0.07	0.34	0.51	0.57	0.76	1.55	1.15	1.53
16~34	0.05	0.23	0.32	0.86	0.65	0.84	1.21	1.50
<16	0.04	0.22	0.33	0.86	0.86	0.89	1.66	1.68

**Effects of salinity on partition coefficient among free metal ions, dissolved organic matter-metal complex, and solid phase ( $K_s^{Me}$ ,  $K_{DOM}^{Me}$ )**

The definition of  $K_s^{Me}$  means the ratio of heavy metal bound to kaolite (g/g) versus heavy metal ion in aqueous phase (g/mL). The definition of  $K_{DOM}^{Me}$  means the ratio of metal-dissolved organic matter complex (g/mL) versus aqueous free metal ion (g/mL) in aqueous phase. The increase of salinity causing the increase of Cu ion concentration in the aqueous phase coincided with the decrease of  $K_s^{Me}$ . The similar result was shown as Pb at Figure 1. The complex ability between free Cu ion and dissolved organic matter decreased with the increase of salinity. It caused the increase of  $K_{DOM}^{Me}$  value (shown as Figure 2). Inversely, the partition coefficient ( $K_{DOM}^{Me}$ ) of Pb increased with the values of salinity.



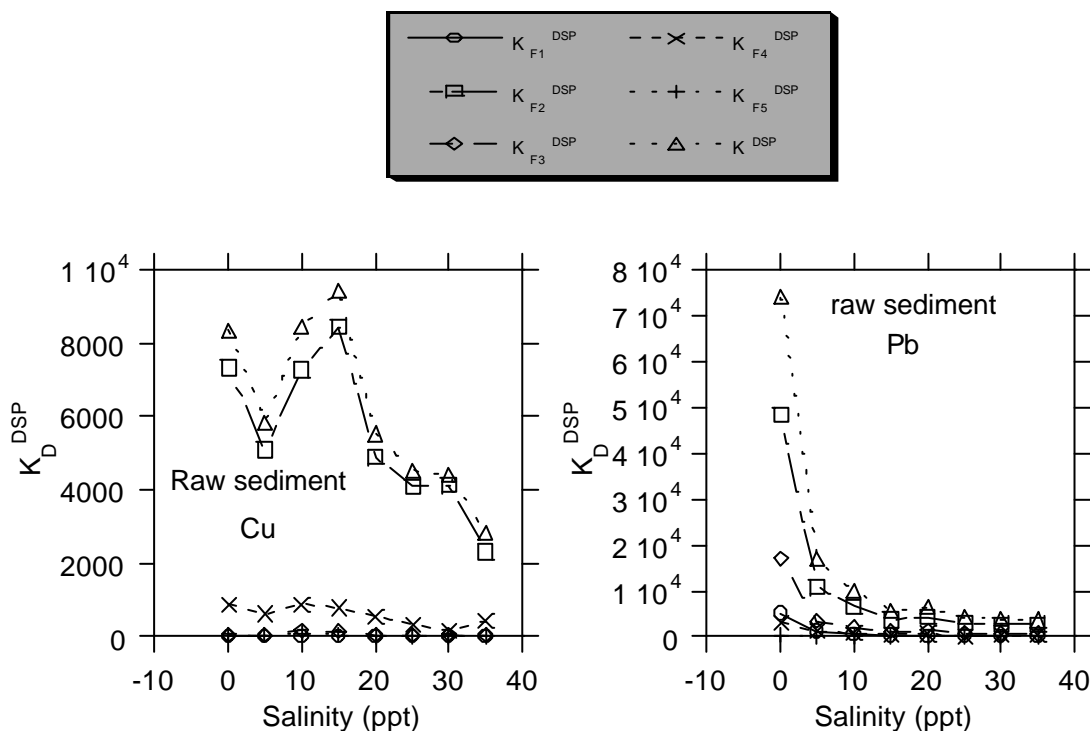
**Figure 1. Effects of salinity on the Partition Coefficient ( $K_s^{Me}$ ) of Cu and Pb between free metal ion and solid phases in different organic matter concentration. The definition of  $K_s^{Me}$  means the ratio of metal bound to kaolite (g/g) versus metal ion in aqueous phase (g/mL).**



**Figure 2.** Effects of salinity on the Partition Coefficient ( $K_{DOM}^{Me}$ ) of Cu and Pb in aqueous tannic acid solution. The definition of  $K_{DOM}^{Me}$  means the ratio of metal-organic matter complex (g/mL) versus aqueous free metal ion (g/mL) in aqueous phase.

**Effects of salinity on partition coefficient ( $k_D^{DSP}$ )**

The heavy metals in the effluent were accumulated in the suspended matter and sediment particle of river. When transported into the ocean, they will go through the estuary channel. Effects of salinity on the partition coefficient ( $k_D^{DSP}$ ) of Cu between aqueous and solid phases will happen in the salinity gradients (as shown in figure 3). The definition of  $k_{F1}^{DSP}$ ,  $k_{F2}^{DSP}$ ,  $k_{F3}^{DSP}$ ,  $k_{F4}^{DSP}$ ,  $k_{F5}^{DSP}$  and  $k_D^{DSP}$  mean the ratios of Cu (g/g) in five binding fractions and sum of metals in five binding fractions versus Cu ions in aqueous phase (g/mL). The higher the salinity existed, the lower the  $k_{F1}^{DSP}$ ,  $k_{F2}^{DSP}$ ,  $k_{F3}^{DSP}$ ,  $k_{F4}^{DSP}$ ,  $k_{F5}^{DSP}$  and  $k_D^{DSP}$  was found. When the salinity in aqueous phase increased, the remobilization of free metal ions increased and the partition coefficient decreased. The concentration of heavy metals in five binding fractions did not affect by the salinity.



**Figure 3.** Effects of salinity on the Partition Coefficient ( $k_D^{DSP}$ ) of Cu between aqueous and solid phases. The definition of  $k_{F1}^{DSP}$ ,  $k_{F2}^{DSP}$ ,  $k_{F3}^{DSP}$ ,  $k_{F4}^{DSP}$ ,  $k_{F5}^{DSP}$  and  $k_D^{DSP}$  mean the ratios of Cu (g/g) in five binding fractions and sum of metals in five binding fractions versus Cu ions in aqueous phase (g/mL).

**CONCLUSION**

The increase of salinity (0-35) can cause the remobilization of heavy metals (Cu and Pb) from all particle sizes partitioning. The associations of particle sizes and metals remobilization did not correlate linearly in fixed salinity. The increase of salinity in aqueous phase will induce the increase of heavy metal concentration (Cu, Pb) in aqueous phase and

the decrease of partition coefficient ( $K_s^{Me}$   $K_{DOM}^{Me}$ ). Salinity affects the partition coefficient ( $k_D^{DSP}$ ) of heavy metals between ion phase and five binding fractions of metals in sediment particle. The increase of salinity induces the decrease of  $k_D^{DSP}$ .

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