CORRELATION OF PARTICLE SIZES AND METALS SPECIATION IN RIVER SEDIMENT

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ABSTRACT

The speciation of heavy metals in polluted river sediment particles can be found as phases as exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. The sediments sampled from upstream and downstream of the Ell-ren river which was seriously polluted with heavy metals in Taiwan, and were separated into different size fractions (2000-600, 600-300, 300-210, 210-65, 65-34, 34-16, 16-8, and <8ìm) with U.S. standard sieves and elutriator apparatus. The speciation of metals in particles was extracted by the sequential extraction procedures and analyzed with atomic absorption spectrometry. The amount of total extractable heavy metal for Cu (TEHM-Cu) correlated with the fractions of particle sizes. However, there weren't a positive or negative linear relationship existing between them. The lowest concentration of TEHM-Cu was found in middle size (65-210ìm), and the higher concentration of TEHM-Cu found in larger and smaller size ranges (300-600 and 16-34ìm) of sediment particles. Similar relationships between TEHMs and particle size were also observed for Cr, Zn, Pb, Fe, and Ni in high or low metal polluted sediment.

The relative order of Cr concentration between each speciation did not affected by the sizes of particles in high and low metal pollution sediment. Similar trends also observed from Cu, Fe, Zn, Pb, and Ni. Cu, Ni, and Pb were bound primarily to organic matter phase for all sizes of sediment particle in high and low metal pollution sediment. However, Cr and Zn were bound primarily to Fe-Mn oxides phase in high metal polluted sediment. The concentration of Cr bound to Fe-Mn oxides varied with the sizes of particle and was larger at size ranges of 600-2000 and 8-16ìm. Similar variation was found for the Zn. The concentration of Pb-organic matter speciation varied with the sizes of particle and was larger at size ranges of 300-600 and 8-16ìm. Similar variations were found for the Cu and Ni. The effects of sediment particle sizes on the variation of relative distribution percentage for each metal speciation (Cu, Ni, Pb, Cr, and Zn) was found significantly at primary binding phase in sediment particles. However, except primary binding phase, the correlation between metal speciation concentration and particle sizes were not significant for Cu, Zn, Pb, Ni, Fe, and Cr.

KEYWORDSs: Elutriator apparatus, Metals speciation, Particle sizes. Sequential extraction procedure.

INTRODUCTION

Trace heavy metals and organic matter pollutants are predominantly transported in association with suspended particulate matter in rivers. Suspended particulates accumulated with heavy metals and organic matter pollutants in low turbulent river, leading to the formation of highly polluted river bottom sediments in industrialized areas (Haag *et al*., 2001). The association of pollutants with sediment particles will be dependent upon the surface area as well as the characteristics of chemical partitioning onto the sediment (Horowitz and Elrick, 1987). Iron hydroxyoxide and natural organic matter surface coatings on sediment particles would be expected to play an important role in controlling the absorption (adsorption) of trace heavy metals (Beckett *et al.*, 1990; Stumm et al., 1992).

Heavy metals existed in river sediment was separated into five speciations: ion-exchangeable (F1), bound to carbonate (F2), bound to Fe and Mn-oxides (F3), bound to organic matters (OM) (F4) and residual (F5) phases (Tessier et al., 1989). Many studies focus on the existence of metal speciation in sediments. However, little is known about variation of heavy metal binding fractions associated with particle sizes in river sediments. The aim of this study is to evaluate the associations of heavy metal chemical fractions with the particle size fractions in high and low heavy metal pollution river sediment.

MATERIAL AND METHODS

Study areas and sample preparation

The Ell-Ren River is 65.1 km in length, and has a catchment area of 350.4 km2, containing a population of 260,000. The river water has been heavily polluted by domestic and industrial wastewaters, especially metal-finishing, electroplating and metal-recycling wastewaters. Sediment samples were collected from between 0–10 cm below the water/sediment interface using a Birge-Ekman grab sampler. Those mixture sediment samples were placed immediately in a polypropylene box to avoid accidental contamination.

Separation of sediment into different particle sizes

The separation of sediment into sizes of 2000-210, 210 -125, 125 -65, and <65.m was finished with the polyethylene or nylon sieves by the flush force of river water. The sediment collected at <65.m fraction was further separated into four particle size fractions of 65-34, 34-16, 16-8,and .8.m with modified elutriator apparatus (Follmer et al., 1973; Muller et al., 1977). All the sediment water mixture were dried with oven at 60.

Sequential extraction procedure

A modified five-step sequential extraction procedure (SEP) (Tessier et al., 1979) was used to extract heavy metals contained in the sediment particle fractions, 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 analysis

The heavy metals (Zn, Pb, Ni, Cr, Cu, and Fe,) from the extracts of the sediment particles were measured by flame atomic absorption spectrometer (GBC, 908AA, Australia). Extracts with heavy metals concentration near three time of detection limit were measured using an atomic absorption spectrometer (GBC, 908AA, Australia), equipped with a graphite furnace (GBC, GF3000) and an auto-sampler (GBC, PAL-3000). According to Tsai *et al*. (1998), total extractable heavy metal (TEHM) is defined as sum of five speciation phases of heavy metal.

RESULTS AND DISCUSSIONS

Variation of particle size fractions versus TEHMs

From high and low heavy metal pollution river sediment (figures 1 and 2), the higher concentrations of TEHM-Zn, TEHM-Pb, TEHM-Ni, TEHM-Cu, TEHM-Cr, and TEHM-Fe (mg/kg) in seriously polluted river sediment were found in size fractions near of 2000-600 and 16-34.m. However, the lowest concentrations of TEHM-metals (Zn, Pb, Cu, Cr, and Fe) (mg/kg) were found in the middle size (65-34.m) fraction of sediment, except the TEHM-Ni (210-65.m). In low heavy metal pollution river sediment, the correlation of particle size and concentration of TEHMs was similar. The higher concentrations of TEHM-Zn, TEHM-Pb, TEHM-Ni, TEHM-Cu, TEHM-Cr, and TEHM-Fe (mg/kg) in low heavy metal pollution river sediment were most abudant in size fractions near of 2000-600 and 16-34.m. However, the lowest concentrations of TEHM-metals (Zn, Pb, Cu, Cr, Ni and Fe) (mg/kg) were found in the middle size (210-65.m) fraction of sediment.

Variation of particle sizes versus metal speciation

From figures 1 and 2, the distribution of heavy metal speciation affected by sediment particles was most significant at bound to organic matter fraction for Zn, Pb, Ni, Cu, Cr, and Fe in low heavy metal pollution sediment, whereas for Pb Ni, Cu, and Fe in serious heavy metal pollution sediment. The most abundant Zn and Cr phases in serious metal pollution sediment were bound to iron- manganese oxides fraction. The other binding fractions in the high or low metal pollution sediment were not affected significantly. In low metals pollution sediment, the highest concentrations of Pb bound to organic matter were found at 650-300.m size fraction, Ni at 16-34.m, Cu at 2000-600.m, Cr at 16-8.m, and Fe at 34-16.m. The smallest concentrations of metal-organic matter were found at 210-65.m for low metal pollution sediment, whereas 65-34.m for high metal pollution sediment, except Ni.

CONCLUSIONS

Whether in high or low metal pollution river sediment, the effects of sediment particle size fraction on the distribution of heavy metal phases were significant at 600-300.m for Pb, 34-16.m for Ni and Fe, 2000-600.m for Cu, 16-8.m for Cr. The metals concentration did not increase with decreasing grain size. The smallest effects of particle size fraction on the speciation of metals was found at 65-34.m for Zn, Pb, Cu, Cr, and Fe in high metal pollution sediment. However, the smallest effect of particle size fraction on the speciation of metals was found at 210-65.m for Zn, Pb, Ni, Cu, Cr, and Fe for low pollution sediment.

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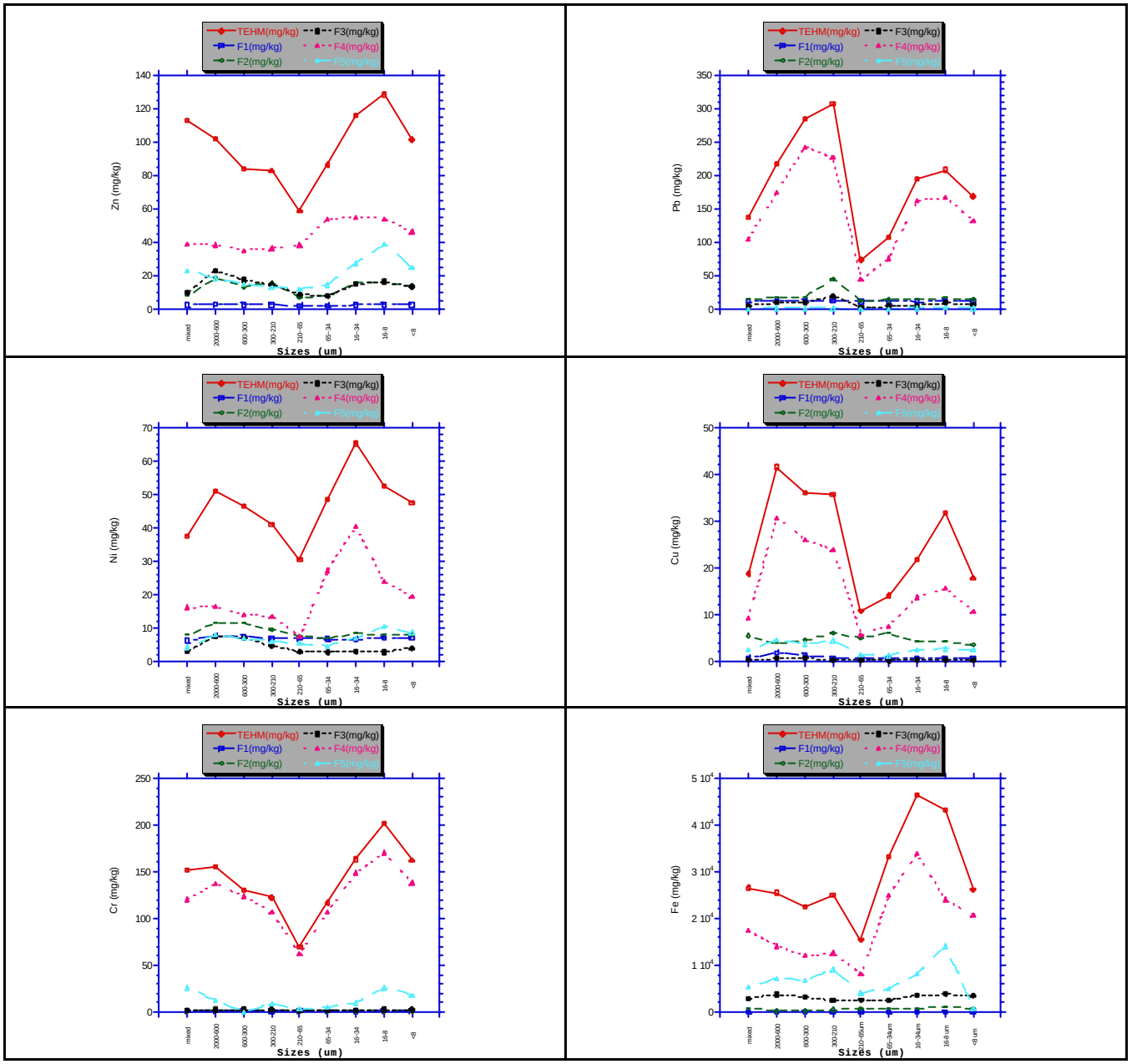

Figure 1. *Correlation of particle sizes and metal speciation (Zn, Pb, Cr, Ni, Cu, and Fe) for low heavy-metal polluted sediment. TEHM: total extractable heavy metal; F1: exchangeable; F2: bound to carbonates; F3: bound to Fe and Mn oxides; F4: bound to organic matter; F5: residual.*

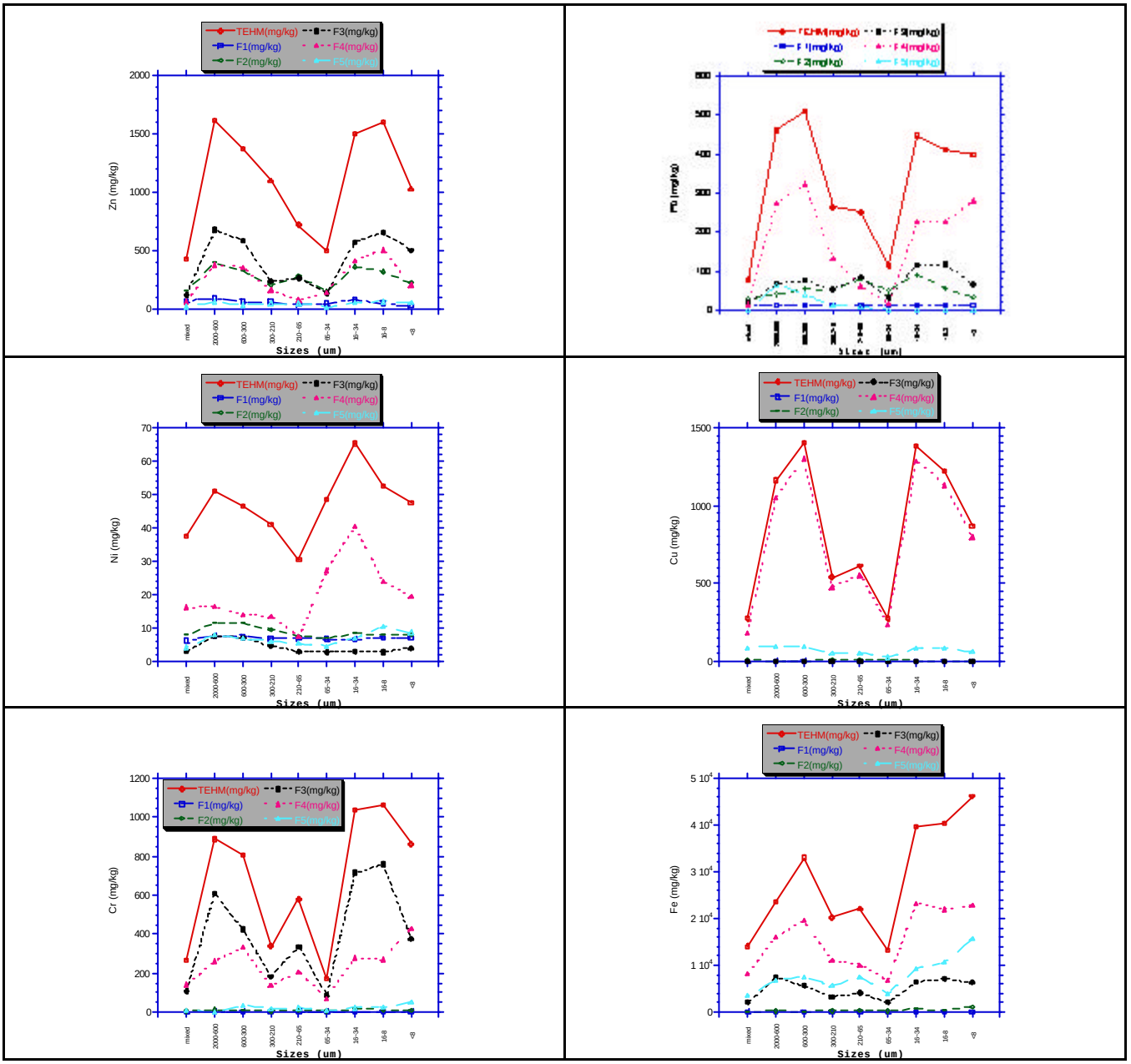

Figure 2. *Correlation of particle sizes and metal speciation for high heavy-metal polluted sediment. TEHM: total extractable heavy metal; F1: exchangeable; F2: bound to carbonates; F3: bound to Fe and Mn oxides; F4: bound to organic matter; F5: residual.*