Correlations of extractable heavy metals with organic matters in contaminated river sediments

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Abstract In southern Taiwan, almost all the main rivers have been contaminated by anthropogenic heavy metals and organic matters. The main pollution sources include agricultural, industrial, and domestic activities. River sediments potentially have large capacities to accumulate heavy metals and organic matters when the river water flows through it. The sediments sampled from high contaminated river (the Yenshui River) and moderately contaminated rivers (the Tsengwen, Chishui, Potzu, and Peikang Rivers) were used to realize correlations between each kind of aqua regia extractable heavy metals (Co, Cr, Cu, Zn, Ni, Pb, Mn, and Fe) and organic matters in vertical sediment cores. Organic matters and aqua regia extractable heavy metal concentrations, analyzed by strong acid-digested extraction, were determined in vertical profile segments from downstream sediments of the five rivers. Sum of six aqua regia extractable heavy metals (Co, Cr, Cu, Zn, Ni, and Pb) were below 3,000 mg/kg in sediments of the Yenshui River, and below 500 mg/kg in the other four rivers' sediments. Strongly positive correlations ($r = 0.83–0.95$) between each kind of aqua regia extractable heavy metals and organic matters (concentration range between 0.6 to 3.8%) were observed in sediments of the Yenshui River. The slopes of the linear regressive lines approximated the average metal complexation ratios with organic matters in the sediments. In sediments of the other four rivers, smaller positive correlation coefficients between aqua regia extractable heavy metals and organic matters (below 2.6%) were observed. The complexation ratios derived from the four moderately polluted river sediments were smaller than those derived from the highly contaminated river sediments, indicating that the importance of organic matters in the accumulation of heavy metals in river sediments.

Keywords Correlation; heavy metal; organic matters, sediment; sediment core

Introduction

By means of decreased flow of river water, flocculation and precipitation of sedimentary particles have the tendency to occur in the downstream river and area of estuaries (Gibbs, 1987). In this study, the five main river systems located in southern Taiwan were selected, which including the highly polluted river (the Yenshui Rivers) and the moderately polluted rivers (the Tsengwen, Chishui, Potzu, and Peikang Rivers). Each river has been polluted for years with heavy metals and organic matter coming from industrial, domestic, and agricultural sources.

In each river, some environmentally relevant trace heavy metals were determined in sediments in order to evaluate their accumulation with organic matter in anthropogenic pollution river systems. For a quantitative evaluation of the organic matter’s influence on the accumulation of heavy metals in river sediments, we selected five main rivers which were situated in different pollution levels of heavy metals.

The main purpose of this study is to verify the correlations of the aqua regia extractable heavy metal pollutants with organic matter in sediment cores. This study also seeks to determine the linear relationships (i.e. complexation ratio) of various heavy metals with organic matter as well as to assess the effects of total anthropogenic heavy metal...
Material and methods

Study areas
The five main rivers flow through the largest plain area of southern Taiwan. The catchments of the Yenshui River have many industrial plants which discharge large amount of wastewater contaminated with high concentration of heavy metals and organic matters. The major pollutions in the catchments of the other four rivers were due to domestic and agricultural activities.

Sediment core samples preparation
Sediment cores from the five main rivers were sampled by a hand-operated sediment corer (Wildco, U.S.A.) for investigation in this study. The sediment cores when taking back to our laboratory were held vertically and cut downwards from the water-sediment interface (by plastic blades) to divide the cores into several 2 cm (between 0–10 cm depth of sediment core) and 5 cm (deeper than 10 cm depth of sediment core) segments. Each sediment core segment was air-dried before chemical analysis.

Chemical analysis
Organic matter (OM) contained in sediment particles was determined using the Walkley-Black method (Walkley et al., 1934) and converted to percent OM (Sims et al., 1991). The concentrations of aqua regia extractable heavy metals were released by strong acid digested extraction. 0.2–0.5 gram of air-dried sediments were added to a plastic centrifuge tube with 3 mL of nitric acid (65%) and 6 mL of hydrochloric acid (37%). This digestion was performed by the Milestone MLS 1200 programmed microwave system. The concentrations of each extractable heavy metals (Co, Cr, Cu, Zn, Ni, Pb, Mn, and Fe) were measured by flame atomic absorption spectrophotometer (GBC, AA960).

Results and discussion

Variation of organic matters and heavy metals in sediment cores

From Figure 1a, the organic matter concentrations at different depths of the Yenshui, Tsengwen, Chishui, Potzu, and Peikang Rivers’ sediments were 0.5–3.8%, 0.5–2.35%, 0.4–1.75%, 0.7–2.6%, and 0.7–1.7%. The concentrations of aqua regia extractable Cu in vertical sediment cores ranged from 5–35 mg/kg in four moderately contaminated rivers to 80–1,000 mg/kg in the highly polluted Yenshui River. Similarly, the concentrations of aqua regia extractable Cr ranged from 13–50 mg/kg to 15–820 mg/kg (Figure 1b). The concentrations of aqua regia extractable Zn ranged from 43–250 mg/kg to 45–830 mg/kg (Figure 1c). The concentrations of aqua regia extractable Ni ranged from 15–38 mg/kg to 15–430 mg/kg (Figure 1d). The concentrations of aqua regia extractable Pb ranged from 10–46 mg/kg to 10–105 mg/kg (Figure 1e). The concentrations of aqua regia extractable Co ranged from 8–26 mg/kg to 8–140 mg/kg (Figure 1f). In the Tsengwen River, the concentration range of aqua regia extractable Mn was from 250 to 710 mg/kg (Figure 1g). However, the concentrations of aqua regia extractable Mn in the other four rivers ranged from 250 to 500 mg/kg. Similarly, the concentrations of aqua regia extractable Fe in the Yenshui and Tsengwen Rivers were also found to have larger variability than the other rivers and ranged from 13,500 to 44,000 mg/kg (Figure 1h). The concentrations of aqua regia extractable Fe in the other three rivers ranged from 20,000 to 40,000 mg/kg.
Correlation of heavy metals with organic matters

Figures 1a–1h shows that the correlations between each kind of aqua regia extractable heavy metals and organic matter have been observed in sediments sampled from high organic matter (the Yenshui River) and low organic matter polluted rivers (the Tsengwen, Chishui, Potzu, and Peikang Rivers) in southern Taiwan.

The strongly positive correlations were found between organic matter and the heavy metals (Cu, Zn, Pb, Cr, Ni, Mn and Fe) in the Yenshui River’s sediments, indicating that complexation of heavy metals with organic matters may be an important factor governing metals uptake into sediment particles in high heavy metals polluted rivers. The correlation coefficients ($r$) were 0.95, 0.89, 0.93, 0.91, 0.88, 0.83, and 0.91 for Cu, Cr, Zn, Ni, Pb, Co, and Fe, except Mn ($r = 0.77$). However, the correlation coefficients between heavy metals

**Figure 1** Correlation of organic matter versus aqua regia extractable heavy metals in sediment cores for the five main rivers. (a) Cu; (b) Cr; (c) Zn; (d) Ni; (e) Pb; (f) Co; (g) Mn; and (h) Fe
(Cu, Cr, Zn, Ni, Pb, Co, and Fe) and organic matter in low heavy metal polluted rivers were lower than those in highly polluted river.

The smaller correlation coefficients between Ni, Pb, and Co with organic matter were found to be 0.48–0.79, 0.53–0.66, and 0.61–0.79 in moderately heavy metal polluted rivers (Figures 1d, 1e, and 1f), which may be explained by the low concentrations of anthropogenic heavy metals and organic matter existing in the rivers. The largest variability of Mn concentration range matched the largest observed correlation coefficient which was found in the Tsengwen River (Figure 1g).

The correlation coefficients between organic matter and the sum of aqua regia extractable heavy metals (Cr, Co, Ni, Cu, Zn, and Pb) in five rivers were shown in Figure 2. Stronger positive correlation was found in the high anthropogenic heavy metal polluted river (the Yenshui River).
Complexation ratio of heavy metal versus organic matter

The complexation ratio of heavy metal concentration and organic matter was defined as the concentration (mg/kg) of each kind of aqua regia extractable heavy metals divided by organic matter (%) in sediments. The value of the complexation ratio for each heavy metal was found as the slope of the linear regressive line in Figures 1a–1h. Complexation ratios in contaminated sediments can be used to compare heavy-metal loads in different rivers. Such kinds of “enrichment factors” are often useful to indicate the degree of river pollution by heavy metals. The complexation ratio for Cu in the Yenshui River was 225.82, but in the other rivers with low Cu pollution, the complexation ratios only ranged from 8.87 to 13.88 (Figure 1a). The variations of complexation ratios for Cr, Zn, Ni, Pb, Co, Mn and Fe in the five rivers were similar (Figures 1b–1h). The complexation ratio correlated with the range of aqua regia extractable heavy metals contamination in sediment. The more the aqua regia extractable heavy metal contaminants contained, the higher complexation ratio observed for each heavy metal.

Figure 1 Continued. (e) Pb; (f) Co

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The high level of organic matters and aqua regia extractable heavy metals in the Yenshui River sediment significantly indicated the strong complexation capacity of organic matter with these heavy metals.

**Conclusions**

The concentrations of aqua regia extractable heavy metals (Co, Cr, Cu, Zn, Ni, Pb, Mn, and Fe) in the sediment core segments correlated strongly with the organic matter in different depth sediments, making an identification of the absorption/complexation of heavy metals by natural organic matter in sediment particles. The more the variability of heavy metal concentration existed in rivers, the stronger positive correlation coefficient will be found. Meanwhile, the larger complexation ratio could also be found.

The evidence of the strong linear relationships between heavy metals and organic matter for the five main rivers’ sediment allows us to realize the high binding affinities of organic matter on heavy metals.
matter with anthropogenic trace heavy metals (Cu, Zn, Ni, Pb, Co, and Cr) and geochemical conservative components (Mn and Fe).

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References

Figure 2 Correlation of organic matter and the sum of six aqua regia extractable heavy metals (Cr, Co, Ni, Cu, Zn and Pb) in sediment core segments for five rivers.