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Fractionation of Heavy Metals in Different Particle-Size Sediments and Its Relationship with Heavy Metal Pollution

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Sediments not only reflect the current quality of surface waters, but also provide vital information on the transportation and fate of pollutants (Santschi, 1984; Finney and Huh, 1989). Numerous reports have highlighted that total concentrations of heavy metals are deficient in predicting toxicity of these pollutants (Förstner and Salomons, 1980; Luoma, 1983; DiToro et al. 1990 Arjonilla et al.1994). A good knowledge of the contamination of sediments requires the identification of speciation in order to known the availability and mobilization of the heavy metals. Generally, sequential extraction procedures have become a common approach for fractionation purposes due to the inherent difficulties in obtaining the real-world chemical speciation nowadays. Of the wide variety of sequential extraction procedures, the most widely used are those proposed by Tessier et al. (1979) and by the Community Bureau of Reference (BCR) (Quevauviller et al., 1993). BCR is now called the Standard Measurements and Testing Program of the European Community (SMT), and the objective of the BCR-program is to improve the quality of measurements and consequently harmonize the results of the measurements obtained within the European Community.

Many factors could influence the chemical speciation of heavy metals, such as sediment particle-size distribution, organic matter content, salinity, pH and redox potential (Soon et al. 1999; Dollar et al. 2001). These factors are not completely understood and simple relationships are seldom found. Of these factors, most frequently the size fraction has been neglected. Almost all the studies deal with sediment speciation are carried out in the unfractionated bulk sediments. Our previous study showed that the total concentrations of heavy metals in sediments were significantly inter-linked to the particle-size distribution. There were also some remarkable changes in the partition of heavy metals among particle-size spectrum between natural and anthropogenic inputs (Zhang et al. 2002). The finer particles showed higher concentration of heavy metals due to increased surface areas, higher clay minerals and organic matter content, and the presence of Fe-Mn oxide phases. What relationship is between speciation distribution and particle-size fractions? We can predict that such kind study by taking account the speciation distribution among particle-size spectrum could provide further detailed information about heavy metal pollution in sediment. For this purpose, an

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attempt has been made to bridge the relationship of pollution of the heavy metals in sediments with fraction distribution among the particle-size spectrum. It seems, to our knowledge, that this is the first time to address this matter by this way.

MATERIALS AND METHODS

The sediments were collected from Guanting Reservoir in October, 2000. The reservoir is situated in the northwest of Beijing and the total capacity is about 2270 million m^3. The water mainly comes from two rivers, Yonghe River and Sanggan River. In recent years, water in the reservoir stopped use as drinking water source because it suffered from the combined stress of pollutant loading, such as atmospheric deposition, hazardous wastes from manufacturing facilities and land leaches. In this study five sediments were collected from different sites. Site 1 is at the mouths of the two rivers from which 90% of water comes. Site 2 is close to the dam in the reservoir. Sites 3 and 4 are in the center of the reservoir. Site 5 is close to the mouth of Guihe River, from which very little water comes.

Sediment samples were partitioned into five particle fractions based on Stoke's Law: coarse sand (150μm), medium sand (63-150μm), coarse silt (20-63μm), medium silt (2-20um) and clay (<2μm). No dispersing agents or inorganic salts were added during these fractionation were dried at 60℃, weighed, and stored for further analysis. All particle-size fractionations were carried out in duplicate. The coefficients of variations of duplicate determination were <5%.

Sequential extraction was performed on the particle-size separated sediments. The three-step extraction scheme proposed by the Community Bureau of Reference (BCR) (Quevauviller et al. 1993) was adopted in this work. Details of the extraction processes are given in Table 1.

Table 1. Sequential extraction scheme for heavy metal fractionation in sediments.

Step	Phases	Procedure
1	B1: water soluble, exchangeable and carbonate bound	0.1 M CH_3COOH, 20 ml, room temperature, shake for 16 h
2	B2: Fe-Mn oxide bound	0.1 M $NH_2OH.HCl$ (pH 2 with HNO_3), 20 ml, room temperature, shake for 16 h
3	B3: organic matter and sulfide bound	30 % H_2O_2, 5 ml, room temperature, 1 h, followed 85 ^{0}C, 1 h, occasionally shake; add 5 ml 30 % H_2O_2, 85 ^{0}C, 1 h; add 1 M NH_4OAc (pH 2 with HNO_3) 25 ml, room temperature, shake 16 h
4^a	B4: residue	HNO_3+HF+HCl, 3ml, under high pressure, 185±5 ^{0}C

a In step 4, 0.100 g of dried residue was attached by 3 ml of HNO_3-HF-$HClO_4$(1+1+1) mixture

Heavy metal concentrations in the sediments were determined by ICP-MS (VG

PlasmaQuard III) after decomposition of samples with a mixture of $HNO_3/HClO_4/HF$ (1:1:1) (Zhang and Shan, 1997). The extractable elements in each fraction were determined after diluting twice for the B1 fraction, and five times each for B2 and B3 fractions. The ICP-MS operating conditions were optimized using a solution of ^{115} In at 10 ng ml^{-1} in 2% HNO_3. An internal standard of ^{115}In at 10 ng ml^{-1} was used to compensate for matrix suppression and signal drifting during analysis. All reagents used were of analytical reagent grade or better.

RESULTS AND DISCUSSION

The heavy metal concentrations in the bulk sediments from each sampling site are summarized in Table 2. High concentration variations were obtained for elements Zn, Cd and Pb and much higher concentration of elements Zn and Pb were observed in sampling sites 1 and 2. Site 1 is at the mouths of Songgan River and Yang River, which are two main rivers run into the reservoir. Pollution, such as wastewater and sewage discharges nearby or upstream, could be carried out and entered the reservoir. Site 2 is close to the dam in the reservoir. Heavy metals could be carried to the dam and then settle down with suspended solid. Therefore, site 2 could become a pollution deposition site.

Table 2. Concentration of heavy metals in different sampling sites ($\mu g\ g^{-1}$).

Element	S1	S2	S3	S4	S5
Cr	56. 4	61. 6	59. 1	59. 3	25. 7
Ni	24. 2	34. 0	39. 6	40. 7	14. 7
Zn	421. 3	339. 5	92. 8	94. 1	41. 4
Cu	47. 7	50. 5	31. 3	41. 4	11. 8
Cd	2. 03	1. 84	0. 31	0. 47	0. 29
Pb	142. 1	148. 7	29. 8	28. 3	18. 2

Sequential extraction of size-separated sediments shows that different metals or different chemical fractions have different distribution patterns among particle-size, see Figure1 to Figure 3. Generally, heavy metals in B1 fraction have an affinity for the finer grain sizes. B2 fraction was evenly distributed among the particle-size fractions for most of elements. B3 fraction are somewhat like B1 fraction, hosted largely by smaller particle-size fractions less than 20 μm. The potentially polluting heavy metals have somewhat different distribution patterns from other metals or the same elements in unpolluted samples.

The heavy metal concentrations in the exchangeable and carbonate bound forms are strongly dependent on particle size, as shown in Fig 1. Chromium, Cu, Ni, Pb, Zn and Cd in B1 fraction in the particle-size-separated sediments show different distribution pattern and we can group them into two categories. The distribution of Cr, Cu and Ni, which are not highly enriched in the sediments, are similar to one another and characterized as hosted largely by the fraction <2 μm, which are over 80% among the total particle fraction. Lead, Zn and Cd behave in a very

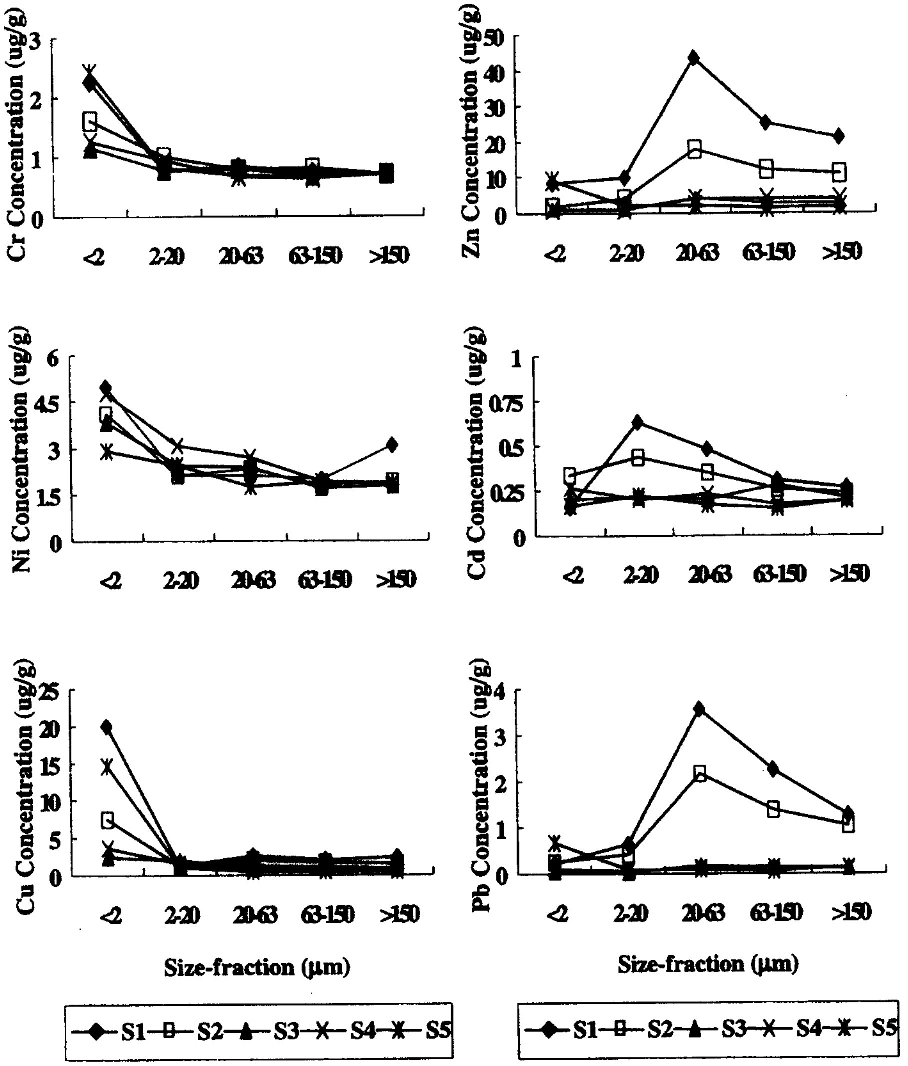

Figure 1. Distribution of heavy metals in B1 among different particle-size fractions

different manner to elements Cr, Cu and Ni. For sediments 1 and 2, the maximum concentration was found in the size of 20-63 μm. For the other three sediments, Pb, Zn and Cd are almost evenly distributed among particle-size spectrum.

When the differences among the samples were considered, sediments 1 and 2 represent different distribution patterns among the size spectrum from other sites for elements Pb, Zn and Cd. From geological point of view, the sample locations are in close proximity to one another and natural changes in mineralogy should be very little. If there is no anthropogenic pollution, the original speciation

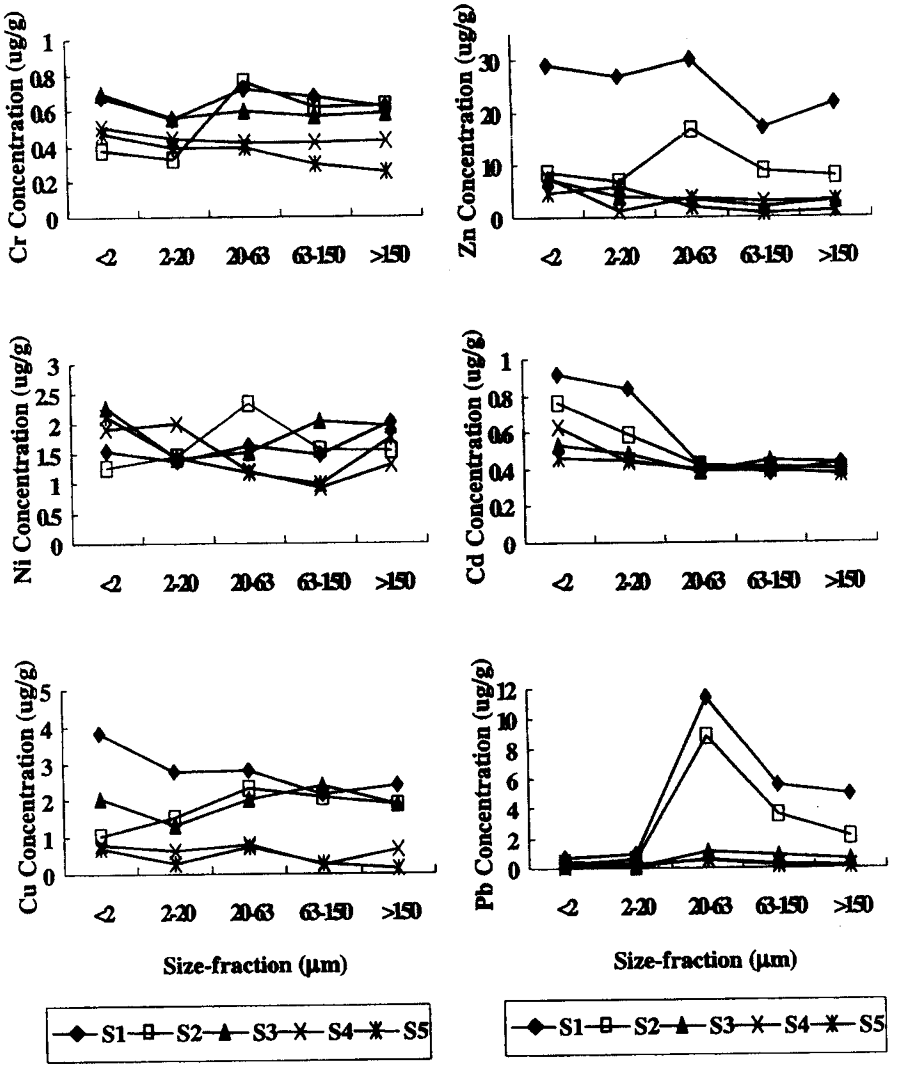

Figure 2. Distribution of heavy metals in B2 among different particle-size fractions

distribution of the sediments should be similar. The differences in speciation distribution should be, therefore, not accounted for by the changes in mineralogy.

The total concentration of elements Pb, Zn and Cd in sediments 1 and 2 are also much higher than in the other samples. Considering high concentration of Pb, Zn and Cd in the sediments 1 and 2, the anthropogenic input in these two sites may play a significant influence on the distribution differences of Pb, Zn and Cd in B1 fraction among size fractions.

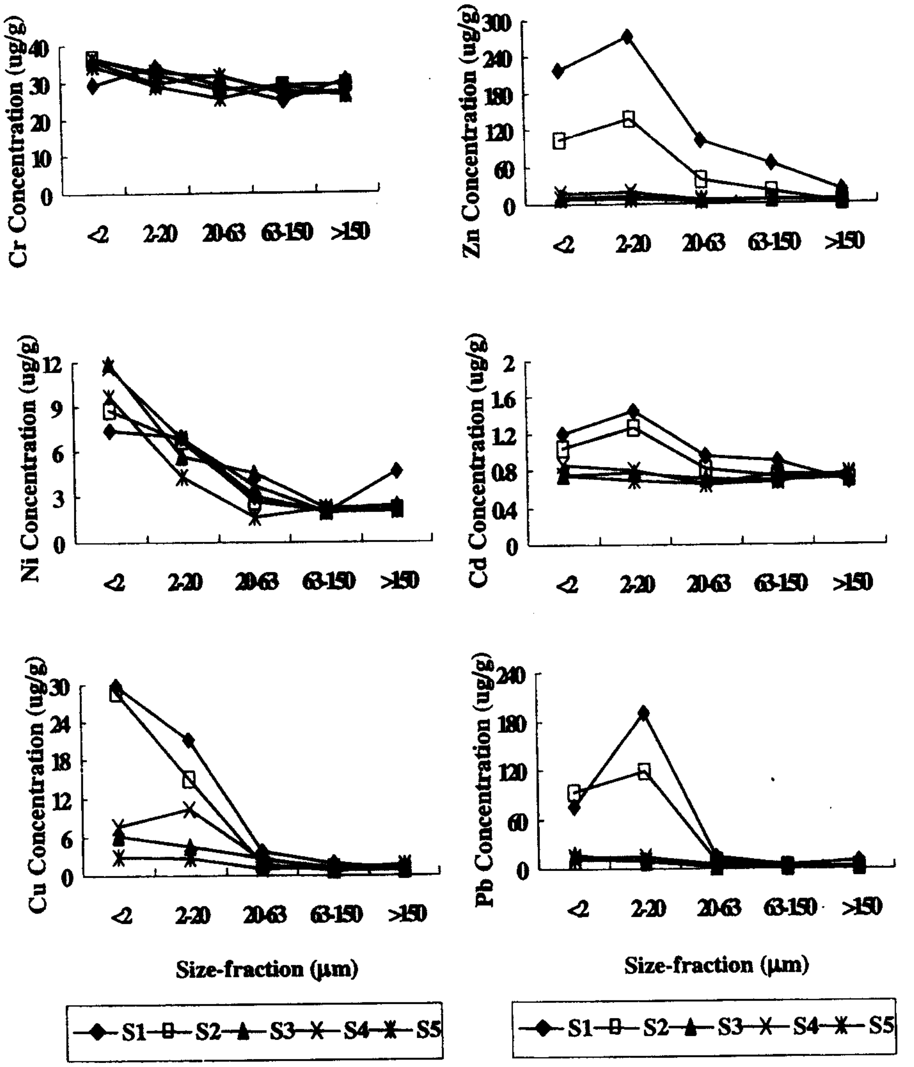

Figure 3. Distribution of heavy metals in B3 among different particle-size fractions

Fresh metallic pollutants were easily adsorbed by the finer particles. However, higher concentrations of Pb, Zn and Cd were observed in the particle size 2-20μm instead of <2 μm. This phenomenon may be attributed to less crystalline or amorphous substances in the fraction <2 μm. Also, the concentrations of elements Pb, Zn and Cd are relatively high, which exert not enough adsorption sites in the fraction <2 μm. As shown in Fig 2 that the metal concentrations in B2 fraction tend to be homogeneously distributed in different grain size expected Pb in sediments 1 and 2. B2 fraction is mainly related to the Fe-Mn oxides, the homogeneous distribution is probably owing to dominant proportion coprecipitation with Fe and Mn oxides or hydrous oxides origination from parent rocks and no significant anthropogenic influence would be expected.

For Pb, the distribution pattern was different from other elements in sediments 1 and 2 by a relative high value in the particle-size 20-63 μm. Our previous study showed that Pb in Fe-Mn oxide form was also relatively high in the bulk sediments (Zhang et al. 2002). Therefore, the different distribution pattern of Pb may to some extent be due to anthropogenic source of Pb. High content of Pb causes the redistribution of Pb on the basis of the geological origin and leading to the different distribution pattern of Pb in the particle size spectrum. Another reason is strong co-precipitation of Pb with manganese oxides. Research on natural biofilms (used to represent lake surface coating materials) by Dong et al. (1999) suggested a strong role of manganese oxides in the retention of Pb. Their results indicated dominant sequestering of Pb by manganese oxides, with lesser adsorption to iron oxides and organic material.

Distribution of B3 fraction among particle-size separated sediments showed similar trends to B1 fraction that Zn, Pb and Cd displayed differences in fractionation between sediments. Although several factors may contribute to the differences in speciation, historic pollution is one obvious explanation for the differences. As shown in Figure 3 that the difference was only observed in the sediments from site 1 and 2, and total concentration of Zn, Pb and Cd was also higher in these two sites. Except carbonate associated metals and exchangeable metals, the oxide coatings are probably another effective scavengers of trace metals in sediments and could be present predominantly as coatings on particle surfaces or as small particulate. The sediments used in this study are surface sediments, most of them are from the oxidized layer and organic matter contents are relatively high. Surface sediments are different from reduced sediments or soil with relative proportions of metals bound by organic matter, especially when the content of the metals are high. The organic carbon was usually found concentrated in the smaller size fractions (Laxen et al.) and in this study we also observed that most of the metals in B3 fraction were concentrated in smaller size fractions. Therefore, from the results of this study we can see expect B1 fraction the organic fraction is another potential pollution bearing phases.

Results of this study showed that in both B1 fraction (water soluble, exchangeable and carbonate bound) and B3 fraction (organic matter and sulfide bound) the distribution of heavy metals among particle-size spectrum was associated with the heavy metal pollution in sediments. The distribution of the heavy metals Cr, Cu and Ni in B1 and B3 fractions displayed similar fractionation patterns among particle-size in all the sediments, characterized as hosted largely by the fraction <2 μm. However, metals Pb, Zn and Cd in polluted sediments were distributed in a different pattern from other metals or the same elements in unpolluted samples with a maximum concentration found in the particle size 20-63 μm. The heavy metals in B2 fraction evenly distributed among different particle-size for all the metals except Pb. The fractionation patterns in particle size fractions exerted some relationship with the pollution of heavy metals in sediments.

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