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The effect of grain size on the Cu, Pb, Ni, Cd speciation and distribution in sediments: a case study of Dongping Lake, China

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Abstract This paper examines the surface sediments collected from Dongping Lake in China for speciation and distribution of toxic heavy metals (Cu, Pb, Ni, Cd) in different grain size fractions, and for the factors that need to be considered in potential hazard of metals to the environment. Four grain size fractions (<63, 63–78, 78–163 and 163–280 µm), divided in wet condition, and bulk samples less than 280 µm in diameter were analyzed for their distribution, density and appearance. A three-stage extraction procedure following the BCR protocol was used to chemically fractionate metals into "acid soluble", "reducible", "oxidizable" and "residual" fractions. Correlation analysis was used to analyze the datasets. The results showed that <63 µm grain size part constitutes the major proportion of the sediments, but its density is the smallest among the four grain size fractions. In general, the metal content curve against grain size presents "S" distribution, and the highest concentrations do not exist in <63 µm grain size. Appearance observation indicates that the adsorbed substance increases gradually along with the decreasing grain size. The dominant speciation of elements and the extent of pollution are responsible for the metal distribution in different grain size sediments. While studying bioavailability and mobilization of metals, it is advisable to take metal speciation, grain size distribution and density into consideration.

Keywords Grain size · Sediments · Heavy metal · Speciation · Fractionation · Dongping Lake · TEM

Introduction

Heavy metal pollution, owing to its permanent existence and biological enrichment, has long been an important subject in the field of international environmental science. As a result of complex physical, chemical and biological processes, a major fraction of trace metals is found to be associated with water body sediments. Sediments are multi-phase solids containing silicates, carbonates, (hydr)oxides, sulfates and organic substances as major components (Bähr et al. 1995). There-fore, their ability and capacity to combine heavy metals differ greatly.

The main factors influencing the heavy metal contents in sediments include the physical and chemical properties (such as grain size, surface to volume ratio, heavy metal contents of the main geochemistry phase), in which grain size is a main control parameter (Ujević et al. 2000; Milligan et al. 1998; Fang et al. 1999). The grain size distribution of sediments varies considerably at different sites and valid inter-site comparisons of metal concentrations cannot be made without a cor-

rection of grain size effect (Förstner et al. 1983). Several methods have been studied to correct the metal contents for grain size effect (Šurija et al. 1995; Szava-Kovats et al. 2002; Loring et al. 1990). It is generally believed that finer sediments contain more heavy metals than coarser ones. The main reason is that smaller grain-size particles have a larger surface-to-volume ratio (Salomons et al. 1984; Martincic et al. 1990). However, some studies have indicated that coarser particles show a similar or even higher heavy metal concentrations than finer ones and the higher residence time and/or the presence of coarser particles are possibly responsible for higher metal content in the coarser size fractions (Tessier et al. 1982; Singh et al. 1999).

In the studies of heavy metal pollution in sediments, the use of sequential extraction schemes to determine metal partitioning has experienced increased attention during recent years. The eco-toxicity and mobility of metals in the environment depend strongly on their specific chemical forms or method of binding rather than on the total element contents. Although many studies have been reported about the grain size effect that sediments adsorb and release the heavy metals (Ergin et al. 1996; Wang et al. 2000), little is known if variation of heavy metal-binding fractions associated with particle sizes has an effect on the total metal contents and heavy metal release. Moreover, some physical characters of particle size are not considered in studying heavy metals' potential pollution to the environment. In this paper, according to grain size distribution characteristics and metal speciation, we are going to analyze the factors influencing the metal concentrations in different grain size sediments from Dongping Lake, and discuss the grain size effect on bioavailability and mobilization of metals.

Materials and methods

Study area

South–North Water transfer is a super strategic project for solving the problem of the water resource shortage in northern China. It can be divided into three zones: east, central and west zones. Dongping Lake is located in the north of Shandong province, extending from 35°30′N to 36°20′N and from 116°00′S to 116°30′S (Fig. 1), which is the last adjusting reservoir of the east zone and the second largest freshwater lake in northern China. In recent years, industrial and municipal sewage goes directly or indirectly into the lake, resulting in serious pollution of heavy metals. Accordingly, in order to guarantee the implementation of this project, it is important to study heavy metal pollution in Dongping Lake.

Sampling and size fractionation

Surface sediment samples were collected in triplicate from Dongping Lake, with a grab, on board. The samples were removed from the surface layer with a polyethylene spoon to avoid contamination, and stored in hermetic polyethylene bottles at 4°C separately. In order to determine the relationship between grain size and metal contents, the sediment samples were fractionated into four sizes by nylon sieves of 280, 163, 78, 63 μm in turn with mechanical shakers. Then the sediment samples were fractionated into four parts: 163–280, 78–163, 63–78 and < 63 μm (the part of grain size > 280 μm is mainly composed of grit, shell and rootstalk so it was discarded). After the sediment samples of different grain sizes were dried at room temperature, they were weighed separately and their densities were determined with a specific gravimeter, then they were preserved in pre-cleaned dry glass vials separately. All the bottles were previously cleaned with 10% (v/v) nitric acid (HNO_3) for 24 h, rinsed with deionized water and were dried.
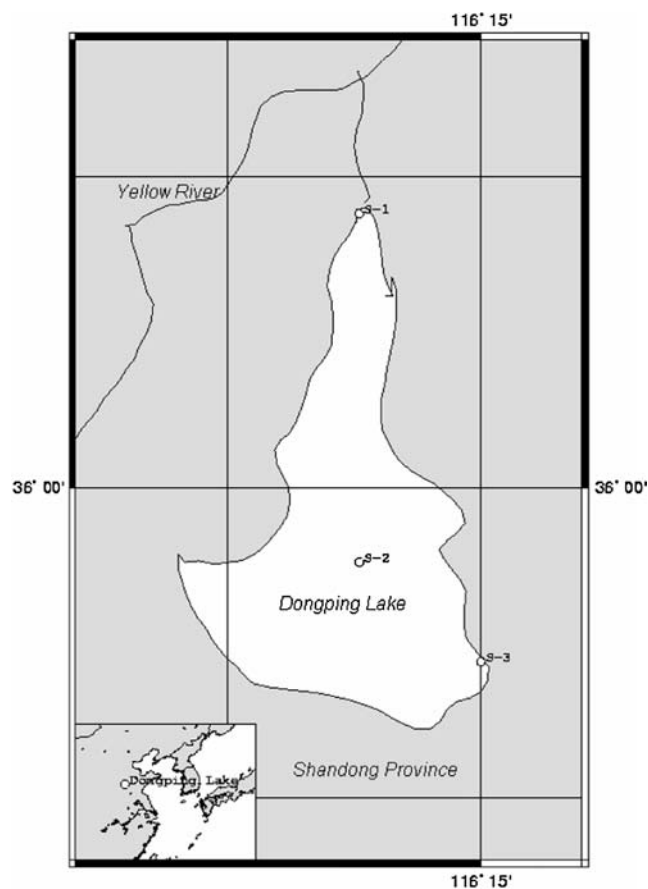

Fig. 1 The map of Dongping Lake with location of sampling sites

Chemical classification for heavy metals

The three-stage sequential extraction procedure by European Community Bureau of Reference (BCR) has been applied to the metal fractionation in sediment samples. Different grain size samples of 1.00 g each were taken from each location and submitted to the BCR sequential extraction procedure (Davidson et al. 1994). According to this method, metals in sediments were separated into four different fractions, which can be described as acid soluble, reducible, oxidizable and residual fractions. The sequential chemical extraction procedure is illustrated as in Table 1. A horizontal mechanical shaker and a centrifuge were used to perform the extractions. The extracts were centrifuged at 5,000 rpm for 20 min by using a centrifuge. The extracts from the samples were stored in PTFE tubes at 4°C in a refrigerator before analysis.

All PTFE tubes, centrifuge vials and transferring pipettes, as well as glass volumetric flasks, were pre-cleaned by being soaked overnight in 10% (v/v) nitric acid (HNO_3) followed by several rinses with deionized water.

Analytical method

The determination of metals was carried out by an Aglent 7500a ICP-MS. Transmission electric mirror of JEM-100X II model was used to observe the appearance characteristics of different grain size sediments.

Quality assurance

In order to guarantee the accuracy of the results, the sums of metal concentrations in each geochemical phase of the sediment samples were compared with the total digestion concentration values. The differences between the total content of sediment and the sums of the individual phase concentrations were not greater than 11%.

Analytical assurance concerning the total digestion was achieved by measuring the standard sample (BCR No. 40) and the results were found to be within ±5% of certified values.

Results and discussion

Grain size distribution and density

The results of weight percentage and densities of different grain size sediments are given in Table 2.

We can see that < 63 μm size is the dominant fraction in all locations, accounting for about 78–89% of the sediments, but its density is the smallest in contrast with that of the other sizes. The possible reason is that this part of sediments contains much smaller density relict of animals and plants, and the proportion of bigger density mineral particle reduces correspondingly. Owing to the smaller density, this part of sediment migrates relatively easily under external forces such as water turbulence and biological activity; then it will play an important role in the migration of heavy metals. In addition, because of the largest percentage, its characters and behavior will exert an important influence on the environment.

The exterior characteristics of different grain size sediments

The appearance characteristics of different grain size sediments were observed by TEM (transmission electron microscopy) at three sampling sites, and these characteristics are similar at each site. The photographs of TEM of S-1 are given (Fig. 2) as an example.

The electron micrograph of 163–280 μm sample indicates that the exterior form of this particles takes on regular crystal brim, and there are less adsorbed matters on the surface. Along with the decrease of grain size, the adsorbed matters increase gradually. The electron micrograph of < 63 μm sample shows that much floc-

Table 1 European Community Bureau of Reference three-stage extraction scheme

Step	Fractions	Reagents	Operating conditions
1	Acid soluble	40 ml of 0.11 mol l^{-1} HAC solution	Room temperature, 16 h, constant agitation
2	Reducible	40 ml of 0.1 mol l^{-1} $NH_2OH \cdot HCl$ (pH = 2 with HNO_3) solution	Room temperature, 16 h, constant agitation
3	Oxidizable	(1) 10 ml of 30% w/v H_2O_2	Room temperature, 1 h, occasional agitation , +85°C 1 h
		(2) 10 ml of 30% w/v H_2O_2	+85°C 1 h, then reduce the volume to 2 ml
		(3) 50 ml of 1 mol l^{-1} NH_4AC solution	Room temperature, 16 h, constant agitation
4	Residual	HNO_3 + $HClO_4$ + HF	Digested in crucible

Table 2 Percentage and density in different grain size fractions of sediments

Location	163–280 µm		78–163 µm		63–78 µm		< 63 µm	
	Percentage	Density[a]	Percentage	Density	Percentage	Density	Percentage	Density
S-1	4	2.63	11	2.56	7	2.53	78	2.42
S-2	5	2.92	4	2.62	2	3.21	89	2.45
S-3	3	2.88	5	2.63	4	2.48	88	2.41

[a]The unit of density is kg/l

Fig. 2 Photographs of TEM (1.9×10^4 times)


163~280µm

78~163µm

63~78µm

< 63µm
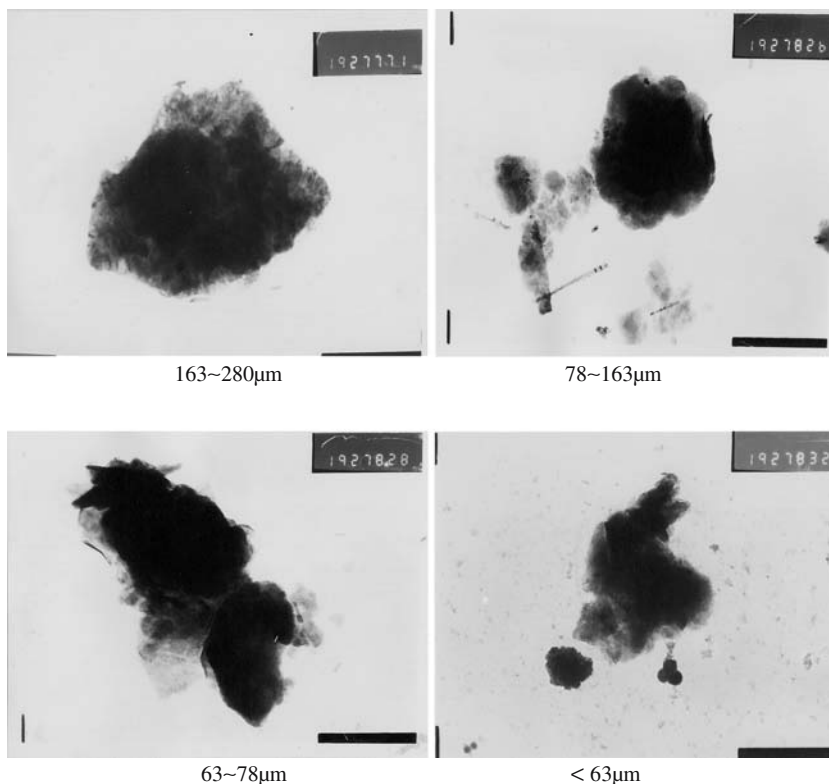
cules are adsorbed by the crystalloid, which makes the brim blurry, and the floccules can adsorb the great mass of pollutants in water. This phenomenon suggests that the heavy metal pollutants are associated with smaller grain size particles. Therefore, the exterior forms cannot explain the metal contents in different grain size sediments either.

The variation regulation of heavy metal contents along with grain size

The variation of metal concentrations to grain size is shown in Fig. 3. We can see that the content curves mainly present "S" distribution (viz. metal concentrations presenting "increase–decrease–increase" or "decrease–increase–decrease" trend along with the increasing grain size), and a few curves show concavity or convexity. The highest concentrations of elements at sites S-1 and S-3

are found in 163–280 µm grain size and the highest concentrations of metals at site S-2 are found in 63–78 µm grain size. In general, there is no gradual decrease or increase in the metal concentrations from finer to coarser sediments in Dongping Lake sediments. Some studies have indicated that higher residence time of the sediment particulates leads to higher metal contents, provided that this theory is also applied to the area we studied, then the residence time of different grain size sediment should be closely related to the density: the bigger the density is, the longer it resides and the more heavy metals are adsorbed on the surface of sediment particulate. But from the correlation coefficients between the density and heavy metal concentrations for the different grain size fractions of the sediments (as is shown in Table 3), we can see that the correlations are not good for some elements; moreover, the highest concentrations at site S-2 exist neither in finer nor in coarser sediment particles. These findings demonstrate that density may be an important factor

Fig. 3 Variation of metal contents against grain size ($n = 3$)
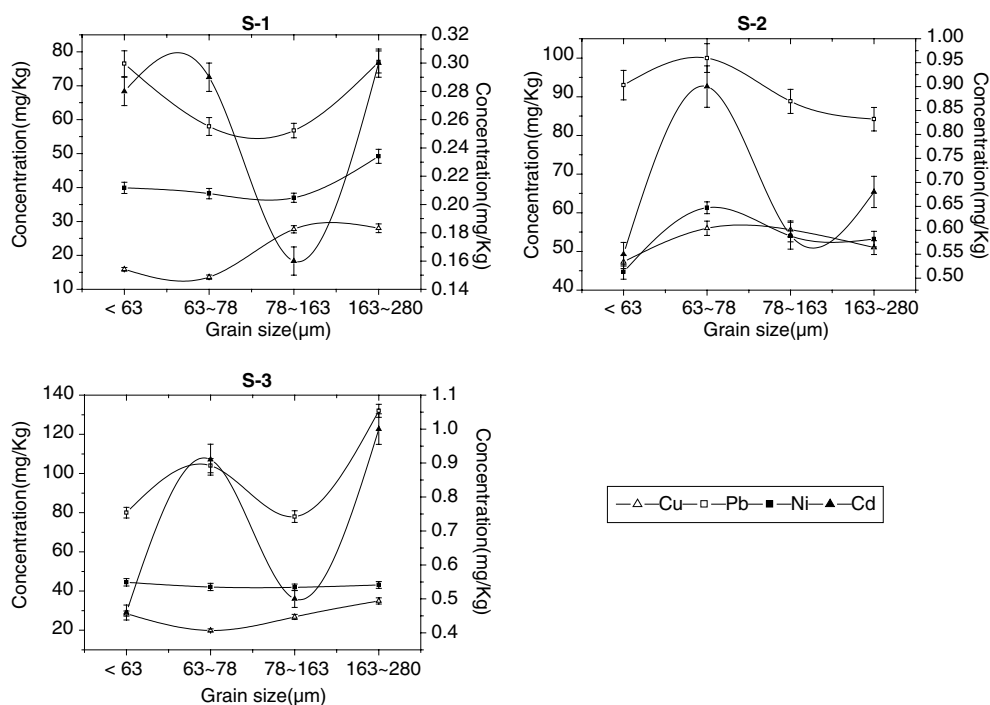
influencing metal concentrations among different grain size sediment fractions; however, the metal concentrations of sediments are also influenced by other factors such as particulate organic carbon content, mineral component, etc. Therefore, the longer residence time theory alone cannot explain why the coarser particles contain more metals than the finer particles for the area we study.

Correlation analysis of total metal concentrations to metal speciation

The correlation analysis of metal contents and speciation were studied (Table 4). The elements Cu, Pb and Ni are associated mainly with residual fraction. Strong correlation, between residual and total metals at S-1 and S-3, shows that Cu, Pb and Ni contents in the original mineral have an important influence on the concentrations of different grain size sediments and that the metal concentrations of dominant speciation are responsible for the total metal contents in different grain size particles.

Table 3 Correlation coefficients of metal contents against density for different grain size sediments ($n = 3$, $p = 0.05$)

Sampling site	Cu	Pb	Ni	Cd
S-1	0.73	−0.12	0.56	−0.07
S-2	0.61	0.38	0.90	0.97
S-3	−0.21	0.74	−0.64	0.91

In the location of S-2, the correlation between residual fractions and total contents is not significant for the elements Cu, Pb and Ni. However, good correlation is found between total metals and oxidizable parts. This can be attributed to more organic pollutants poured into S-2 site than into the other two sites, which leads to higher organic bound metals at this site. Then we can conclude that the highest metal contents in 63–78 μm grain size sediments are not only decided by the dominant speciation metals, but by the quantity of pollutants.

Acid soluble part is the dominant speciation for Cd, and it correlates well with all the elements we studied. The high concentrations in this fraction are due to the special adsorption manner and active chemical property. Study showed that Cd is combined in the exchangeable position of the sorption, but not the inside of the crystal lattice. At these three sampling sites, the total contents of Cd are determined by the content distributions of dominant speciation in this four grain size parts.

Biological toxicity is related more closely to particular chemical forms, and heavy metals are not permanently fixed on sediments and can be released back into the water as a result of environmental change such as pH, redox potential and the presence of organic chelator (Campbell PGC et al. 1987). However, residual fraction cannot be released into bulk water in natural conditions so we compared the extractable heavy metal contents in different grain size sediments (given in Fig. 4) with predictable potential bioavailability and mobilization to the environment.

Table 4 Correlation coefficients for chemical form and total heavy metal contents in different grain size sediments ($n = 3$, $p = 0.05$)

| Element	S-1				S-2				S-3			
	I	II	III	IV	I	II	III	IV	I	II	III	IV
Cu	−0.14	−0.67	0.12	0.99	–	–	0.82	0.74	–		0.69	1.00
Pb	0.51	0.15	−0.23	0.96	–	1.00	0.88	−0.60	0.56	0.69	0.80	0.97
Ni	0.93	−0.40	0.90	0.86	0.90	0.56	0.94	0.20	−0.56	−0.56	−0.82	0.93
Cd	1.00	0.57	0.99	−0.99	0.96	0.86	0.28	−0.91	0.96	0.84	–	0.59

I Stands for acid soluble—total, *II* Stands for reducible—total, *III* Stands for oxidizable—total, *IV* Stands for residual—total, – Stands for non-existence

At site S-1, the highest extractable contents are found in < 63 or 163–280 μm grain size. The largest percentage of < 63 μm grain size in the sediment will increase the environmental pollution, and the smallest density also can increase it's mobilization. Because of smaller proportion and larger density, the latent contamination of 163–280 μm grain size part will not be serious. Accordingly, we should pay more attention to the potential pollution caused by < 63 μm grain size sediments at this site. At sites S-2 and S-3, the most extractable metal contents exist in 63–78 and 163–280 μm grain size, respectively, but relative smaller proportion and larger density will weaken the potential bioavailability and mobilization.

Conclusions

Owing to the largest part and smallest density among the four fractions (< 63, 63–78, 78–163 and 163–280 μm), < 63 μm grain size sediments will exert an important influence on the environment. The highest concentrations of elements Cu, Pb, Ni, Cd at sites S-1 and S-3 are found in 163–280 μm grain size, and the highest metal concentrations at site S-2 are found in 63–78 μm grain size. In general, there is no gradual decrease or increase in metal concentrations from finer to coarser sediments in Dongping Lake sediments. Correlations of metal contents against density and appearance observed by

Fig. 4 Extracted heavy metal contents in different grain size sediments
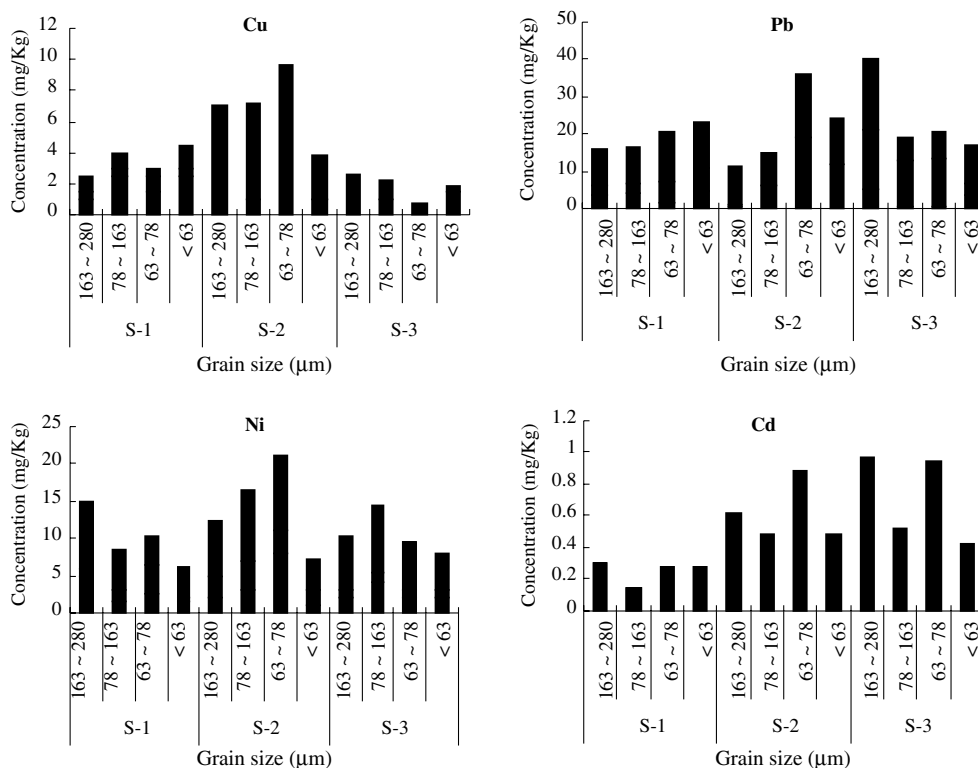
TEM cannot explain the distribution of metal concentrations in different grain size sediments. Correlations of metal concentrations to chemical forms show that metal contents are mainly related to the dominant forms of elements and the extent of pollution at any sites. When we study the release and mobility of metals, we should take into account metal speciation, grain size distribution and density comprehensively.

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