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## Heterogeneous distribution of copper in different grain size and density fractions of contaminated surface sediment from Nansi Lake (China)

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**Abstract** The copper (Cu) distributions and speciation in the surface sediment collected from Nansi Lake (NL) (China) were investigated by chemical and physical fractionation methods. Sediment was first fractionated into four grain size fractions (< 63, 78–163, 163–280, and > 280  $\mu\text{m}$ ) in wet condition. Each fraction was then further divided into two density sub-fractions (low and heavy) by flotation in sodium-polytungstate solution ( $\rho = 2.0 \text{ g/cm}^3$ ). In addition, a three-stage extraction procedure following the European Communities Bureau of Reference (BCR) protocol was applied to study the speciation distribution of Cu among grain size fractions. It was found that the speciation distributions of Cu among different grain size fractions were quite close to each other, although the total Cu concentrations were different in the individual fractions. Moreover, Cu mainly occurred in the coarser, low density,

OC-rich fractions. Extractable Cu, which was dominated by reducible and oxidizable parts, occupied almost 80% of the total Cu concentration. Total Cu concentrations in grain size fractions and density sub-fractions ranged from 29.6 to 72.9 and from 21.4 to 156 mg/kg dw, respectively. It was noted that low-density fractions had 4–7 times higher Cu concentrations and 5–12 times higher organic carbon (OC) content than those in high-density fractions. The results demonstrated that OC was a main factor influencing Cu distributions in either grain size or density fractionated sediment. This study suggests that the role of the Cu-rich fraction should be considered when conducting the remediation of Cu contamination in NL.

**Keywords** Copper · Sediment · Grain size fraction · Density fraction · Speciation · Organic matter

### Introduction

Copper (Cu) is an essential micronutrient for living organism growth and development, but it is potentially toxic to living organisms at higher concentrations. Now Cu pollution in natural environment has become a widely concerned problem (Hummel et al. 1997; Fortunati et al. 2005). This phenomenon is especially significant in the lake, which usually acts as a reservoir to provide fresh water for cities. An intensive use and dis-

charge of Cu led to a widespread accumulation of Cu in sediment where it often remains in surface layers (Brun et al. 1998; Miko et al. 2003). Therefore, Cu deposited in sediments may be directly available to benthic fauna (Zarcinas and Rogers 2002) or be released to the overlying water through sediment resuspension, adsorption/desorption reactions, reduction/oxidation reactions, and degradation of organism (Santschi et al. 1990). Thus, major risks for environmental pollution are generated, in particular with regards to water quality.

In general, bioavailability and toxicity of sediment-associated heavy metal are largely influenced by its speciation (Miller and McFee 1983; Tessier and Campbell 1988; O'Day et al. 2000). Although many single and sequential extraction procedures have been widely used for speciation analysis, there is no satisfactory method permitting an unambiguous determination of the metal speciation in sediment because of technical limitations nowadays, such as non-selectivity of the chemical reactants or artifacts due to metal elements re-distribution during extraction procedures (McGrath and Cegarra 1992; Schramel et al. 2000). As a result, chemical extraction methods might be insufficient to reveal the distribution information of heavy metals in sediments.

On the other hand, physical fractionation based on grain size and density, etc., was attempted to investigate the metal behaviors in aquatic environment (Fang and Hong 1999; Singh et al. 1999; Zhu et al. in press). Spatial and temporal distributions of metal concentrations in sediments are influenced by many factors in which it is generally difficult to find the dominant one. Many studies indicated Cu may be bound to various forms of organic matter (Spark et al. 1997; Sun and Puttmann 2000; Calace et al. 2005). Over the last decade, grain-size fractionated methods were widely used for studying particulate organic matter (POM) dynamics (Jones and Turki 1997; Paetzel and Schrader 2003). Moreover, density fractionation had been used to investigate the distribution of metal elements among different re-suspended particles (Titova et al. 1996; Breslin and Sanudo-Wilhelmy 1999; Besnard et al. 2001). These studies revealed that Cu is mainly concentrated in the finer grain-size grade or low-density fraction and seems to be strongly fixed by organic matter. However, some researchers found that Cu usually accumulates not in the fine grain size fraction but in the coarse particles (Stone and Droppo 1996). Thus, the distribution property of Cu might depend on the specific characteristics of sediment.

Nansi Lake (NL) is the largest freshwater lake in Shandong province, China. It is also one of the largest adjusting reservoirs in the East Route of China's South-North Water Transfer Project. In recent years, NL was receiving industrial waste water from a large number of nearby factories, resulting in serious pollution of Cu in surface sediments (Zou 2004). Thus, it is necessary to investigate the characteristics of Cu pollution and further perform remediation of Cu contamination in NL surface sediments.

This study is undertaken for examining the Cu speciation and distribution in the surface sediment collected from NL (China). Both chemical (BCR sequential extraction procedures) and physical methods (grain size and density fractionation) were employed to provide more scientific information for further contaminant removal in terms of Cu. The joint application of physical

and chemical fractionation methods was expected to achieve some basic understanding about the Cu behaviors in surface sediment.

## Materials and methods

### Study site and sampling

In this study, nine surface 0–3 cm layer sediment samples were collected from NL in July 2002 (Fig. 1). The samples were transferred with a polyethylene spoon to avoid contamination and stored in hermetic polyethylene bottles at 4°C. To achieve greater homogeneity, surface sediment collected from nine sampling sites (each 0.5 kg) was well blended to prepare a bulk sediment sample with the wet mass of 4.5 kg. Here only reported results for the bulk sediment are indicated.

### Grain size fractionation

The bulk sediment was wet-divided into four-grain size fractions (< 63, 78–163, 163–280, and > 280  $\mu\text{m}$ ) through a mechanical shaker with a series of nylon

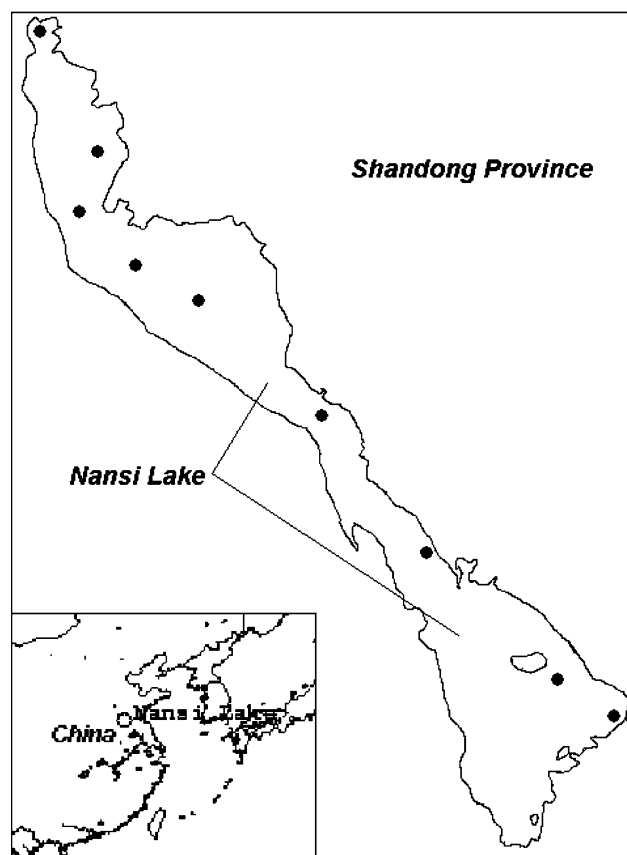


Fig. 1 Map illustrating the sampling sites in the NL

sieves. After grain size fractionation, the sediment was immediately dried at 60°C for 12 h in a drying oven. After cooling down to room temperature, each fraction was weighed to calculate the percentage in terms of the total dry weight.

#### Density fractionation

Density fractionation was conducted for both bulk and grain size fractionated sediment samples, respectively (Golchin et al. 1994). Briefly, to separate light sub-fraction (L,  $\rho < 2.0 \text{ g/cm}^3$ ) and heavy sub-fraction (H,  $\rho > 2.0 \text{ g/cm}^3$ ), sodium polytungstate (TC-Tungsten Compounds, Germany) was dissolved in distilled water in a ratio which gave the densities of  $2.0 \text{ g/cm}^3$ . Five grams of dry sediment was put into a 50 ml centrifuge tube. Twenty-five ml of sodium-polytungstate solution was added and the tube was then vortically mixed to suspend the solids. The floating particulate fraction obtained thus was L sub-fraction, whereas the settled particulate fraction was H sub-fraction. The light fraction was filtered through a quantitative Whatman no. 40 filter. Both sub-fractions were dried at 60°C for 12 h in a drying oven before being weighed and tested.

#### Organic matter analysis

Sediment POM was presented by OC in this study. Dry sediment samples were homogenized, acidified with HCl to remove carbonates, and dried at 60°C before analysis. OC contents of each size fraction and density sub-fraction were determined by a Multi N/C 3000 Elemental Analyzer (Analytik Jena, Germany).

#### Cu analytical procedures

##### *Microwave assisted digestion*

Sample digestions were performed in a programmable focalized microwave oven following a three-step digestion procedure (Sandroni et al. 2003). Briefly, each sediment sample (0.025 g) was placed in Teflon vessel with  $\text{HNO}_3$  (4 ml), HF (200  $\mu\text{l}$ ), and  $\text{H}_2\text{O}$  (4 ml). It was then subjected to a heating program: 400 W (6 min), 1,000 W (15 min), and 0 W (15 min). Each set of digestion included a certified reference material (NIES no.12) and a reagent blank, respectively.

##### *Sequential extraction*

The three-stage sequential extraction procedure, proposed by the BCR, has been applied for speciation of Cu

in grain size separated sediment. A detailed description of the BCR-protocol is described by Quevauviller et al. (1994). The extractants and operationally defined chemical fractions are described in Table 1. The treatment of sample was carried out in a 50 ml centrifuge tube, placing 0.5 g of grain size separated sediment sample. Sum value of steps 1–3 was regarded as the extractable Cu concentration. Extracts were separated from solid residues by centrifugation at 6,000 g for 15 min. The complete procedure for each step analyses using the same reagents was carried out on blank extractions. Metal concentrations in blank extracts were found negligible.

##### *Analysis*

The determination of Cu was carried out using an Atomic Absorption Spectrophotometer (model 3110, Perkin-Elmer, Boston, MA, USA) with an acetylene-air flame. Hollow cathode lamps (Perkin-Elmer) were used as a radiation source. The instrumental parameters employed were spectral bandwidth of 0.7 nm, 30 mA lamp intensity, and 324.8 nm wavelength.

##### Quality assurance

Bulk sediment analyses, physical fractionations, and chemical analyses were carried out in three replicates. The fractions obtained from these three replicates were analyzed independently. Analytical assurance concerning the microwave digestion was achieved by measuring the certified reference material (NIES no.12). The results were found to be within  $\pm 5\%$  of certified values.

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## Results and discussion

### Sediment characteristics

Characteristics of NL surface sediment are shown in Table 2. As compared by dry weight (dw), fractions of grain size in  $< 63$ , 78–163, and 163–280  $\mu\text{m}$  were prominent components in NL sediment, especially the  $< 63 \mu\text{m}$  fraction (42.1%). Particulate OC contents ranged between 2.2 and 25.4%, with the highest value occurring in the coarsest fraction ( $> 280 \mu\text{m}$ ). In the coarse grain size fraction, water plant debris were prominent components, while only few inorganic particles such as bivalve shell fragments and coarse sand were found. This demonstrated particulate OC has positive relationship with classical characteristics of decomposing plant debris (Balesdent 1996). Generally, when the grain size decreased, mass contribution to total dw increased and OC content decreased, respectively

**Table 1** BCR three-stage extraction scheme

Step	Fractions	Reagents	Operating conditions
1	Acid soluble	40 ml of 0.11 mol/l HAC solution	Room temperature, 16 h, constant agitation
2	Reducible	40 ml of 0.1 mol/l NH <sub>2</sub> OH·HCl (pH = 2 with HNO <sub>3</sub> ) solution	Room temperature, 16 h, constant agitation
3	Oxidizable	10 ml of 30% w/v H <sub>2</sub> O <sub>2</sub>  10 ml of 30% w/v H <sub>2</sub> O <sub>2</sub>  50 ml of 1 mol/l NH <sub>4</sub> AC solution	Room temperature, 1 h, occasional agitation , + 85°C 1 h + 85°C 1 h, then reduce the volume to 2 ml Room temperature, 16 h, constant agitation
4	Residual	HNO <sub>3</sub> + HClO <sub>4</sub> + HF	Digested in crucible

(Table 2). Similar sediment characteristics were found by Ahrens and Depree (2004) in Auckland Harbor, New Zealand.

#### Distribution and speciation of Cu in different size fractions

As shown in Fig. 2, the extractable Cu of NL surface sediment was dominated by steps 2 (Reducible) and 3 (Oxidizable). Concentrations of acid soluble-Cu were 10–30 times lower than reducible-Cu or oxidizable-Cu in each grain size fraction. The speciation distributions of Cu were observably similar among the four grain size fractions analyzed, i.e. acid soluble-Cu, reducible-Cu, oxidizable-Cu, and residual-Cu contributed about 2, 25, 50, and 23% of the sum-total Cu, respectively. It was noted that the extractable Cu occupied high percentage of the sum-total Cu (near 80%). Therefore, if environmental conditions such as pH, redox potential changed, Cu in sediment might be easily released back into overlying water (Campbell and Tessier 1987).

Although the relative Cu composition was remarkably identical among different grain size fractions, absolute concentrations varied for both total and each speciation of Cu. Higher Cu concentrations occurred in the coarser grain size fractions (> 280, 163–280 μm)

while the finer fractions (< 63, 63–163 μm) had lower Cu concentrations. This was different from previous literature reports (e.g. Jones and Turki 1997; Paetzel and Schrader 2003) and very much dependent on the specific characteristics of sediments, such as OC content, density, etc. Total and extractable Cu concentrations for each particle size fraction presented a range of 29.6–72.9 and 21.1–60.7 mg/kg dw, respectively (Table 2, Fig. 3). As to the bulk sediment, total and extractable Cu concentrations were 48.0 and 38.5 mg/kg dw, respectively. It was noted that Cu concentrations showed general trends in agreement with OC contents. This indicated that plant debris retained larger amounts of Cu (Hughes et al. 1980; Harter and Naidu 1995). Increases of Cu concentrations could simply be due to increases in the organic matter.

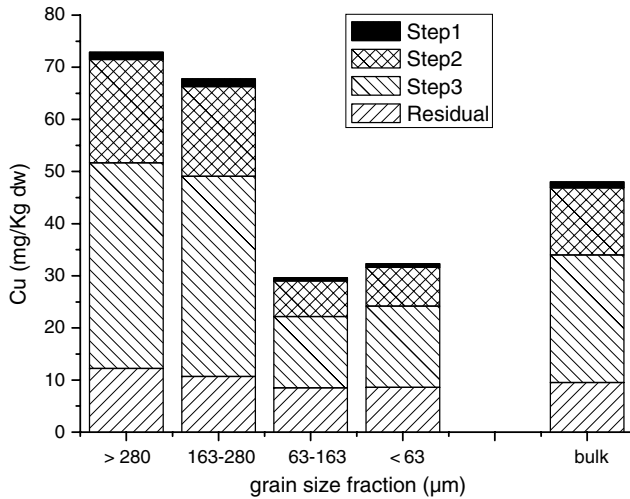
Considering Cu might be bound to various forms of organic matter (Sun and Puttmann 2000; Calace et al. 2005), normalization of weight-referenced Cu concentrations to OC content was conducted. The results showed it further amplified the differences of Cu concentrations among grain size fractions (range: 287–1,345 mg/kg OC) and shifted the maximum value of Cu concentration from the > 280 μm fraction to the 63–163 μm fraction (Fig. 3).

To calculate the contribution of each size fraction to the composite sediment Cu concentration, total and

**Table 2** Sediment characteristics of NL sediment (standard deviations shown in parentheses)

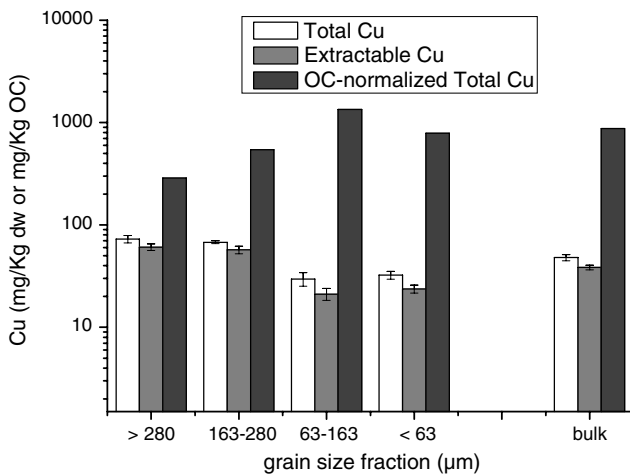
Grain size (μm)	Mass contribution to total dw (%)	Particulate organic carbon (%)	Total Cu (mg/kg dw)	Extractable Cu (mg/kg dw)	OC-normalized total Cu (mg/kg OC)
> 280	5.1(0.4)	25.4 (0.5)	72.9 (6.1)	60.7 (4.5)	287
163–280	29.3 (1.2)	12.5 (0.2)	67.8 (2.2)	57.1 (4.8)	542
63–163	23.5 (1.7)	2.2 (0.1)	29.6 (4.5)	21.1 (2.8)	1,345
< 63	42.1 (2.8)	4.1 (0.2)	32.3 (2.9)	23.7 (2.1)	788
Composite <sup>a</sup>		7.2	44.1	34.8	613
Bulk		5.5 (0.2)	48.0 (3.4)	38.5 (2.0)	873

<sup>a</sup>Composite reflects the mass-weighted average of all grain size fractions

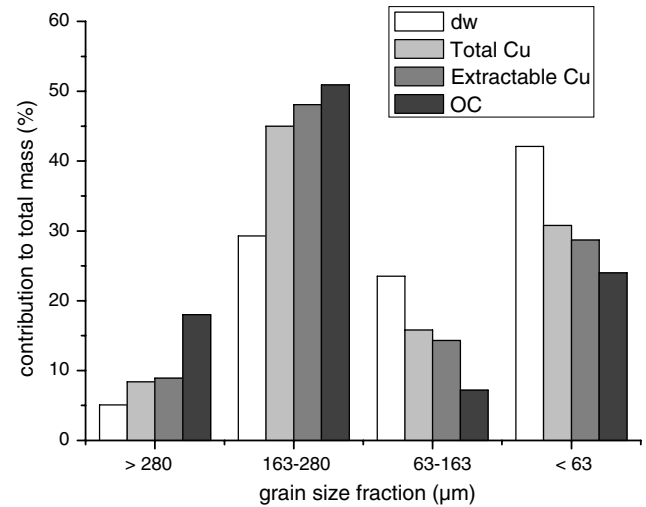


**Fig. 2** Distribution and speciation of Cu in NL surface sediment

extractable Cu concentrations for individual particle size class were multiplied by their proportion of sediment dry mass. This procedure revealed that the 163–280  $\mu\text{m}$  fraction accommodated the largest proportion both of the total (45%) and extractable (48%) Cu concentrations in NL sediment (Fig. 4), while it comprised only 29% of the sediment mass. In contrast, the abundant < 63  $\mu\text{m}$  fraction, which accounted for over 40% of the sediment mass, contributed merely 30.8% of the total Cu and 28.7% of the extractable Cu, respectively. These results revealed that the distribution of Cu among grain size fractions in NL surface sediments was heterogeneous and concentrated in a specific fraction (163–280  $\mu\text{m}$ ).



**Fig. 3** Total and extractable Cu concentrations for bulk and size-fractionated NL sediments



**Fig. 4** Relative contribution of each grain size fraction to composite sediment dry mass, total Cu concentration, extractable Cu concentration, and particulate OC content

Sediment characteristics and distribution of Cu in different density fractions

The results of relative contributions of L and H sub-fractions to grain size fraction mass and to total (composite) sediment mass are shown in Table 3, respectively. To examine mass balance, the bulk sediment sample, which was only density-fractionated, was analyzed as well. The contribution of the L sub-fraction to the respective size fraction mass ranged between 7.1 and 57.5%. In general, the L sub-fraction of coarser grain size fractions contributed a greater proportion of the fraction mass, and for the finer fractions, which only contributed a smaller proportion. By summing up the mass-weighted contributions, it was revealed that L sub-fractions proportioned 19.0% of the composite sediment mass. The result indicated that a good mass-balance was achieved as the value was close to that of the L fraction contribution in density-fractionated bulk sediment (16.9%).

On the other hand, OC contents of L sub-fractions were about 5–12 times higher than that of H sub-fraction (Table 3). The results indicated that in the case of NL surface sediment, low-density fractions might have a larger capability of accommodating OC (Avnimelech et al. 2001). In both L and H sub-fractions, the highest OC content values occurred in the coarsest particle fractions. Furthermore, OC contents decreased when grain size decreased with the exception of the value in heavy density of < 63  $\mu\text{m}$  fraction, which was slightly higher than that of 63–163  $\mu\text{m}$  fraction. In addition, composite sediment OC contents in both L sub-fractions and H sub-fractions were calculated to examine mass balance. The values in composite samples were 26.5 and 3.1%, respectively, which were closely consistent with that in bulk sediment (28.3 and 3.4%).

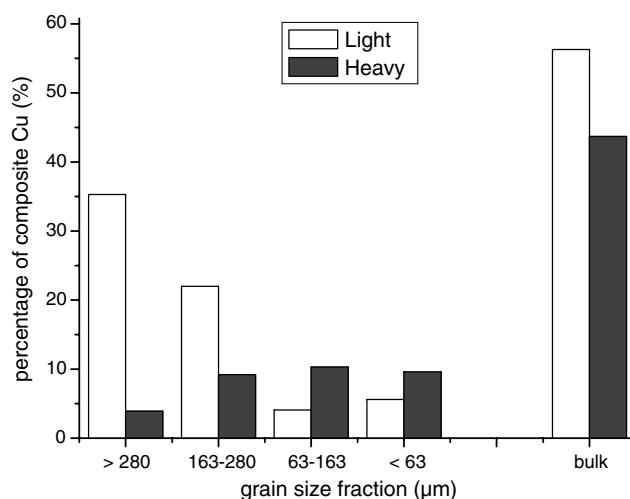
**Table 3** Sediment characteristics of NL surface sediment fractionated by grain size and density (standard deviations shown in parentheses)

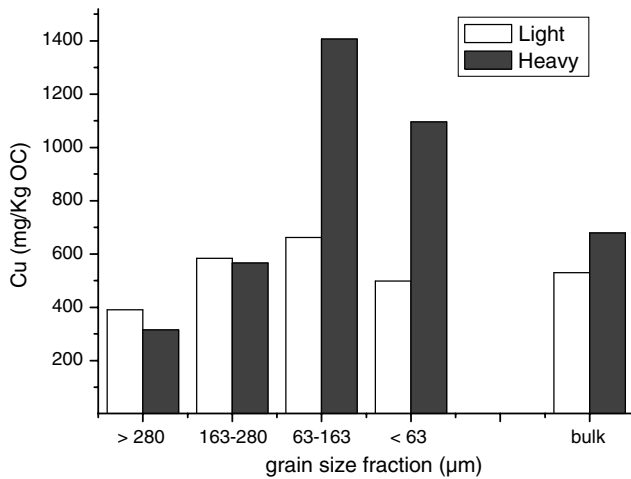
Grain size fraction ( $\mu\text{m}$ )	Mass contribution to fraction dw (%)		Mass-weighted contribution to total sediment dw (%)		OC (%)		Mass-weighted contribution to total sediment OC (%)		Cu (mg/kg dw)		OC-normalized Cu (mg/kg OC)		Mass-weighted contribution to total Cu (%)	
	Light	Heavy	Light	Heavy	Light	Heavy	Light	Heavy	Light	Heavy	Light	Heavy	Light	Heavy
> 280	57.5 (3.2)	42.5(2.0)	2.9	2.2	36.3(1.3)	6.8(0.3)	14.1	1.9	142(6)	21.4(5)	391	315	35.3	3.9
163–280	32.6 (1.7)	67.4(2.5)	9.6	19.7	26.7(1.5)	5.6(0.2)	33.7	14.6	156(9)	31.7(3)	584	566	22.0	9.2
63–163	7.1 (0.8)	92.9(3.0)	1.7	21.8	20.4(0.2)	1.8(0.1)	4.5	5.3	135(10)	25.6(2)	662	1,407	4.1	10.3
< 63	11.6(0.1)	88.4(2.4)	4.9	37.2	22.5(1.2)	2.3(0.1)	14.5	11.3	112(8)	25.2(2)	498	1,096	5.6	9.6
Composite <sup>a</sup>			19.0	81.0	26.5	3.1	66.8	33.2	143	26.3	537	930	67.0	33.0
Bulk	16.9(0.7)	85.1(3.2)	16.9	85.1	28.3(1.0)	3.4(0.1)	62.3	37.7	150(7)	23.1(5)	530	679	56.3	43.7

<sup>a</sup>Composite reflects the mass-weighted average of all grain size fractions

The copper concentrations ranged from 112 to 156 and from 21 to 31 mg/kg dw in the L-fraction and the H sub-fraction, respectively. In each grain size class, Cu concentrations in L sub-fraction were about 4–7 times higher than those in H sub-fractions (Table 3). However, it should be noted that as L sub-fractions had lower density, a majority of Cu could be more easily re-suspended and transferred with L sub-fractions given the water turbulence condition changed (Saulnier and Mucci 2000; Martino et al. 2002). The highest Cu concentration values of both L and H sub-fractions (156 and 31.7 mg/kg dw, respectively) were found in the 163–280  $\mu\text{m}$  grain size. In addition, variation of Cu concentrations was relatively lower compared to that in non-density fractionated grain-size fractions (Tables 2, 3). This might indicate particle density was a dominant factor controlling the Cu distribution in the NL surface sediment.

As to the mass-weighted contribution to total Cu in the composite sediment, the L sub-fractions of the coarser grain size fractions, i.e. > 280 and 163–280  $\mu\text{m}$ , proportioned over 55% (Table 3 and Fig. 5). And the remaining six fractions contributed about 45%. L sub-fractions totally contributed 67.0% of total Cu concentration in the composite sediment, although they only contributed 19.0% of the sediment dw. In addition, the results of mass balance analysis of Cu concentrations in grain size and density fractionated (composite) sediment were satisfactory. For example, calculated results of Cu in composite sediment (grain size and density separated) and bulk sediment (only density separated) from Table 3 were practically identical to bulk sediment (un-sieved and non-density separated) in Table 2 (48.5, 45.0, and 48.0 mg/kg, respectively). The results demonstrated quite negligible loss of Cu occurred during the sieving, extraction, and density-flotation procedures.

**Fig. 5** Relative contribution of L and H sub-fractions to total Cu concentration of composite sediment



**Fig. 6** Copper concentrations (OC-normalized) for density and size separated sub-fractions

As OC was more abundant in the L sub-fractions, normalization of Cu concentrations to OC content could change the distribution mode. In this study, it was noted that the H sub-fractions of the finer grain size fractions (63–163, < 63 µm) became the dominant proportions (Table 3 and Fig. 6). As to the coarser size fractions (> 280, 163–280 µm), OC-normalized Cu concentrations in H sub-fraction were fairly close to those in the corresponding L sub-fractions. In general, the distributions of OC-normalized Cu concentrations in the L sub-fractions were apparently decreased compared with that of the absolute Cu concentrations. These findings demonstrated that particulate OC was a main factor influ-

encing Cu distributions in either grain size or density fractionated sediment fractions. This result was consistent with those of other researchers (e.g. Besnard et al. 2001; Calace et al. 2005). In addition, the results suggested that, despite being of fewer amounts, OC in the H sub-fractions of the finer grain size fractions might have relatively higher affinity in terms of Cu binding.

## Conclusions

This paper presented that chemical and physical fractionation methods could be successfully applied to study the distribution of Cu in NL sediments. It was found that there was an observably similar speciation distribution of Cu among grain size fractions and extractable Cu (dominated by reducible and oxidizable parts) occupied almost 80% of the total Cu concentration, although total Cu concentrations in sediments had a heterogeneous distribution throughout bulk sediment. Main carriers for Cu were the coarser grain size, low density, and OC-rich particles, which comprised only a small proportion of the sediment mass. Thus, our study partially accounted that POM had a direct effect on the distribution of Cu in sediments. Furthermore, since low-density fraction contributed a relatively higher proportion of Cu contribution in the bulk sediment mass, the fate and behavior of Cu in this fraction might play an important role on the mobility and bioavailability of Cu in the overlying water and benthic biota, respectively. It is implied that interception or post-depositional removal of this Cu-rich light fraction may be an efficient way to mitigate Cu pollution from NL sediments.

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