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Sediment quality in the water-level-fluctuation-zone of the Three Gorges Reservoir, China

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Abstract The water-level-fluctuation-zone (WLFZ) of the Three Gorges Reservoir (TGR) acts as an important area for sediment and associated contaminants deposition and remobilization. Knowledge of sediment quality in the WLFZ of the TGR plays an important role in evaluating geochemical baselines and understanding human influences on sediment geochemistry. When the water level of the TGR was low in summer 2010, sediment samples in the WLFZ were collected for the determination of heavy metals (Pb, Cr, Cu, Zn, Cd), and nutrients (TP, OM). Generally, concentrations of TP and heavy metals, except for Zn, in most of the sediment samples exceeded the Lowest Effect Levels, and the maximum concentrations of these elements were below the Severe Effect Levels. The results indicated the sediments were contaminated by Cu, Cd, Pb, Cr and phosphorus to some extent. In the sediment profiles, higher concentrations of Pb, Cr, Cu, Cd and TP were associated with subsurface sediment rather than surface material. In contrast to the nutrients, the generally higher concentration of heavy metals, except for Zn, in the lowland at lower elevations rather than the higher elevation sloping land. Many of the spatial trends for heavy metals and nutrients were explained by the element properties, particle-size-selective deposition and post-depositional remobilization. As sensitive indicators of contaminants in aquatic systems, the heavy metals and nutrients in the sediments in the WLFZ reflect human activities in the TGR region and have implications for environmental management.

Key words Three Gorges Reservoir; water-level-fluctuation-zone; heavy metals; nutrients; sediment; pollution extent

INTRODUCTION

Globally, large reservoirs intercept between 25 and 30% of sediments, which poses problems at their deposition sites, particularly when they are contaminated (Salomons, 2005). Generally, fluctuation of the reservoir's pool level is regulated off-season, which results in periodic exposure of the WLFZ in summer. Therefore, the WLFZ serves as a key area for deposition and remobilization of the sediment and sediment-associated contaminants. Remobilization of contaminated sediments deposited in the WLFZ can re-introduce nutrients or contaminants into the water column long after the activities of contamination ceased. Such potential situations have been referred to as "chemical time-bombs" (Walling *et al.*, 2003; McLaughlin *et al.*, 2011). Hence, the quality of sediments deposited on the WLFZ is a matter of increasing concern with implications for environmental management.

The Three Gorges Reservoir (29°16′–31°25′N, 106°–111°50′E) lies in a 600-km valley stretching from Chongqing upstream to Yichang, and draining the upstream of the Yangtze River, the largest river in China (Fig. 1). Its pool level is 145 m in summer and 175 m in winter since the reservoir fully functioned in 2009. A 30-m high WLFZ, which is historic arable land with a total area of 348.9 km², contributes 32.2% to the total drawdown area of the TGR.

Since the TGR is one of the largest and most controversial reservoirs in the world, the maintenance of good water quality and ecological status within the reservoir is of strategic importance for the sustainability of the reservoir. However, eutrophication and algal blooms have been occurring ever since the reservoir's impoundment in 2003 (Fu *et al.*, 2010; Cao *et al.*, 2011). The increasing application of mineral fertilizers due to intensive agricultural activities leads to nutrient enrichment in the sediments eroded from the sloping land (Zhu *et al.*, 2012). Extremely high concentrations of Cd have been found in the river sediment from the upper stream of the Yangtze River before the reservoir's impoundment (Cheng *et al.*, 2005). Increased shipping and industrial wastes have deposited large amounts of heavy metals which have accumulated in the WLFZ during its submergence period (Song *et al.*, 2008; Chen *et al.*, 2011).



Fig. 1 Location of study area.

Although several articles written in Chinese have documented the background levels of heavy metals on the soils at the WLFZ of the TGR (Chen *et al.*, 2001a,b; Xu *et al.*, 2003) and reported elevated levels of heavy metals, such as Pb, Cd, Cu on the surface soils at the WLFZ, since the reservoir's impoundment in 2003 (Xu *et al.*, 2003; Yang *et al.*, 2006; Cheng *et al.*, 2009), few studies have attempted to document the quality of sediments at different depositional environments of the WLFZ, particularly since the TGR began functioning fully in 2009. A few previous studies have indicated that the reservoir's sediments in a tributary of the Yangtze River have been slightly polluted and the sediments at the WLFZ have adverse effects on aquatic life (Ji *et al.*, 2009; Ling *et al.*, 2010). Such information is needed to inform the development of reservoir management strategies aimed at controlling environmental problems associated with sediment-associated nutrients and contaminants in the riparian ecosystems.

This paper aims at evaluating sediment quality in a variety of depositional environments in the WLFZ of the TGR. This study: (1) presents the data on concentrations of heavy metals (Pb, Cr, Cu, Zn, Cd), nutrients (TP, OM) in the sediments collected during an expedition in May 2010 from a WLFZ in the middle of the TGR; (2) assesses the pollution extent of heavy metals and phosphorus in the sediments, using the technical guidance of the New York State Department of Environmental Conservation (NYSDEC, 1999); (3) discusses the vertical distribution pattern of heavy metals and nutrients in the sediment profiles; and (4) discusses the longitudinal distribution pattern of heavy metals and nutrients in the bulk sediments along elevations of the reservoir's pool level (145–175 m).

MATERIALS AND METHODS

The study area is located in the middle of the Three Gorges Reservoir, at ZhongXian of Chongqing Municipality (30°03′–30°35′N, 107°–108°14′E) (seen in Fig. 1). Annual mean temperature is 16.5–19°C, ranging from 3.4–7.2°C in January to 28–30°C in July. Annual mean precipitation is 1100 mm, 80% of which occurs in April–October. The study area is characterized by a diversity of morphological patterns reflecting a broad spectrum of geochemical and ecological variation.

When the WLFZ of the TGR was exposed in May 2010, the pool level was close to 145 m. A total 48 sediment samples were collected at three sampling plots with different vegetation covers (*Cynodon dactylon, Paspalum paspaeoides, Hemarthria compressa*).

Sampling strategies

Along the elevations (145–175 m) of each sampling plot, the sediment samples sediment were collected by manual dredging. At different depositional environments, the sediment depth varied

from <1 cm to tens of centimetres. The subsamples were sectioned into 10 cm, if the sediment depth was >10 cm in a sediment profile. The sediment samples including all the subsamples were sealed in plastic bags and then air-dried, gently disaggregated, and sieved through a mesh. The samples finer than 1 mm were re-evaluated.

Analytical methods

The concentrations of Pb, Cr, Cu, Zn, Cd were measured by flame atomic absorption spectrometry (FAAS) following direct acid digestion (HCl and HNO₃) (Allen, 1989). The concentration of organic matter (OM) in the sediment was determined using the UV/visible spectrophotometer after $K_2Cr_2O_7$ -H₂SO₄ low-temperature digestion (Lu, 1999). The concentration of total phosphorus (TP) was determined by the AMAA (Ammonium-Molybdate-Ascorbic-Acid) method using the UV/visible spectrophotometer after digestion with H₂SO₄ and KClO₄ (Lu, 1999).

Every extraction batch of three samples included a blank extraction in order to control accuracy and to determine the uncertainty of heavy metal determination. Analytical results of the quality control samples indicated a satisfactory performance for heavy metals, TP and OM determinations with overall uncertainties between 5% and 15%.

Assessment of pollution extent

To assess the pollution extent of heavy metals and nutrients in the sediments, the sediment criteria for metals and phosphorus was applied. Two levels of risk have been established for metals contamination in sediments. These are the Lowest Effect Level and the Severe Effect Level. The sediment is considered contaminated if either criterion is exceeded. If both criteria are exceeded, the sediment is considered to be severely impacted. If only the Lowest Effect Level criterion is exceeded, the impact is considered moderate. It proposes Lowest Effect Levels (LELs) for Pb, Cr, Cu, Zn, Cd and TP of 31, 26, 16, 120, 0.6, and 600 μ g/g, respectively, and Severe Effect Levels (SELs) of 110, 110, 270, 9.0 and 2000 μ g/g, respectively (NYSDEC, 1999).

RESULTS AND DISCCUSION

Assessment of pollution extent for heavy metals and phosphorus in sediment

Table 1 presents ranges and arithmetic means of heavy metal concentrations in the sediment samples of the TGR's WLFZ. Generally, the average concentrations of TP and heavy metals, except for Zn, in the sediment samples were higher than the LELs at all sampling plots, but lower than the SELs. The results show that the sediments at the WLFZ have been moderately contaminated and enriched in Cu, Cd, Pb, Cr and phosphorus.

The Cu and Cd maximum concentrations were 91.1 and 2.97 μ g/g, approximately six and five times as much as the LEL values, and they appeared at elevations of 148 and 152 m in sampling plot 1, respectively. The results were consistent with the previous literature that reported the sediments highly polluted with Cu and Cd due to anthropogenic activities (Zhao *et al.*, 2009; Chu *et al.*, 2011). The peak levels of Pb (89.9 μ g/g) and Cr (43.3 μ g/g) were nearly three and two times as much as the LEL values at the elevations of 157 m and 160 m, respectively, in sampling plot 3, Compared with Cu and Cd, the sediments were slightly contaminated with Pb and Cr. The maximum of Zn concentration was only 53.9 μ g/g, which was much lower than the LEL value. The average concentration of Zn in all the sediment samples was far below the LEL value (120 μ g/g). It should be confirmed that the sediments at the reservoir's WLFZ were not enriched in Zn.

At all the sampling plots, the average concentration of TP in the sediment samples ranged from 696.7 to 741.7 μ g/g, which was slightly higher than the LEL value (600 μ g/g) and much lower than the SEL value (2000 μ g/g). TP peak level of 859.1 μ g/g was only 1.4 times as much as the LEL value, whilst the valley level of 553.8 μ g/g was lower than the LEL value. Compared with great variance of the heavy metals concentrations determined in the sediment samples, TP

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concentrations were relatively constant level throughout the study area. In total, the sediments at the reservoir's WLFZ were slightly enriched in phosphorus.

Element	Plot 1	Plot 2	Plot 3
	(Paspalum aspaeoides)	(Hemarthria compressa)	(Cynodon dactylon)
Pb(µg/g)	10.3–66.6	34.0-63.6	34.0-89.9
	35.9±14.6	45.3±16.0	54.0±15.5
Cr(µg/g)	17.4–37.2	27.0–37.3	31.2–43.3
	28.6±5.5	31.8±5.2	35.8±5.2
$Cu(\mu g/g)$	14.3–91.1	50.3–65.0	56.9–73.9
	54.4±21.0	58.1±7.4	62.3±6.9
$Zn(\mu g/g)$	31.4–53.8	47.9–53.9	45.8–50.1
	45.2±7.4	51.7±3.3	48.7±1.8
$Cd(\mu g/g)$	1.69–2.97	2.26–2.60	2.07–2.47
	2.36±0.40	2.45±0.17	2.32±0.15
$TP(\mu g/g)$	553.8–859.1	615.9-821.2	584.9–854.4
	741.7±86.0	697.4±78.3	696.7±106.3
OM(%)	1.52–2.58	1.50–1.99	1.50–2.44
	2.20±0.34	1.70±0.26	1.85±0.39

Table 1 Range of element concentrations and arithmetic mean \pm confidence interval (P = 95%) in sediments of the TGR's WLFZ.

Table 2 Concentrations of heavy metals and nutrients in sediment profiles of the TGR's WLFZ.

Plot	Elevation	Depth (cm)	Pb (µg/g)	Cr (µg/g)	Cu (µg/g)	Zn (µg/g)	Cd (µg/g)	TP (µg/g)	OM (%)
Plot 1	148.7 m	0-10	39.0	34.3	64.8	53.7	2.81	778.3	1.43
		10-20	42.2	34.1	68.7	54.7	2.89	779.4	1.78
		20-30	45.3	34.2	72.6	55.7	2.97	775.9	1.41
		30–40	67.3	33.2	73.0	52.2	2.60	730.5	1.28
	151.3 m	0-10	19.6	20.8	41.3	53.3	2.11	680.4	1.87
		10-20	36.1	31.2	68.3	53.8	2.44	778.3	1.81
		20-26	42.5	35.3	78.9	52.5	3.13	816.5	2.20
Plot 2	150.2 m	0-10	73.7	31.2	66.7	53.7	2.71	699.5	1.94
		10-20	68.7	35.1	69.8	52.6	1.02	821.2	1.50
		20-24	65.9	32.2	66.4	51.6	2.86	795.3	1.42
Plot 3	150.6 m	0-10	38.3	34.2	63.7	55.4	2.92	699.5	1.79
		10-20	89.9	31.2	64.6	51.7	2.81	821.2	1.86
		20-35	75.1	35.2	70.8	50.6	2.92	795.3	0.98

Vertical distribution pattern of heavy metals and nutrients in sediment profiles

Table 2 presents the concentrations of heavy metals and nutrients in the sediment subsamples at various depths. The higher concentrations of Cu, Cr and Cd appeared in the subsurface sediments rather than surface materials. Similarly, this pattern is observed for Pb at both sampling plot 1 and plot 3. In contrast, this pattern is reversed for Pb at the sampling plot 2. All the sediment profiles contain concentrations of Zn averaging $53.2 \pm 1.5 \,\mu$ g/g, reflecting the homogeneous distribution of Zn through the sediment depths.

A significant increase for TP in the subsurface sediments has been observed at all sampling plots except for the sediment profile sampled at plot 1 (elevation 148.7 m). The result indicates that phosphorus would rather be associated with subsurface sediment. OM has no clear pattern, although constant level or a slight increase for OM in the subsurface sediments has been observed in all the sampling sites except for sampling plot 2 (elevation 150.2 m).

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The generally higher concentrations for TP and heavy metals, except for Zn, may be explained by the fact that finer material in the top layer is diffused downward with gravity water into coarser material towards the bottom, during the water level (WLFZ) drawdown in summer.

Longitudinal distribution pattern of heavy metals in sediments

Generally, the concentration of Zn in the bulk sediment samples remained at average level of $45 \ \mu g/g$ between the elevation of 145 m and 175 m, showing no clear spatial trends (Fig. 2(e)). Compared with other heavy metals, Zn is generally believed to be more mobile in aqueous systems. Therefore, it would be expected to remain in the dissolved phase rather than in the sediment (Nagorski *et al.*, 2002). That would be the reason why Zn showed a generally constant level throughout the study area.



Fig. 2 Longitudinal distribution of heavy metals in sediments collected from sampling plot 1.

A sharp decline in concentrations of Pb, Cu, Cd and Cr is seen in the bulk sediments sampled along the elevation of 145 m to 160 m (Fig. 2(a)–(e)). The bulk sediment collected around the elevation of 150 m contained the highest concentrations of Pb, Cu, Cd and Cr, whereas the lowest concentrations of these elements appeared in the bulk sediment collected close to the elevation of 160 m. The spatial trends of heavy metals may be explained by different depositional environments. Variations in the thickness of the sediment deposited on the WLFZ ranged from >40 cm to as little as 3 cm. The lowland at lower elevations is a good depositional environment for the finer sediment associated with relatively high concentrations of heavy metals. Conversely, the sloping land at higher elevations is dominated by erosion, where only the coarser sediment associated with relatively low concentrations of heavy metals could be retained.

Although the thickness of the bulk sediments was <1 cm at the elevation of 170 m, the slightly higher concentrations of Pb, Cu, Cd and Cr were observed in comparison with those of the bulk sediments sampled from elevation 160 m (Fig. 2(a)–(e)). The result may reflect seasonal change of the sediments. When the reservoir operates at the pool level of 175 m in winter, the reservoir sediment is characterised finer particulates associated with relatively more pollutants.

Compared with vertical variation in the sediment profiles, large variance has been shown in the longitudinal distribution of heavy metals along the elevations (Fig. 2). For example, the maximum concentration of Cu was elevated over the minimum concentration of Cu by up to one order of magnitude. The results showed the sediment quality varied greatly within different pool levels during the reservoir's impoundment period, reflecting anthropogenic pollution and the geochemistry of sediments in the TGR. The generally higher concentrations of heavy metals in the sediments collected at lower elevations indicate that the upstream input could be the major source of heavy metals to the sediments of the WLFZ in the TGR.

Longitudinal distribution pattern of nutrients in sediments

In contrast to the distribution pattern of the heavy metals, the concentration of OM in the sediments presented a sharp increase with increasing elevation, shown in both sampling plots 1 and 3 (Figs 3(a) and 4(a)). The sediment samples collected at the elevation of 145 m contained the lowest concentration of OM, possibly because the sediment-associated organic matter could be easily released to the water column when the sediment was submerged by water. At all the sampling plots except for the plot 1, the concentration of TP in the sediments showed a slight increase with increasing elevation (Figs 3(b) and 4(b)). There was a slight positive increase, and approximately linear relationship between the concentrations of TP and OM at the sampling plot 3 (Fig. 4(a)–(b)). The relatively higher concentrations of TP and OM in the sediments appeared at higher elevations, indicating that the sloping upland is the major source of nutrients to the sediments of the WLFZ in the TGR.



Fig. 3 Longitudinal distribution of nutrients in sediments collected from sampling plot 1.



Fig. 4 Longitudinal distribution of nutrients in sediments collected from sampling plot 3.

In sum, the spatial trends of TP and OM in the sediments is more complicated, because they are nutrients for vegetation and easily mobile in aqueous systems as well as being affected by sediment erosion or post-depositional remobilization.

CONCLUSION

This paper reports the pollution severity and spatial trends of heavy metals (Pb, Cr, Cu, Zn, Cd), and nutrients (TP, OM) in the sediments deposited along the pool level from 145 m to 175 m in the riparian zone for the first time, since the Three Gorges Reservoir fully functioned in 2009.

Average concentrations of Pb, Cr, Cu, Cd and TP in the sediments at the WLFZ exceeded the LELs, and the maximum concentrations of these elements were below the SELs. The results indicated that the sediments at the TGR's WLFZ were contaminated and enriched in Pb, Cr, Cu, Cd, and phosphorus to some extent.

Generally, Pb, Cr, Cu, Cd and TP were associated with subsurface sediment rather than surface material. The generally higher subsurface sediment concentrations for heavy metals and phosphorus may be the result of post-depositional remobilization, where finer sediments are downward diffused with gravity water and subsequently precipitated in the subsurface after the drawdown of the WLFZ.

The generally higher concentrations of heavy metals such as Pb, Cr, Cu and Cd in the sediments appeared at lower elevations, whereas those of TP and OM appeared at higher elevations. Apart from differences of element properties and particle-size-selective depositional environments, much of the results indicated that the sediment-associated heavy metals in the reservoir's WLFZ originate from the upstream input, whilst the source of nutrients is mainly from the sloping arable land.

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