

Accumulation and risk assessment of heavy metals in water, sediments, and aquatic organisms in rural rivers in the Taihu Lake region, China

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Abstract Concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) were measured in water, sediments, *Ceratophyllum* (hornwort), and *Bellamya sp.* (edible snail) from residential, mixed (industrial and commercial), and agricultural areas with rural rivers in the Taihu Lake region, China. Zn concentrations were the highest, whereas Cd concentrations were the lowest among the six metals in water, sediments, and aquatic organisms. Cd was mainly present in the acid-soluble fraction, Cr in the residual fraction, and Pb in the reducible fraction of sediments. Heavy metal concentrations in water, sediments, and aquatic organisms in the three areas followed the order of the mixed area > residential area > agricultural area. Heavy metal concentrations in aquatic organisms were not only related to total metal concentrations in water and sediments but also to metal speciation concentrations in sediments. In addition, the bio-concentration factor (BCF) values of Cr, Cu, Pb, and Zn for *Bellamya sp.* were higher than those for *Ceratophyllum*, whereas the BCF values of Cd and Ni for *Bellamya sp.* were lower than those for *Ceratophyllum*. An ecological risk assessment of heavy metals in sediments showed that Cd posed the highest ecological risk to the environment. A health risk assessment showed that consuming *Bellamya sp.* from the mixed area could cause a potential health risk.

Keywords Heavy metals · Sediment · Rural · Aquatic organisms · Accumulation · Risk assessment

Introduction

The Taihu Lake region, one of the most economically developed regions in China, is located in the Yangtze River Delta (Yu et al. 2012). It covers 36,900 km² and has the highest population density, exceeding 1000 persons/km² (Zhang et al. 2007). Rivers are spread across most of the region with a total length of 1.2 × 10⁵ km. Rivers play an extremely important role in the economic and social development in the region (Jiao et al. 2010).

The rapid development of industrialization and urbanization in recent decades has resulted in a substantial volume of untreated or inadequately treated wastewaters from industrial, agricultural, and domestic discharge into rivers, which has deteriorated the water quality and produced significant negative impacts on aquatic ecosystems (Lin et al. 2010; Wang et al. 2008). Heavy metals from these anthropogenic sources pose serious threats to the environment and human health and have become a widespread concern due to their toxicity, persistence, abiotic degradation, and bioaccumulation (Bonanno and Lo Giudice 2010). Sediments are both sinks and sources of heavy metals in water and also provide habitats and food sources for benthic organisms. However, heavy metals accumulate to toxic levels in aquatic flora and fauna under certain conditions, leading to ecological damage and endangering human health through the food chain (Götze et al. 2014). Investigation of heavy metals in water, sediments, and aquatic organisms are indispensable for assessing heavy metal contamination and its potential risks to aquatic ecosystems and human health.

In this study, we examined the behavior of six heavy metals in water, sediments, and aquatic organisms from residential,

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mixed, and agricultural areas with rural rivers in the Taihu Lake region, China. We also explored the relationships among heavy metal concentrations in water, sediments, and aquatic organisms. In addition, we also assessed potential heavy metal ecological and health risks in sediments and aquatic organisms from these three areas with rural rivers. Our results will provide the direct evidence needed by local environmental authorities to warn about the potential ecological risks caused by heavy metals in sediments and the potential health risks caused by consuming aquatic products.

Materials and methods

Study area and sampling

The study area was located in Yangyuan town, Changshu city in southern Jiangsu Province, China (120° 38' N, 31° 33' E) (Fig. 1). Thirty-four sampling sites were selected along rivers that run through residential, mixed (industrial and commercial), and agricultural areas. The R1–R7 sampling sites were located in the residential area. Pollutants at these seven sites were mainly from domestic village wastewaters. The M8–M27 sampling sites were situated in a mixed industrial and commercial area (mixed area). This area includes several industrial factories (three printing and dyeing mills, three chemical plants, five garment factories, and three machinery factories), commercial shops, and villages. Therefore, a considerable amount of industrial and domestic wastewater drains directly into the rivers. The remaining sampling sites (A28–A34) were located in an agricultural area where agricultural runoff could increase pollutant loads.

Sampling was conducted in November 2012. Sediment and water samples from the rivers were collected at the

corresponding sampling locations. *Ceratophyllum* (hornwort) and *Bellamya sp.* (edible snail) of similar sizes (2–3-cm shell length, 20 snails/site) were obtained at every second site. Surface sediment (0–10 cm) samples were collected using a core sampler equipped with Perspex tubes (8-cm inner diameter, 30 cm long). Water samples were collected at a depth of 50 cm below the water surface, filtered through a 0.45- μm membrane filter, and maintained in 1 % nitric acid in polyethylene bottles. The water, sediments, and aquatic organism samples were kept in plastic bags and transported to the laboratory at 4 °C until analysis.

Sample preparation and analysis

The sediment samples were freeze dried, homogenized, and sieved through a 63- μm sieve. Total heavy metals were extracted using a mixture of HF-HNO₃-HClO₄ in an open system. A 0.5-g dry sediment sample was digested in 15 mL of HF and 10 mL of a 1:1 (v/v) mixture of HNO₃ and HClO₄. After digestion, the final residue was dissolved in 5 mL of 2 M HCl and the volume was brought up to 25 mL with deionized water.

DTPA-extractable metals were obtained from all sediment samples using 0.005 M DTPA + 0.01 M CaCl₂ + 0.1 M triethanolamine at pH 7.3 (Lindsay and Norvell 1978). The Community Bureau of Reference sequential extraction procedure (BCR-SEP) was applied to all sediment samples using the conditions given in Table 1 (Rauret et al. 1999; Sahuquillo et al. 1999; Ure et al. 1993).

The hornwort samples were washed with tap water, rinsed with deionized water, dried at 80 °C, and pulverized. The samples (0.8 g) were weighed and digested with 20 mL of HNO₃ and 1 mL of HClO₄ until digestion was completed. The

Fig. 1 Distribution of sampling sites in Yangyuan town, southern Jiangsu Province

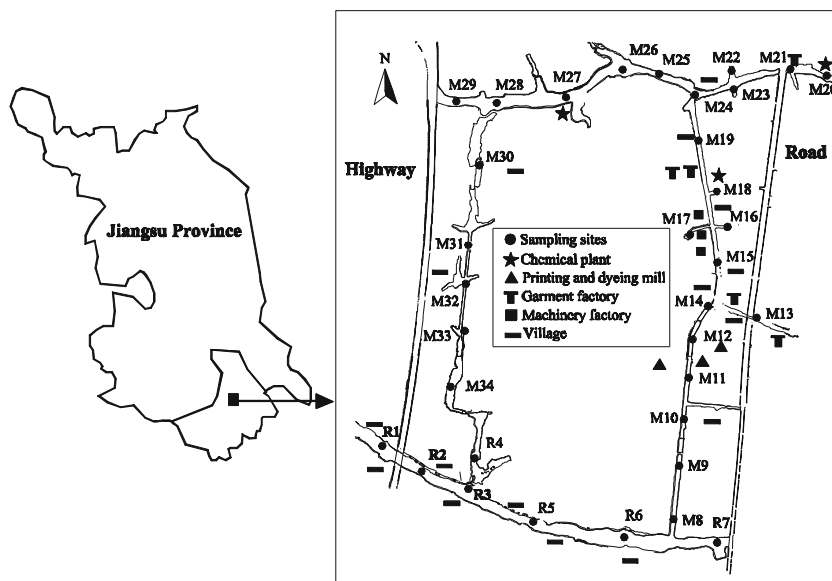


Table 1 The modified Community Bureau of Reference (BCR) sequential extraction procedure used for operational speciation of metals

Step	Metal fraction	Extractant	Experimental conditions
F1	Acid-soluble fraction	40 mL 0.11 M CH ₃ COOH	Shake 16 h at 22±5 °C
F2	Reducible fraction	40 mL 0.5 M NH ₂ OH·HCl (pH 2.0)	Shake 16 h at 22±5 °C
F3	Oxidizable fraction	10 mL 8.8 M H ₂ O ₂ (twice) 50 mL 0.5 M NH ₄ OAc	1 h at 22±5 °C and 1 h at 85 °C Shake 16 h at 22±5 °C
R ^a	Residual fraction	Similar to total metal digestion	Heating on hot plate to dryness

^a Digestion of residual material is not a BCR protocol step

solution was cooled at room temperature, diluted, and adjusted to 25 mL with deionized water.

The foot muscle and visceral mass were dissected from *Bellamya sp.*, dried at 80 °C, and pulverized. The snail samples (0.5 g) were weighed and digested with 10 mL of HNO₃ and 1 mL of HClO₄. The solution was cooled at room temperature, diluted, and adjusted to 25 mL with deionized water.

Three replicate samples were measured in all cases. All reagents used were analytical grade or better, and double-deionized water was used for preparing the solutions and all dilutions. Heavy metals were determined by a flame atomic absorbance spectrophotometer equipped with a heated graphite tube atomizer (Hitachi Z-2000, Tokyo, Japan) for Cd, Cr, Cu, Ni, Pb, and Zn. The absorption wavelengths and detection limits were 228.8 nm for Cd, 359.3 nm for Cr, 324.8 nm for Cu, 232.0 nm for Ni, 283.3 nm for Pb, and 213.8 nm for Zn.

Two standard reference materials (GSS3 and GSS27) were used for total metal analysis, and a certified sediment reference material (BCR-701) was analyzed using the BCR-SEP to ensure good quality results. Recoveries were 87–101 % for GSS3, 98–114 % for GSS27, and 94–111 % for BCR-701.

Bio-concentration factor

The bio-concentration factor (BCF) of a heavy metal from the sediment to an aquatic organism is defined as the ratio of the metal concentration in the aquatic organism to that in the corresponding sediment (Agoramoorthy et al. 2008). The BCF is used to evaluate the potential ability of an aquatic organism to accumulate a heavy metal from the sediment.

The BCF was computed as follows:

$$BCF = C_{org} / C_s$$

Where C_{org} and C_s represent the metal concentrations in the aquatic organism and sediment extracts, respectively, on a dry weight basis.

Potential ecological risk index

The risk index (RI) was applied to assess the potential ecological risk of heavy metals in sediments. The RI was

originally proposed by Hakanson (1980) and is widely used in many studies. The metal RI was defined as follows:

$$RI = \sum_{i=1}^m Er^i = \sum_{i=1}^m T_r^i (C_m^i / C_b^i)$$

Where E_r^i is the potential ecological risk factor for a given contaminant, T_r^i is the toxic-response factor for a given contaminant, C_b^i is the background heavy metal concentration in Jiangsu Province soil (Wei et al. 1990), and C_m^i is the measured heavy metal concentration in sediments. T_r^i for the eight metals is described as follows: Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, and Zn=1 (Hakanson 1980; Sheykhi and Moore 2013).

According to the literature (Hakanson 1980), the values used to describe the risk factor E_r^i and the RI are as follows: $E_r^i < 40$ and $RI < 150$, low potential ecological risk; $40 \leq E_r^i < 80$ and $150 < RI < 300$, moderate potential ecological risk; $80 \leq E_r^i < 160$ and $300 \leq RI < 600$, considerable potential ecological risk; $160 \leq E_r^i < 320$, high potential ecological risk; $E_r^i \geq 320$ and $RI \geq 600$, very high ecological risk.

Target hazard quotient

The potential health risk from consuming *Bellamya sp.* by local people was characterized using the target hazard quotient (THQ) and total THQ (TTHQ) of heavy metals. The THQ and TTHQ were calculated using the following equations:

$$THQ = \frac{EF \times ED \times FIR \times C}{RfD \times BW \times AT} \times 10^{-3}$$

$$TTHQ = \sum_{i=1}^6 THQ$$

Where E_F is the exposure frequency (365 days/year); E_D is exposure duration (70 years); F_{IR} is food ingestion rate, considered to be 16.7 g/person/day for adults and 9.0 g/person/day for children (Yu et al. 2012); C is the metal concentration in food (mg/kg, wet weight); R_fD is the oral reference dose (mg/kg/day); BW is the average body weight (kg/person), considered to be 63 kg for adults and 33 kg for children (Yu

et al. 2012); and AT is the average time for non-carcinogens (365 day/year×exposure years, assuming 70 years). The RfD values for Cd, Cr, Cu, Ni, Pb, and Zn are 0.001, 1.5, 0.04, 0.02, 0.0035, and 0.3 mg/kg/day, respectively (Hang et al. 2009). If the THQ or TTHQ is <1, there is no obvious risk, whereas there is a potential health risk if the THQ or TTHQ is ≥ 1 (Zheng et al. 2007).

Statistical analysis

The means and standard errors of the metal concentrations in water, sediment, and aquatic organisms were calculated. Two-way analysis of variance followed by least significant difference tests (SPSS 13.0; SPSS, Inc., Chicago, IL, USA) was used to analyze differences in the heavy metal concentrations at the different areas. Pearson's bivariate correlation analysis was used to evaluate the relationships among heavy metal concentrations in water, sediments, and aquatic organisms. A $p < 0.05$ was considered significant.

Results and discussion

Heavy metal concentrations in water

The heavy metal concentrations in water from the residential, mixed, and agricultural areas are presented in Table 2. Zn, Ni, and Cu were the heavy metals at the highest concentrations in the residential, mixed, and agricultural areas, respectively. Cd was the heavy metal at the lowest concentration in all three areas. The mean heavy metal concentrations in water were in the following decreasing order: Zn>Ni>Cu>Pb>Cd in the residential, mixed, and agricultural areas. In addition,

mean Cd concentrations in the residential, mixed, and agricultural areas were 4.0, 6.0, and 2.5 times higher than the background values, respectively. Moreover, mean Ni concentrations in the residential, mixed, and agricultural areas were 7.7, 9.1, and 7.3 times higher than the background values, respectively. However, none of the heavy metals exceeded the safe limit in irrigation water for agricultural purposes. Samples from the rural rivers in the three areas were slightly polluted based on a comparison of the heavy metal concentrations in these rivers in our study with values in other rivers (Abdel-Baki et al. 2013; Ahmed et al. 2012; Aktar et al. 2010; Fernandes et al. 2008; Klavinš et al. 2000).

Heavy metal concentrations in sediments

Total heavy metal concentrations

Sediments in the mixed area had the highest mean concentrations of Cr, Cu, Ni, and Pb, whereas Zn and Cd were highest in sediments in the residential area (Table 3). Mean concentrations of heavy metals were lowest in sediments in the agricultural area. Heavy metal concentrations in sediments displayed the following decreasing order: Zn>Cr>Cu>Ni>Pb>Cd in the residential and mixed areas, whereas in the mixed area, they display the following order: Cr≈Zn>Pb≈Ni>Cu>Cd. Mean concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the residential area were 78.6, 1.6, 3.6, 2.7, 2.1, and 6.8 times higher than the background values in the Jiangsu Province soil (Wei et al. 1990), respectively. Mean concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the mixed area were 52.0, 2.6, 7.5, 3.9, 3.3, and 7.1 times higher than the background values (Wei et al. 1990), respectively. However, heavy metal concentrations in the agricultural area were less than two times higher than the background values (Wei et al. 1990). Cd, Cr, and Zn

Table 2 Heavy metal concentrations in rural river water and other study areas and the guidelines ($\mu\text{g/L}$)

		Cd	Cr	Cu	Ni	Pb	Zn
Residential area	Range	0.05–0.11	1.76–2.26	0.37–0.53	1.89–2.91	0.15–0.22	1.89–3.12
	Mean	0.08±0.02	1.90±0.20	0.43±0.06	2.30±0.36	0.19±0.03	2.45±0.43
Mixed area	Range	0.07–0.21	1.18–3.11	0.41–1.59	1.78–3.68	0.19–0.50	1.98–3.89
	Mean	0.12±0.04	2.44±0.82	0.74±0.31	2.72±0.95	0.25±0.07	2.59±0.54
Agricultural area	Range	0.02–0.07	1.01–2.01	0.40–0.62	1.49–2.65	0.16–0.29	1.88–3.00
	Mean	0.05±0.02	1.53±0.38	0.52±0.07	2.20±0.39	0.24±0.04	2.49±0.41
Background ^d	0.02	–	1.00	0.30	0.20	10.0	
Safe limit ^b	10.0	100	200	200	500	2000	
Latvia river ^a	0.02	–	0.56	0.34	0.10	3.35	
Wadi Hanifah ^c	0.87	6.40	43.7		0.95		
Ganga rive ^d	5.00	–	10.0	140	120	60.0	
Dhaleshwari river ^e	1.00	130	0	–	201	–	
Esmoriz Paramos lagoon ^f	–	–	12.0	–	18.0	264	

^a (Klavinš et al. 2000), ^b (Ahmad and Goni 2010), ^c (Abdel-Baki et al. 2013), ^d (Aktar et al. 2010), ^e (Ahmed et al. 2012), ^f (Fernandes et al. 2008)

Table 3 Heavy metal concentrations in sediments and other study areas and the guidelines (mg/kg)

		Cd	Cr	Cu	Ni	Pb	Zn
Residential area	Range	0.12–21.8	71.7–170	23.2–147	31.3–109	22.0–87.7	43.5–876
	Mean	10.2±9.90	121±39.0	80.1±52.9	72.0±30.8	56.0±29.4	425±351
Mixed area	Range	0.48–28.1	104–621	45.0–443	59.0–274	40.7–310	141–934
	Mean	6.77±6.75	200±119	168±98.0	104±48.0	85.4±60.4	447±227
Agricultural area	Range	0.05–0.37	91.5–103	26.9–66.8	40.1–66.8	21.6–80.7	52.0–148
	Mean	0.15±0.1	95.9±3.81	40.7±13.5	49.2±9.95	52.0±19.4	95.2±37.6
Background ^a	0.13	77.8	22.3	26.7	26.2	62.6	
Luan river ^b	0.15	71.5	46.0	–	22.1	75.5	
Yangtze River ^c	1.0	107	61.4	41.6	50.0	231	
Pearl River ^d	1.7	93.1	348	–	103	38	
Hindon River ^e	2.3	102	59.3	–	41.2	58.3	
Tigris River ^f	1.8	84.8	345	146	265	203	
Kor River ^g	0.2	83.4	20.3	104	7.5	46.6	

^a(Wei et al. 1990), ^b(Liu et al. 2009), ^c(Yang et al. 2009), ^d(Niu et al. 2009), ^e(Suthar et al. 2009), ^f(Varol 2011), ^g(Sheykhi and Moore 2013)

concentrations in river sediments from the residential and mixed areas were significantly higher than those in other selected rivers around the world (Liu et al. 2009; Niu et al. 2009; Sheykhi and Moore 2013; Suthar et al. 2009; Varol 2011).

The different metal accumulation behavior may be related to the intensity of human activities, such as the volume of domestic sewage and industrial wastewater discharge (Long et al. 2009; Ongley ED and Tao 2010), limited wastewater treatment capacity (Wang et al. 2008), and increased heavy traffic activity (Pérez et al. 2008). The high levels of Cd could be due to excess use of Cd-based products (pesticides) in chemical plants and an electroplating factory, which have been relocated. In addition, a large amount of domestic sewage and industrial wastewater is discharged into rivers, which might explain the high level of Cu and Zn accumulation in sediments (Dummee et al. 2012). Furthermore, interactions among dissolved oxygen, temperature, salinity, and detritus may have had a significant effect on heavy metal accumulation and their potential ecological risks (Guhathakurta and Kaviraj 2004; Karadede-Akin and Ünlü 2007), which will be discussed in the next sections.

Metal speciation

Metal speciation in sediments was divided via the BCR-SEP, as shown in Fig. 2. Cd was mainly present in the acid-soluble fraction (Fig. 2-Cd), indicating extraordinary mobility and bioavailability (Yu et al. 2010), which was similar to Cd concentrations described by Yang et al. (2009) in sediments from a Yangtze River catchment. For example, the percentages of Cd in the acid-soluble fraction from the three areas followed the order of mixed area (64.8 %)>residential area (56.8 %)>agricultural area (32.4 %). Furthermore, 33.5, 29.4,

and 40.3 % of total Cd in the sediment samples was found in the reducible fraction from the residential area, mixed area, and agricultural area, respectively. In addition, <2 % of total Cd was found in the oxidizable fraction.

More than 75 % of the total Cr was found in the residual fraction (Fig. 2-Cr), indicating relatively less bioavailability and potential risk to the environment (Yu et al. 2010), which was similar to Cr found by Nemati et al. (2011) in sediments from Sungai Buloh. The proportions of Cr in the residual fraction followed the decreasing order of the agricultural area (91.8 %)>residential area (80.6 %)>mixed area (75.2 %). Moreover, <2 and 10 % of total Cr was associated with the acid-soluble and reducible fractions, respectively.

The proportions of Cu in each fraction were relatively distributed evenly in sediments of the three areas, with slightly higher proportions of Cu being found in the reducible and residual fractions than in the acid-soluble and oxidizable fractions (Fig. 2-Cu).

The residual fraction contained a mean of 48.0, 37.5, and 58.4 % of the total Cr in the residential, mixed, and agricultural areas, respectively. Less than 13 % of total Ni was found in the oxidizable fraction. The rest of the Ni was distributed equally in the acid-soluble and reducible fractions (Fig. 2-Ni).

The reducible fraction contained most of the Pb, with mean values of 61.8, 68.6, and 55.2 % of total Pb in the residential, mixed, and agricultural areas, respectively (Fig. 2-Pb), indicating relatively higher mobility and bioavailability under reducing conditions (Passos et al. 2010). These results were in agreement with the Pb concentrations observed in sediment from the Yamuna River by Jha et al. (1990) and Jain (2004). No more than 4 and 9 % of total Pb was found in the acid-soluble and oxidizable fractions, respectively.

The behavior of the four Zn fractions revealed a similar distribution pattern (Fig. 2-Zn). In addition, Zn was mainly

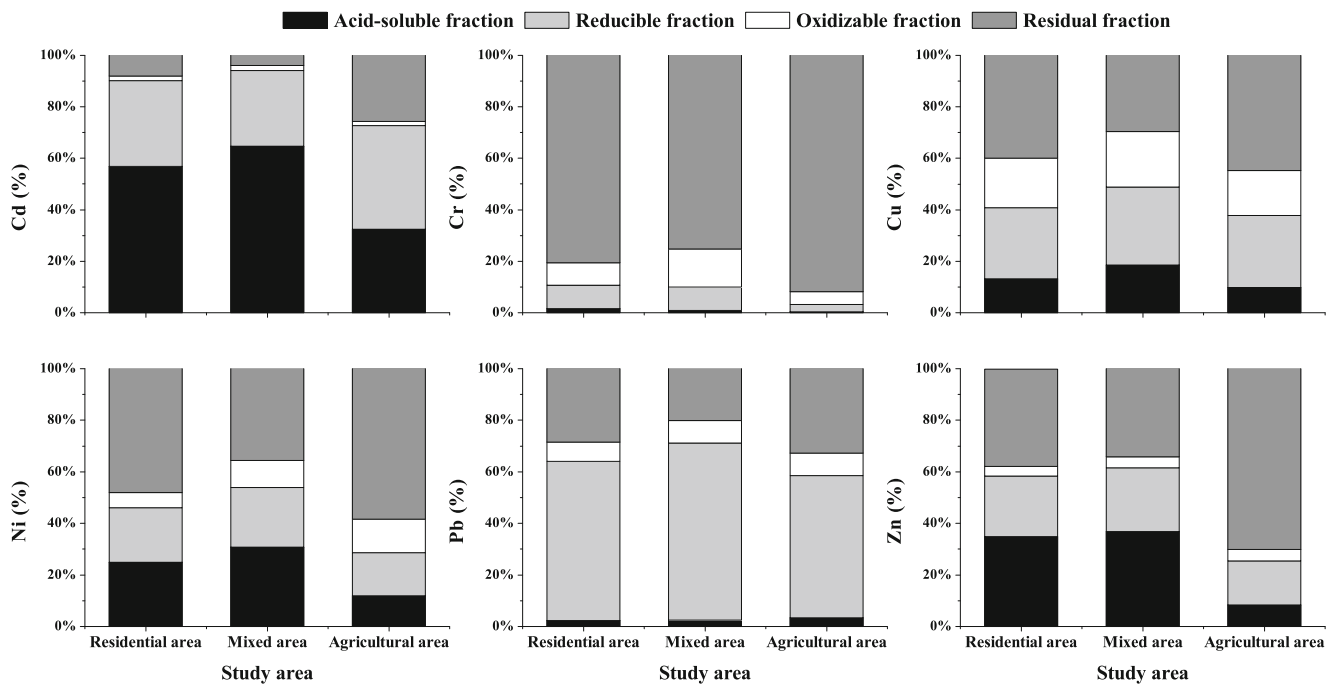


Fig. 2 Metal speciation in sediments from rural rivers in the residential, mixed, and agricultural areas

associated with the acid-soluble (34.9 and 36.8 %), reducible (23.4 and 24.8 %), and residual fractions (37.6 and 34.2 %) in the residential and mixed areas, respectively. However, Zn was mainly associated with the residual fraction (70.1 %) in the agricultural area.

Heavy metal concentrations in aquatic organisms

Submerged plants in rural rivers in Yangyuan town are dominated by *Ceratophyllum*. The heavy metal concentrations in *Ceratophyllum* from the three areas are given in Table 4. Zn

concentrations were the highest, whereas Cd concentrations were the lowest among the six metals in *Ceratophyllum* from the three areas, which was similar to the results reported for plankton from Taihu Lake (Yu et al. 2012). Ni was the second highest element in *Ceratophyllum*, varying from 20.4–197 mg/kg in the residential area, 20.2–149 mg/kg in the mixed area, and 9.58–19.3 mg/kg in the agricultural area. In general, metal concentrations appeared to decrease in the order of Zn>Ni>Cu>Cr>Pb>Cd in the residential and mixed areas and Zn>Ni>Cr>Cu>Pb>Cd in the agricultural area. Additionally, the concentrations of Cd, Cr, Cu, and Pb in

Table 4 Heavy metal concentrations in *Ceratophyllum* and *Bellamya sp.* (dry weight, mg/kg)

		Cd	Cr	Cu	Ni	Pb	Zn
<i>Ceratophyllum</i>							
Residential area	Range	0.11–2.54	7.54–23.9	12.2–56.8	20.4–197	3.80–9.69	102–1622
	Mean	0.95±1.14	13.3±7.64	26.0±20.1	95.3±87.1	5.72±2.74	496±751
Mixed area	Range	0.88–2.66	9.20–39.8	12.0–55.4	20.2–149	6.36–46.4	128–1066
	Mean	1.59±0.66	20.7±11.4	28.8±13.0	78.4±38.2	13.6±13.3	451±299
Agricultural area	Range	0.05–0.12	7.47–8.78	4.86–8.26	9.58–19.3	4.04–7.02	116–121
	Mean	0.10±0.04	7.96±0.72	6.63±1.71	12.9±5.50	5.15±1.63	119±2.78
<i>Bellamya sp.</i>							
Residential area	Range	0.03–0.65	1.19–45.96	89.9–284	6.51–65.1	7.26–78.2	475–887
	Mean	0.20±0.30	20.2±22.6	165±85.5	33.2±31.2	25.2±35.3	613±188
Mixed area	Range	0.12–0.74	2.85–54.4	92.3–410	8.20–58.8	9.6–163	489–684
	Mean	0.36±0.23	28.8±23.9	264±109	35.7±21.4	65.4±55.0	598±68.4
Agricultural area	Range	0.02–0.04	1.18–2.18	31.1–60.2	5.18–6.06	5.81–10.2	526–547
	Mean	0.03±0.01	1.55±0.55	44.6±14.7	5.52±0.47	7.56±2.30	535±10.8

Table 5 Correlation of metal concentrations between aquatic organisms (*Ceratophyllum* and *Bellamya sp.*) and the environment medium (water and sediment)

Water		Sediment					
		Total	DTPA	Aci.	Red.	Oxi.	Res.
<i>Ceratophyllum</i>							
Cd	0.673**	0.712**	0.643**	0.705**	0.733**	0.428	0.752**
Cr	0.144	0.153	0.340	0.457	0.378	0.179	0.111
Cu	0.186	0.504*	0.544*	0.533*	0.453	0.373	0.616*
Ni	0.139	0.225	0.324	0.396	0.522*	0.012	0.063
Pb	0.668**	0.529*	0.348	0.521*	0.516*	0.422	0.482
Zn	0.519*	0.598*	0.655**	0.668**	0.656**	0.309	0.046
<i>Bellamya sp.</i>							
Cd	0.578*	0.605*	0.567*	0.601*	0.632**	0.251	0.640**
Cr	0.262	0.089	0.466	0.660**	0.388	0.074	0.045
Cu	0.216	0.505*	0.466	0.502*	0.420	0.400	0.687**
Ni	0.413	0.178	0.335	0.449	0.605*	-0.070	-0.023
Pb	0.627**	0.449	0.021	0.211	0.429	0.497	0.099
Zn	0.341	0.592*	0.591*	0.619*	0.642**	0.239	0.226

Total total heavy metal, DTPA DTPA-extractable metals, Aci. acid-soluble fraction, Red. reducible fraction, Oxi. oxidizable fraction, Res. residual fraction

*Correlation significant at 0.05 level

**Correlation significant at 0.01 level

the three areas followed the order of the mixed area>residential area>agricultural area, whereas the concentrations of Ni and Zn in the three areas followed the order of the residential area>mixed area>agricultural area.

Bellamya sp. is a major macro-benthic species in rural rivers in Taihu Lake region, China, and it can survive in polluted environments (Yu et al. 2012). Heavy metal concentrations detected in *Bellamya sp.* are shown in Table 4. Among the six metals, Zn had the highest concentrations and Cd had the lowest concentrations in all *Bellamya sp.* samples, which were similar to the results obtained for *Ceratophyllum*. Cu was the second highest element in *Bellamya sp.*, with an average of 165, 264, and 44.6 mg/kg in the residential, mixed, and agricultural areas, respectively, which was contrary to the

findings in *Ceratophyllum*. The metal concentrations were observed in the order of Zn>Cu>Ni>Pb>Cr>Cd in the residential area and Zn>Cu>Pb>Ni>Cr>Cd in the mixed and agricultural areas. Additionally, the concentrations of Cd, Cr, Cu, Ni, and Pb in the three areas followed the order of the mixed area>residential area>agricultural area, whereas the Zn concentrations in the three areas followed the order of the residential area>mixed area>agricultural area.

Heavy metal concentrations in aquatic organisms in the three areas varied widely depending on the distribution of heavy metals in sediments and where the organisms were caught, because sediments are the major sink for heavy metals in water and play an important role in heavy metal uptake by aquatic organisms (Yi et al. 2011).

Table 6 Heavy metal bio-concentration factor (BCF) in *Ceratophyllum* and *Bellamya sp*

	Cd	Cr	Cu	Ni	Pb	Zn
<i>Ceratophyllum</i>						
Residential area	0.51±0.45	0.12±0.03	0.45±0.12	1.31±0.79	0.14±0.03	1.60±0.88
Mixed area	0.45±0.56	0.12±0.11	0.26±0.22	0.88±0.73	0.18±0.12	1.22±1.28
Agricultural area	0.66±0.16	0.08±0.00	0.16±0.03	0.24±0.05	0.13±0.05	1.28±0.49
<i>Bellamya sp.</i>						
Residential area	0.12±0.11	0.16±0.16	3.23±1.32	0.45±0.33	0.42±0.32	5.18±4.93
Mixed area	0.12±0.17	0.18±0.18	2.48±2.30	0.39±0.31	0.96±0.81	1.72±1.29
Agricultural area	0.19±0.01	0.02±0.00	1.13±0.13	0.11±0.01	0.19±0.07	5.77±2.20

Relationships among heavy metals in aquatic organisms, water, and sediments

Significant relationships were observed between the concentration of Cd or Pb in *Ceratophyllum* and *Bellamya sp.* and that in water and between the total concentrations of Cd, Cu, and Zn in *Ceratophyllum* and *Bellamya sp.* and those in sediments (Table 5). Additionally, significant relationships for Zn were found between *Ceratophyllum* and water and for Pb were found between *Ceratophyllum* and sediments. These results suggest that *Ceratophyllum* is more suitable as a metal pollution biomonitor in water and sediments. Moreover, significant relationships were observed between the concentrations of Cd and Zn in *Ceratophyllum* and *Bellamya sp.* and DTPA-extractable Cd and Zn in sediments, indicating that metal concentrations in aquatic organisms were closely related to available metals in sediments. In addition, the Cd concentrations in *Ceratophyllum* and *Bellamya sp.* were significantly related to the acid-soluble, reducible, and residual fractions. The Cu concentrations in *Ceratophyllum* and *Bellamya sp.* were significantly related to the acid-soluble and residual fractions. The Ni concentrations in *Ceratophyllum* and *Bellamya sp.* were significantly related to the reducible fraction. The Zn concentrations in *Ceratophyllum* and *Bellamya sp.* were significantly related to the acid-soluble and reducible fractions. Significant relationships for Pb were found between *Ceratophyllum* and the acid-soluble and reducible fractions.

Heavy metal concentrations in aquatic organisms were not only related to total metal concentrations in water and sediments but also to metal speciation concentrations in sediments (Pempkowiak et al. 1999; Yap et al. 2002). As a consequence, controlling the heavy metal sources in water and sediments in an aquatic system is a key method for protecting aquatic plants and animals.

Bioaccumulation of heavy metals in aquatic organisms

The BCF of Zn was the highest of the six metals for *Ceratophyllum* (Table 6), indicating the strong capability of *Ceratophyllum* to enrich Zn and suggesting that *Ceratophyllum* is suitable for treating Zn-polluted rivers. The BCF of other metals for *Ceratophyllum* displayed the decreasing order of Ni>Cd>Cu>Pb>Cr. The BCF of Cu and Zn exceeded 1 for *Bellamya sp.*, indicating the high tolerance of *Bellamya sp.* for Cu and Zn. In addition, the BCF of Zn was the highest, whereas the BCF of Cd was the lowest for *Bellamya sp.* Moreover, the BCF of Cr, Cu, Pb, and Zn for *Bellamya sp.* was higher than that for *Ceratophyllum*, and the BCF of Cd and Ni for *Bellamya sp.* was lower than that for *Ceratophyllum* because of selective accumulation of heavy metals by aquatic organisms (Nakajima and Sakaguchi 1986).

Ecological risk and health risk assessment

Potential ecological risk assessment

Comparing the heavy metal E_r^i criterion, Cd posed a very high ecological risk at four sites in the residential area and 18 sites in the mixed area, but a low ecological risk at five sites in the agricultural area (Table 7). Additionally, E_r^i of Cr, Cu, Ni, Pb, and Zn at all sampling sites was <40, except site 17 for Pb and sites 13–17 and 21 for Cu, indicating a low potential

Table 7 Potential ecological risk assessment of heavy metals in sediments at the sampling sites

Sampling sites	E_r^i						RI
	Cd	Cr	Cu	Ni	Pb	Zn	
R1	4903	3.9	27.9	17.9	16.0	10.3	4979
R2	4238	4.1	29.7	19.4	16.7	12.8	4320
R3	5179	4.4	33.0	20.4	16.5	14.0	5267
R4	2371	2.7	13.9	12.6	8.8	6.3	2416
R5	277	2.5	9.1	9.9	7.8	2.4	309
R6	28.7	1.8	5.2	5.9	4.2	0.7	46.4
R7	34.2	2.3	6.8	8.3	4.6	1.2	57.5
M8	1320	3.1	18.3	14.7	7.8	6.0	1370
M9	499	2.9	16.5	13.6	8.5	4.8	546
M10	209	2.7	10.1	11.0	7.8	2.3	243
M11	422	2.9	15.7	12.9	8.3	4.3	466
M12	1778	3.5	36.4	21.0	15.1	10.4	1865
M13	1351	6.5	99.4	26.1	24.9	8.3	1517
M14	3463	7.6	51.7	26.2	18.7	14.7	3582
M15	6700	8.8	67.9	23.9	19.5	14.9	6835
M16	4727	6.3	65.9	17.5	23.2	12.8	4853
M17	1462	4.4	43.3	16.5	59.2	9.4	1595
M18	612	3.1	19.2	11.9	10.0	3.5	659
M19	794	16.0	25.1	51.4	10.0	4.8	901
M20	115	3.9	33.3	15.2	9.4	4.0	181
M21	688	5.8	49.9	17.2	19.3	7.0	787
M22	1201	4.8	31.7	14.4	18.9	5.5	1277
M23	1357	4.3	34.7	16.8	13.9	6.0	1433
M24	1384	4.8	51.6	28.5	20.5	8.1	1497
M25	1520	3.9	34.1	18.7	11.7	6.1	1595
M26	1274	4.3	30.9	18.9	10.6	5.9	1345
M27	1346	3.2	17.8	14.1	8.8	4.2	1394
A28	54.1	2.7	14.9	12.5	12.8	2.4	99.3
A29	88.0	2.4	10.6	11.0	11.4	2.3	126
A30	11.3	2.5	6.1	7.5	15.4	0.8	43.7
A31	32.7	2.4	9.3	8.1	9.1	1.5	63.1
A32	20.5	2.4	8.6	7.8	9.5	1.3	50.0
A33	22.2	2.5	8.2	8.4	7.2	1.3	49.7
A34	19.4	2.4	6.0	9.2	4.1	1.1	42.3

E_r^i potential ecological risk factor for a given contaminant, RI risk index

Table 8 Target hazard quotient (THQ) for heavy metals in *Bellamya sp.* in the rivers

Exposure group	THQ						TTHQ
	Cd	Cr	Cu	Ni	Pb	Zn	
Children							
Residential area	0.01±0.01	0.001±0.001	0.19±0.09	0.08±0.06	0.33±0.40	0.09±0.03	0.71±0.57
Mixed area	0.02±0.01	0.001±0.001	0.31±0.13	0.08±0.05	0.87±0.73	0.09±0.01	1.36±0.91
Agricultural area	0.001±0.001	0.000±0.000	0.05±0.02	0.01±0.001	0.10±0.03	0.08±0.002	0.25±0.05
Adult							
Residential area	0.01±0.01	0.001±0.001	0.18±0.08	0.07±0.06	0.32±0.39	0.09±0.02	0.68±0.55
Mixed area	0.02±0.01	0.001±0.001	0.30±0.12	0.08±0.05	0.84±0.70	0.09±0.01	1.32±0.88
Agricultural area	0.001±0.001	0.000±0.000	0.05±0.02	0.01±0.001	0.10±0.03	0.08±0.002	0.24±0.05

ecological risk at these sites. The average E_r^i of the six heavy metals in sediments decreased in the order of Cd>Cu>Ni>Pb>Zn>Cr.

Based on the RI values, 28.6, 14.3, and 57.1 % of all samples in the residential area were classified to have low, high, and very high potential ecological risks, respectively, and 10.0, 10.0, and 80.0 % of all samples in the mixed area were classified to have moderate, high, and very high potential ecological risks, respectively. In addition, all samples in the agricultural area were in the low ecological risk category. The RI values of heavy metals in the residential and mixed areas were higher than those found in the Yangtze River (Yi et al. 2011) and Kor River (Sheykhi and Moore 2013).

Potential health risk assessment

Bellamya sp. is a favorite daily food for local people. Therefore, it is necessary to assess the potential health risk caused by consuming *Bellamya sp.* The THQ values of individual metals and the TTHQ values of all metals from *Bellamya sp.* consumption for the different exposure groups are listed in Table 8.

THQ value of none of the metals >1 for children as well as adults, suggesting that the potential health risk was lower for ingesting heavy metals by consuming *Bellamya sp.*

Furthermore, the TTHQ values were <1 in the residential and agricultural areas. However, the TTHQ values in the mixed area were >1, which exhibited potential health risks for children and adults. The health risk caused by consuming *Bellamya sp.* in the three areas followed the order of the mixed area>residential area>agricultural area.

The heavy metal levels in *Bellamya sp.* from rural rivers in the three areas and the international standards are listed in Table 9. Cd concentrations in the three areas and Cr concentrations in the agricultural area were safe in terms of the international standards (Demirak et al. 2006; Yu et al. 2012). Moreover, Cu concentrations were safe in comparison with the Chinese limit (Yu et al. 2012). However, the concentrations of the remaining metals exceeded the international standards (Demirak et al. 2006; Yu et al. 2012), indicating that local people should be cautious when consuming *Bellamya sp.*

Conclusions

Heavy metal concentrations in water, sediments, and aquatic organisms in the three areas with rural rivers followed the order of the mixed area>residential area>agricultural area. In

Table 9 Comparison of metal concentrations in *Bellamya sp.* (wet weight, mg/kg) and the relevant standards

		Cd	Cr	Cu	Ni	Pb	Zn
<i>Bellamya sp.</i>	RA	0.03±0.05	3.43±3.82	27.9±14.5	5.63±5.29	4.27±5.99	104±31.9
	MA	0.06±0.04	4.87±4.04	44.8±18.4	6.05±3.62	11.1±9.31	101±11.6
	AA	0.005±0.002	0.26±0.09	7.55±2.49	0.94±0.08	1.28±0.39	90.7±1.83
Chinese limit ^a	0.1	2	50	0.3	0.5	50	
Turkish Guidelines ^b	0.1	–	20	–	1	50	
FAO ^f limit ^a	0.1	1	20	–	0.5	50	

RA residential area; MA mixed area; AA agricultural area; FAO Food and Agriculture Organization

^a(Yu et al. 2012), ^b(Demirak et al. 2006)

addition, the Zn concentration was the highest, whereas the Cd concentration was the lowest among the six metals in water, sediments, and aquatic organisms in the rural rivers. Heavy metal accumulation in aquatic organisms was not only related to total heavy metal concentrations in water and sediments but also to metal speciation concentrations in sediments. Cd in sediments posed the highest ecological risk to the environment. Furthermore, considerable attention should also be paid to the potential health risks of heavy metals through aquatic product consumption.

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