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RESEARCH ARTICLE

Health risk assessment for consumption of fish originating from ponds near Dabaoshan mine, South China

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Abstract Mining effluents are a potential source of toxic metals in the surrounding aquatic ecosystem and pose a potential health risk to humans from fish consumption. The objective of this paper is to assess the impact of the long-term Dabaoshan mining operation on heavy metal accumulation in different fish species. Heavy metal accumulation (lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu)) in four tissues (liver, muscle, intestine, and gills) of five carp species (*Hypophthalmichthys molitrix*, *Ctenopharyngodon idellus*, *Megalobrama amblycephala*, *Aristichthys nobilis*, and *Carassius auratus auratus*) from two fishponds exposed to effluent waters from Dabaoshan mine, South China. The bioaccumulation factor (BAF) and target hazard quotients were calculated to assess potential health risks to local residents through fish consumption. Levels of heavy metals varied depending on the analyzed tissues. *C. auratus auratus* accumulated the higher Pb, Cd, Zn, and Cu in the intestine compared with other fish species. Liver of all five species contained high concentrations of Pb, Cd, Zn, and Cu. The BAF for the studied metals showed a descending order of Cd>Zn>Cu>Pb for fishpond 1 and Zn>Cd>Cu>Pb for fishpond 2. Risk assessments suggested that potential human health risk may be present due to high Pb and Cd concentration in the muscle of some fish species exceeding the national and international limits, although the target hazard quotients were less than one.

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Introduction

Rapidly expanding industrial and agricultural activities have led to heavy metal contamination in the environment of China (Cheng 2003). Mining and processing of metal ores can be a significant source of heavy metal contamination of the environment (Dudka and Adriano 1997; Navarro et al. 2008). The environmental concern in mining areas is primarily related to spilled mine tailings, emitted dust, and acid mine drainage (AMD) transported into aquatic ecosystems (Tarras-Wahlberg et al. 2001; Riba et al. 2005; Mayes et al. 2010). Heavy metals are highly persistent and nonbiodegradable contaminants that have been reported to cause toxic effects in animals and may be bioaccumulated through food chain to hazardous levels, thus posing potential health risks to the local inhabitants by fish consumption (Bogut 1997; Eimers et al. 2001; Castro-González and Méndez-Armenta 2008; Qiu et al. 2011). Moderate exposure to non-essential metals (e.g., lead (Pb) and cadmium (Cd)) can lead to gradual accumulation in the human body, where they are associated with a number of diseases, especially cardiovascular, kidney, nervous system, and bone diseases (Telišman et al. 2000). Therefore, there is an urgent need to investigate the biological impacts of mining activities and bioaccumulation of toxic metals in fish cultured in the vicinity of metal mining.

Fish have been reported to accumulate large amounts of some metals and are often at the top of the aquatic food chain (Mansour and Sidky 2002; Bidar et al. 2009). As an important constituent of the human diet, fish can represent a major dangerous source of certain heavy metals (Bogut 1997). Numerous investigations and monitoring programs have been carried out worldwide on heavy metal accumulation in fish, particularly in the last decade (Wong et al. 2001; Brumbaugh et al. 2005; Reynders et al. 2008; Yi et al. 2011). Fish accumulate metals in their body by direct absorption via gills from water as well as through diet by consumption of contaminated food and sediments, although there can be considerable variability in bioaccumulation among species depending on their life history (Chen and Chen 1999). Most of the previous studies have demonstrated the variability in accumulation of heavy metals in different tissues of various fish species (Wong et al. 2001; Has-Schön et al. 2008; Liu et al. 2012). It has been recognized that determination of metal levels of fish muscle is extremely important for human health owing to levels in edible portions of some fish in polluted regions exceeding acceptable levels, although muscle is not an active tissue in accumulating metals (Yilmaz 2003; Qiu et al. 2011).

The present work aimed to:

1. Determine the concentration of heavy metals (Pb, Cd, zinc (Zn), and copper (Cu)) in the liver, muscle, intestine, and gills of silver carp (*Hypophthalmichthys molitrix*), grass carp (*Ctenopharyngodon idellus*), wuchang carp (*Megalobrama amblycephala*), bighead carp (*Aristichthys nobilis*), and crucian carp (*Carassius auratus auratus*) collected from two fishponds near the Dabaoshan mine;
2. Determine the bioaccumulation of heavy metals in the different organs of fish species in relation to superficial sediment in the fishponds; and
3. Assess the potential health risk of heavy metals to local residents by fish consumption.

Materials and methods

Sampling site

The study area (24°31′37″ N, 113°42′49″ E) is located in northern Guangdong, China. The mining activities of Dabaoshan metal mine, the largest mine in south China, initiated since the 1970s (Fig. 1). It has a subtropical humid monsoon climate, with annual average temperature and precipitation of 20 °C and 1,800 mm, respectively. The Dabaoshan mineral deposit is a well-known polymetallic sulfide meso-hypothermal deposit. The minerals in the ore mainly consist of pyrite, pyrrhotite, and chalcopyrite with minor components of sphalerite, chalcocite, galena, limonite, calaverite, and native bismuth. Oxidation of sulfide-bearing minerals exposed to weathering has resulted in AMD, which is characterized by extreme acidity and a high level of dissolved metals (e.g., Pb, Cd, Cu, and Zn) and anions (e.g., sulfates and carbonates, Zhou et al. 2005). Previous investigations have shown that the mining activities polluted 83 villages, $585 \times 10^4 m^2$ paddy fields, and 21×10^4 m^2 ponds around the mine. Fandong village (24°33′78″ N, 113°43′94″ E) is downstream from the heavily polluted AMD and mud-retaining impoundment/dams, the latter being tailing reservoirs containing contaminated sediment. AMD discharged from the mine has been shown to exert an impact on water quality around mine area and pose great potential health risk from heavy metals, and residents are suffering from serious cancers (Zhuang et al. 2009a, b; Wang et al. 2011).

Sampling and preparation

Sampling sites were chosen according to their downstream distances from the mud-retaining impoundment of the Dabaoshan mine. Fishpond sediment samples were collected from the surface down to a depth of 10 cm at five different locations, and these samples were pooled together. Sampled fish included silver carp (*H. molitrix*), grass carp (*C. idellus*), wuchang carp (*M. amblycephala*), bighead carp (*A. nobilis*), and crucian carp (*C. auratus auratus*). All fish and sediment samples were sealed in polyethylene bags and kept cold on ice during transportation to the laboratory. Sediment samples were air-dried, crushed, sieved through a 2-mm screen, then pulverized and passed through a 0.2-mm mesh sieve. The number of fish, total length, wet weight (ww) and habitat of fish samples are shown in Table 1. After the fish were rinsed with de-ionized water, each fish was dissected using stainless-steel implements to extract liver, muscle, intestine, and gill tissues. Polyethylene gloves were worn during dissection of fish tissues to reduce surface contamination of samples. After dissection, 20-g samples of each tissue were dried at 60 °C until they reached a constant weight. Dried tissues were ground, sieved, and transferred to porcelain dishes.

Chemical analysis

The sediment pH was measured in H_2O (1:2.5, sediment: solution ratio, dry (*w*/*v*)). One gram of powdered tissue sample was digested in 65 % HNO_3 (5 ml for 0.5 g of dried sample) and 2 ml 30 % H_2O_2 (Uluturhan and Kucuksezgin 2007). All the digested liquors were diluted to 25 ml in volumetric flasks with double-distilled water and stored in acid-washed polyethylene bottles. The sediment samples were digested using a concentrated acid mixture (HNO_3/$HClO_4$/HF=5/1/1 (*v*/*v*)). Blank digestions were also carried out in the same way. Heavy metal concentrations in the sediments were measured using ICP-AES. The concentrations of heavy metals in the fish tissues were determined by ICP-MS, and expressed as milligrams per kilogram of ww. All reagents used were of analytical grade. Standard working solutions of the different elements analyzed were

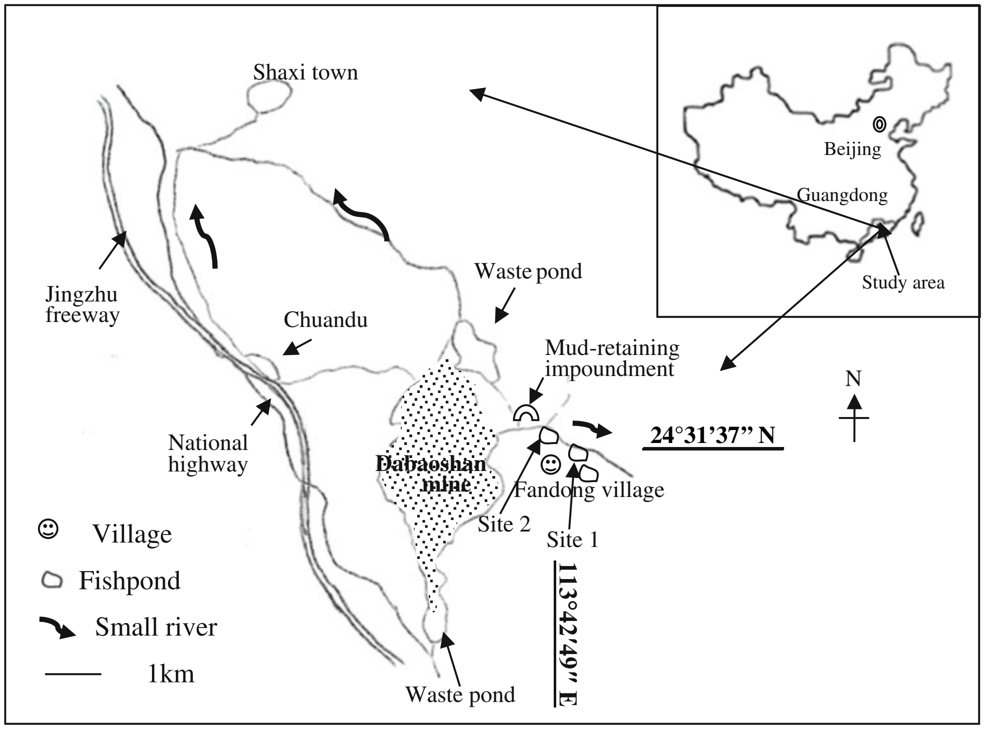

Fig. 1 Map of the Dabaoshan mine showing the location of studied fishponds at the Fandong village

prepared from the corresponding 1,000 $mg L^{-1}$ Merck Titrisol solution. Standard reference materials, including soil (GBW 08303) and *Pseudosciaena crocea* (GBW 08573) were employed to verify the accuracy and precision of metal determination. Replicate analysis of these reference materials showed good accuracy, with recovery rates of metals between 93 and 102 % for fish and 95 and 103 % for sediment. Blank and drift standards were run after every 20 determinations to maintain instrument calibration.

Risk assessment

The bioaccumulation factors (BAFs) were measured according to the following formula by Barron (1995):

$$BAF = (Ct/Cs) \times 100\% \tag{1}$$

Ct is the metal concentration (in milligrams per kilogram dry weight (dw)) in tissue, and Cs is the metal concentration (in milligrams per kilogram dw) in sediment.

The target hazard quotient (THQ) of heavy metals (Pb, Cd, Zn, and Cu) for fish was calculated by the following formula (USEPA 2000; Chien et al. 2002):

$$THQ = \frac{EF \times ED \times FI \times MC}{RfDo \times BW \times AT} \times 10^{-3} \tag{2}$$

where EF is exposure frequency (365 $days year^{-1}$); ED is exposure duration (70 years), FI is fish ingestion (in grams per person per day); MC is metal concentration in fish (in milligrams per kilogram, ww); RfDo is the oral reference dose (in milligrams per kilogram per day); BW is the average adult body weight (60 kg); AT is averaging time for noncarcinogens (365 $days year^{-1} \times$ number of exposure years, assuming 70 years). According to our questionnaire of 100 adult living in Fandong village, the average ingestion rate of fresh fish for the general population is 33.5 $g day^{-1}$. Oral reference doses were based on 4×10^{-3}, 1×10^{-3}, 3×10^{-1}, and $4\times10^{-2} mg kg^{-1} day^{-1}$ for Pb, Cd, Zn, and Cu, respectively (USEPA 2009). If the THQ value is less than

Table 1 Number of samples, average length, wet weight, and habitat of selected five fish species caught in two fishponds near Dabaoshan mine

Site	Species	Number	Total length (cm)	Weight (g)	Age (years)	Habitat
Fishpond 1	*Hypophthalmichthys molitrix*	10	43.2±0.95	935±0.06	2	Middle upper
	Ctenopharyngodon idellus	11	39.2±0.51	686±0.04	2	Middle lower
	Megalobrama amblycephala	10	28.1±1.2	289±26.9	2	Middle lower
Fishpond 2	*H. molitrix*	5	30.5±3.5	355±10.6	1	Middle upper
	Aristichthys nobilis	7	45.3±3.3	836±18.5	1	Middle upper
	Carassius auratus auratus	10	21.4±2.6	161±5.5	1	Bottom

1, there will be no obvious risk. Conversely, an exposed population of concern will experience health risks if dietary intake is greater than the RfDo (Chien et al. 2002).

Statistical analysis

The one-way analysis of variance and Tukey's test were performed for each heavy metal, either to compare the mean values in the same tissue of different fish species or in the different tissues of the same fish species. All tests were regarded as statistically significant when $p<0.05$. To assess the differentiation among the four analyzed tissues based on the heavy metal accumulation, the tissues were also compared by means of the canonical discriminant analysis.

Results

Heavy metal concentration in sediment

Metal concentrations in the sediments from the two sampled fishponds are summarized in Table 2. Both fishponds showed signs of heavy metal pollution. Sediments from fishpond 2 contained significantly higher concentrations of all the tested metals compared with fishpond 1. The sediment concentrations of Cu and Zn were the highest, followed by Pb, with Cd being the lowest. The concentrations of Pb, Cd, Zn, and Cu in sediments were found to be 4.4–5.4, 1.6–18, 2.6–3.9, and 7–20 times higher than the national guideline (GB-18668, CSBTS, 2002), respectively. The pH value of fishpond 1 water was lower than in fishpond 2.

Heavy metal contamination in fish

The concentration of heavy metals (Pb, Cd, Zn, and Cu) in the liver, muscle, intestine, and gills of the five fish species from mining-affected fishponds are listed in Table 3. All five fish species contained higher concentrations of Zn and Cu than Pb and Cd, reflecting the order of concentrations observed in sediment from the polluted fishponds. Different species and tissues showed different capacities for accumulating heavy metals. Muscle tended to accumulate less metal than the other tissues.

Table 2 Concentrations of heavy metals in sediment of two fishponds and background values (in milligrams per kilogram, dry weight)

	Fishpond 1	Fishpond 2	Background values[a]
pH	5.22±0.61	6.67±0.29	
Pb	262±13.5	327±7.48	60
Cd	0.83±0.09	8.91±1.76	0.5
Zn	386±80.2	581±17.3	150
Cu	239±48.3	743±30.1	35

[a] Marine sediment quality (GB-18668, CSBTS, 2002), set by China

Pb concentrations in most tissues varied greatly and inconsistently among all five species from two sites. Mean Pb concentration varied from 1.30 to 6.83 $mg kg^{-1}$ in the liver, with the highest level in *H. molitrix* at fishpond 1. Muscle of all fish species contained Pb ranging from 0.29 to 3.21 $mg kg^{-1}$ ww, with the highest in *H. molitrix* at fishpond 1. Intestine of *C. auratus auratus* seemed to accumulate significantly ($p<0.01$) higher Pb quantity than intestines of other species at two fishponds.

Cd concentrations ranged between 0.31 and 7.08 $mg kg^{-1}$ in the liver, 0.02 and 0.24 $mg kg^{-1}$ in the muscle, and 0.04 and 0.42 $mg kg^{-1}$ in the gills. The highest Cd concentration was found in liver of *A. nobilis* compared with those of other fish species at the two sites. Muscle of *C. idellus* seemed to accumulate significantly higher ($p<0.01$) Cd than muscle in other species. Cd level (6.94 $mg kg^{-1}$) in the intestine of *C. auratus auratus* was significantly higher than those of other fish species.

Zn concentrations in all tissues at both sites differed marginally among species, except for *C. auratus auratus.* In comparison, muscle of all five fish species contained lower concentration of Zn than other tissues. In *C. auratus auratus*, all tissues accumulated the highest level of Zn, with 278, 13.5, 649, and 55.2 $mg kg^{-1}$ in liver, muscle, intestine, and gills, respectively.

Cu levels in all tissues varied greatly and inconsistently among all fish species. The concentrations of Cu in liver of *A. nobilis* (1,053 $mg kg^{-1}$) and in intestine of *C. auratus auratus* (332 $mg kg^{-1}$) were significantly higher ($p<0.01$) than those of other fish species. In *H. molitrix* at fishpond 1, Cu levels in liver, muscle, and gills were several times as high as those of other fish species at both sites, except for *A. nobilis.*

Bioaccumulation factors of heavy metals

The BAFs, (in percent) of heavy metals, calculated for liver, muscle, intestine, and gills of *H. molitrix*, *C. idellus*, *M. amblycephala*, *A. nobilis*, and *C. auratus auratus* at both fishponds, are shown in Fig. 2. Generally, the BAFs were different when comparing different heavy metals of same tissues or different tissues of same metal at the two sites. The BAF values among heavy metals showed the descending order of Cd>Zn>Cu>Pb for fishpond 1 and Zn>Cd>Cu>Pb for fishpond 2. The highest BAF of Cd (1,204 %) was found in the intestine of *C. idellus.* The BAFs of Pb in gills of three fish species at fishpond 1 were significantly higher than those in other tissues. Muscle of three fish species at site 1 had the lowest BAFs for Zn, which ranged between 12.5 and 16.7 %. The highest BAFs for Cu of 128, 11, and 36 % were found for the liver tissues of *H. molitrix*,

Table 3 Heavy metal concentrations in tissues of five fish species from two sites (means±SE, in milligrams per kilogram, wet weight)

	Site	Fish species	Liver	Muscle	Intestine	Gills
Pb	Fishpond 1	*Hypophthalmichthys molitrix*	6.83±0.34 b, A	3.21±0.29 b, A	NA	28.9±1.68 a, A
		Ctenopharyngodon idellus	3.92±0.21 b, B	2.33±0.17 b, A	5.00±0.17 b, B	11.5±0.73 a, B
		Megalobrama amblycephala	6.53±0.13 b, A	2.03±0.16 c, A	5.63±0.23 b, B	15.5±0.32 a, A, B
	Fishpond 2	*H. molitrix*	5.16±0.21 a, A	0.29±0.04 c, B	NA	2.34±0.12 b, C
		Aristichthys nobilis	3.77±0.15 a, B	0.37±0.08 b, B	4.72±0.21 a, B	2.91±0.14 a, b, C
		Carassius auratus auratus	1.30±0.09 c, C	0.29±0.05 d, B	95.6±1.46 a, A	4.03±0.12 b, C
Cd	Fishpond 1	*H. molitrix*	0.31±0.02 a, B	0.02 ±0.01 b, B	NA	0.04±0.001 b, C
		C. idellus	1.08±0.08 a, B	0.24±0.04 b, c, A	0.03±0.001 c, D	0.42±0.01 b, A
		M. amblycephala	0.42±0.04 b, B	0.03±0.01 c, B	1.95±0.08 a, B	0.08±0.01 c, C
	Fishpond 2	*H. molitrix*	0.40±0.06 a, B	0.03±0.001 c, B	NA	0.16±0.01 b, B
		A. nobilis	7.08±4.11 a, A	0.04±0.001 c, B	0.28±0.02 b, C	0.28±0.03 b, A
		C. auratus auratus	0.73±0.24 b, B	0.10±0.01 c, A, B	6.94±0.51 a, A	0.18±0.01 c, B
Zn	Fishpond 1	*H. molitrix*	39.5±2.46 a, B	9.44±0.44 c, A	NA	22.0±1.40 b, B
		C. idellus	37.6±1.06 a, B	11.2±1.70 c, A	20.4±0.29 b, B	22.0±1.01 b, B
		M. amblycephala	45.6±1.54 a, B	8.07±2.36 c, A	18.0±1.39 b, B	18.4±0.45 b, B
	Fishpond 2	*H. molitrix*	37.0±1.17 a, B	8.03±0.25 b, A	NA	28.6±1.64 a, B
		A. nobilis	57.7±1.95 a, B	8.50±0.73 c, B	34.3 ±2.83 b, B	19.5±1.02 b, c, B
		C. auratus auratus	278±1.97 b, A	13.5±1.06 c, A	649±45.5 a, A	55.2±0.84 c, A
Cu	Fishpond 1	*H. molitrix*	126±11.5 a, B	4.89±1.76 b, A	NA	12.4±2.30 b, A
		C. idellus	12.6±0.76 a, D	1.10±0.09 c, B	4.29±1.05 b, C	2.09±0.64 b, c, C
		M. amblycephala	35.5±2.19 a, C	0.57±0.02 b, C	3.26±1.30 b, C	1.90±0.13 b, C
	Fishpond 2	*H. molitrix*	36.4±2.75 a, C	2.35±0.16 c, B	NA	10.1±0.47 b, A
		A. nobilis	1,053±40.7 a, A	1.83±0.29 c, B	12.9±1.36 b, B	9.43±1.28 b, A
		C. auratus auratus	12.0±0.18 b, D	0.61±0.09 d, C	332±7.69 a, A	4.20±0.24 c, B

Values followed by the same letter in a column (small letter) or row (capital letter) were not significantly different at the 0.05 levels according to Tukey's test. *NA* no analysis

C. idellus, and *M. amblycephala*, respectively. The BAFs of Pb, Cd, and Zn in the intestine showed the highest values in *C. auratus auratus* when compared with the BAFs of the other tissues analyzed in this species. Cd and Cu displayed the highest BAFs of 194 and 346 % in the liver of *A. nobilis*, which were 10–18 and 29–88 times higher than those in the liver tissue of *H. molitrix* and *C. auratus auratus*, respectively.

Discussion

Comparison of metal accumulations in fish with published data

The liver Pb concentrations (3.17–16.5 $mgkg^{-1}$ dw, estimated from ww concentrations and moisture) in all fish species tested here were higher than those in carp and bass (mean= 3.34 $mgkg^{-1}$ dw) from other mining-influenced sites (Brumbaugh et al. 2005) and in *Campostoma oligolepis*, *Lepomis megalotis*, and *Hypentelium nigricans* (0.03–9.82 $mgkg^{-1}$ dw) from a Pb–Zn mining areas of the USA (Schmitt et al. 2007). The livers of four fish species from the Lot River polluted by effluents from a Zn-mineral-processing plant in Bouillac (France), had Zn levels of about 50 $mgkg^{-1}$ ww (Andrés et al. 2000), which were within the range of our data for all species (Table 3). Liver Cd averaged 17.9 $mgkg^{-1}$ dw in carp fish from mining-influenced water reported by Brumbaugh et al. (2005), which was similar to liver Cd concentration (17.3 $mgkg^{-1}$ dw estimated from ww concentrations and moisture) in bighead carp *A. nobilis* (Table 3). Livers were the major tissues of Cu accumulation in all fish species, and the levels (30–2,574 $mgkg^{-1}$ dw estimated from ww concentrations and moisture) were higher than those reported (4.94–104 $mgkg^{-1}$ dw) in many other studies (Wong et al. 2001; Jarić et al. 2011; Liu et al. 2012). These results demonstrated that the high metal-accumulating ability of the liver is possibly attributed to the activity of metallothioneins, proteins that bind heavy metals such as Cu, Cd, and Zn, thus reducing their toxicity and allowing the liver to accumulate high levels of metal pollutants from the environment (Al-Yousuf et al. 2000; Karadede and Ünlü 2000; Usero et al. 2003).

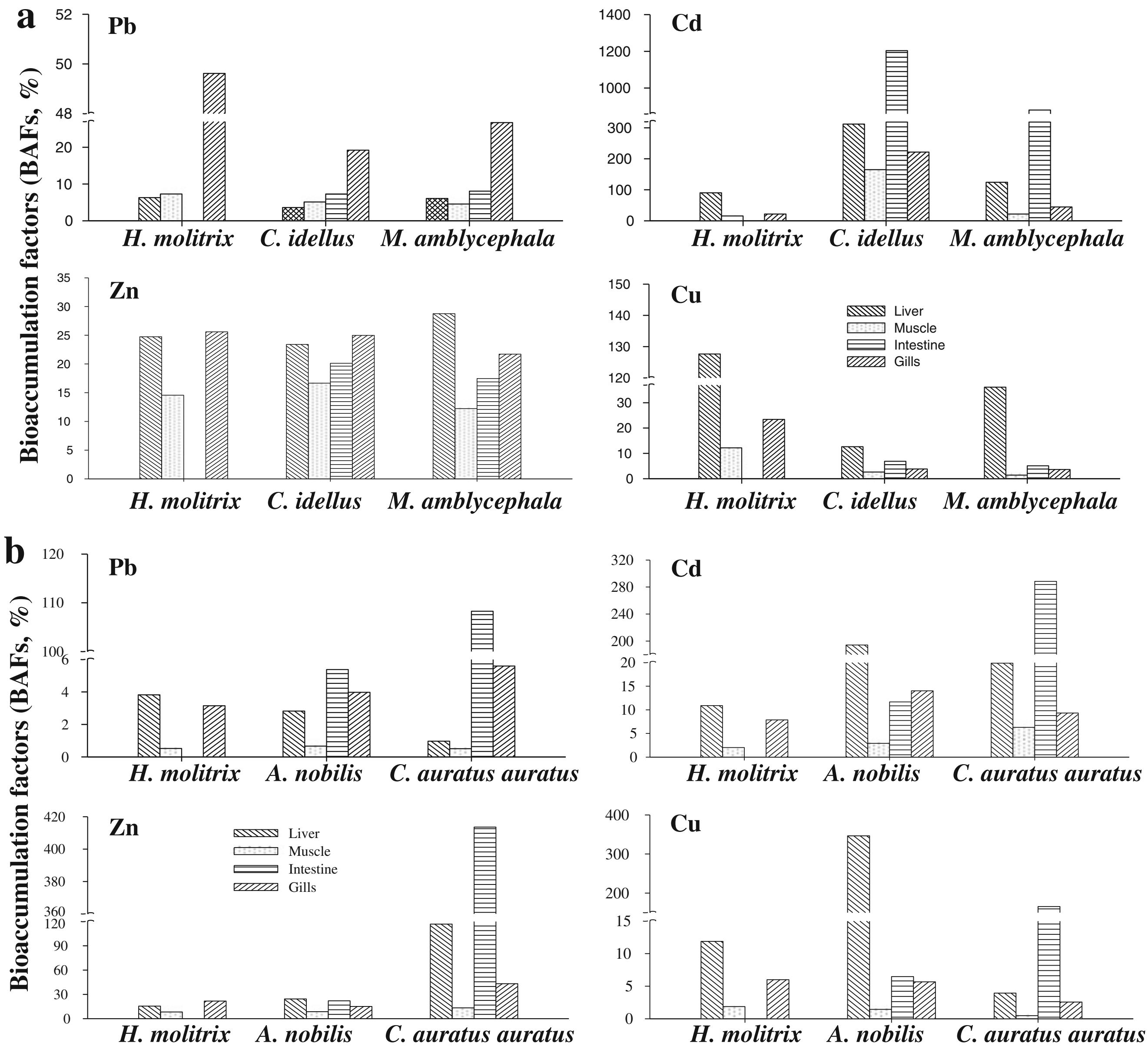

Fig. 2 Bioaccumulation factors (*BAFs* (in percent)) of heavy metal in tissues of three fish species from fishponds 1 (**a**) and 2 (**b**)

It has been recognized that fish muscle always contains lower concentrations of metals than other tissues in a number of fish species in many water bodies around the world (Yilmaz 2003; Reynders et al. 2008; Jarić et al. 2011), due to its low metabolic activity (Uluturhan and Kucuksezgin 2007). Muscle levels of Pb of five fish species (0.29–3.21 mgkg^{-1} ww) were higher compared with the same fish species (0.25–0.89 mgkg^{-1} ww) from the Yangtze river (Yi et al. 2011) and six fish species (0.01–0.12 mgkg^{-1} ww) reported by Has-Schön et al. (2008). Muscle concentrations of Cd in the carp analyzed by Yi et al. (2011) were 0.054–0.17 mgkg^{-1} ww and in the *C. idellus* reported by Liu et al. (2012) averaged 0.128 mgkg^{-1} ww, which were within the range of the means (0.02–0.24 mgkg^{-1} ww) for the same fish species in this study. The concentrations of Zn in the muscle (8–13.5 mgkg^{-1} ww or 47–77 mgkg^{-1} dw) of all fish species were within the range of those reported in *Solea vulgaris*, *Anguilla anguilla*, and *Liza aurata* (3.1–13 mg kg^{-1} ww) from salt marshes of Spain (Usero et al. 2003) and fish species (16–130 mgkg^{-1} dw) from the Taihu Lake, China (Chi et al. 2007).

Although gill is not a tissue with high metabolic activity, it still showed a modest accumulation of heavy metals. This could be explained by increased metal adsorption on the gill surface from higher metals in water (Canli and Atli 2003). Pb concentrations in the gills of *H. molitrix*, *C. idellus*, and

M. amblycephala were significantly higher ($p<001$) than those in liver and muscle, which agreed with the finding by Has-Schön et al. (2006). Gill Zn levels in this study, ranging from 18.4 to 55.2 $mgkg^{-1}$ ww, were higher than those reported (13–29 $mgkg^{-1}$ ww, Yilmaz et al. 2007) previously. Compared with other internal tissues, the gill is the first tissue exposed to water and resuspended sediment particles, the metal concentration which could show the availability of waterborne metal to fish (Chen and Chen 1999; Karadede and Ünlü 2000; Reynders et al. 2008). High heavy metal loads in gills can reveal water or sediment to be the main source of contamination (Bervoets and Blust 2003).

Among all the fish species, intestine of *C. auratus auratus* accumulated exceptionally high levels of Pb, Cd, Zn, and Cu compared with other tissues, which might be related to the different feeding habits of *C. auratus auratus* and high metal levels in fishpond 2. Because *C. auratus auratus* is a bottom-feeding fish, it showed evidence of heavy metal uptake via the intestine by consumption of contaminated food and organic matter in sediment. Thus, *C. auratus auratus* might represent a good biomonitor of metals present in the surrounding environment. Reynders et al. (2008) and Jarić et al. (2011) also reported the highest Zn levels in intestine of carp and starlet, respectively, compared with other tissues. A similar accumulation pattern for Cd, Zn, and Cu in intestine of all fish species monitored in this study was found in grey mullet (*Liza macrolepis*) as well (Chen and Chen 1999).

Figure 3 shows canonical discriminant analysis of the tissue metal data, suggesting a high differentiation among the four tissues and fish species. Two canonical functions (CV) together accounted for 95.4, 100, and 99.9 % of the total heterogeneity of *C. idellus* (CV1, 64.4 % and CV2, 31 %), *H. molitrix* (CV1, 90.4 % and CV2, 9.6 %), and *C. auratus auratus* (CV1, 99.4 % and CV2, 0.5 %), respectively. In *C. idellus*, intestine was primarily separated from the other three tissues by the first CV, based on the high concentrations of Pb and Cd, while liver was separated along the second CV based on high concentrations of Cu, a pattern similar to that of starlet (*Acipenser ruthenus*) reported by Jarić et al. (2011). *C. auratus auratus* showed the clearest separation between the intestine and the other three tissues, with heavy metal concentrations in liver, muscle, and gills being

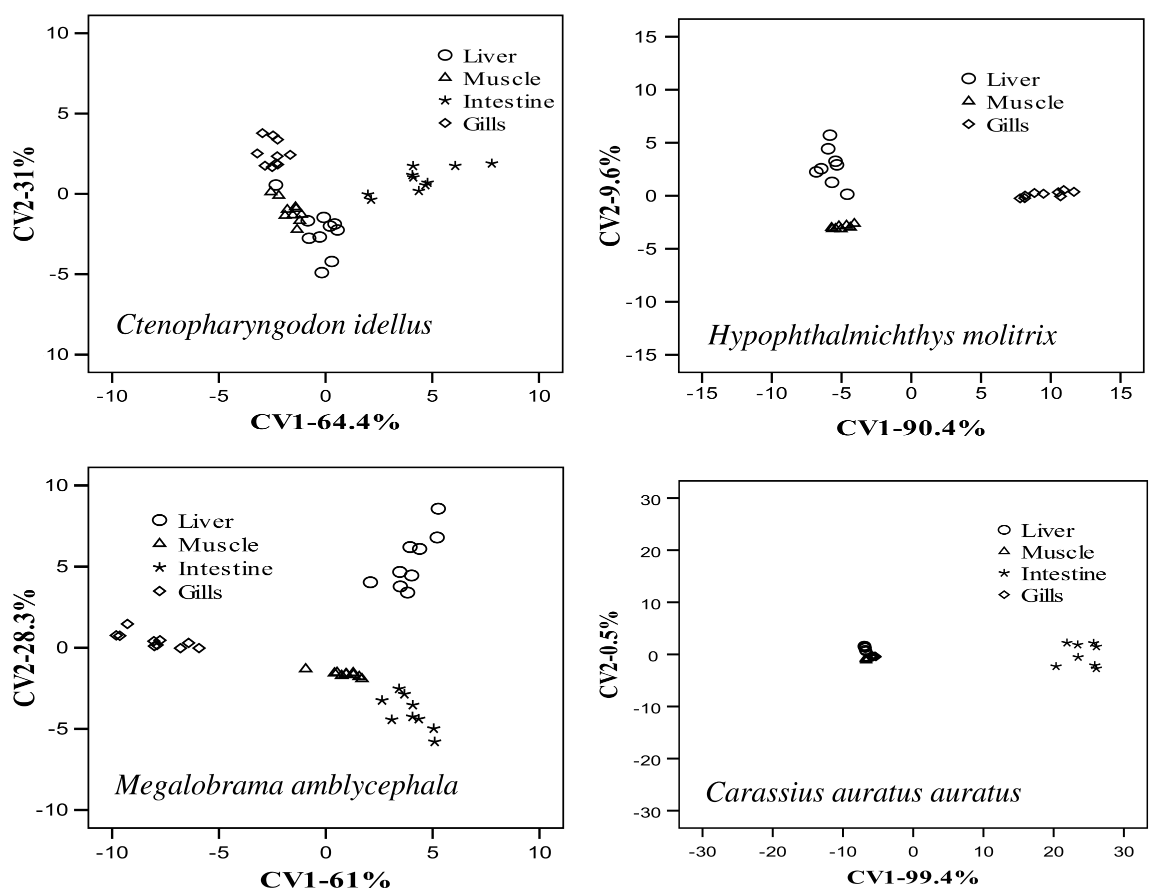

Fig. 3 Canonical discriminant analysis applied on the heavy metal concentrations in four tissues of four selected fish species (ellipses show 95 % confidence intervals)

Table 4 Comparison of metal concentrations in fish (muscle) and relevant standards (in milligrams per kilogram, ww)

	Pb	Cd	Zn	Cu
In this study	0.29–3.21 (61 %)[a]	0.02–0.24 (28 %)	8.03–13.5 (0)	0.57–4.89 (0)
National limit	0.5[b]	0.1[b]	50[c]	50[b]
FAO limit	0.5	0.1	50	20
EC limit	0.3	0.05	–	–

[a] The number in parentheses indicated the percentage of metals concentration exceeding the national and FAO limits

[b] The limits of pollutants in foods (NY-5073, MAPRC, 2006)

[c] The limits of pollutants in foods (GB-13106 for Zn, MHPRC, 1991)

relatively uniform. Al-Yousuf et al. (2000) and Usero et al. (2003) reported that the differences in metal concentrations of the tissues might be a result of their capacity to induce production of metal-binding proteins such as metallothioneins. Thus the present study confirmed that the accumulation pattern between the organs for elements was very highly species dependent.

Bioaccumulation in relation to heavy metals in sediment

BAFs significantly differed among all the metals and fish species (Fig. 2). The highest liver Cd-BAFs of *C. auratus auratus* (312 %) and *A. nobilis* (194 %) in this study were, nevertheless, lower than those of *Pagellus erythrinus* from the Eastern Aegean Sea, Turkey (610 %; Uluturhan and Kucuksezgin 2007) and of *L. macrolepis* (521 %; Chen and Chen 1999). The BAF of Cu was highest in the liver, implying these metals were regulated in the liver tissue (Hamilton and Mehrle 1986; Chen and Chen 1999). The BAFs of Zn and Cu in gills of all fish species were lower than those found in *Liza saliens* by Fernandes et al. (2007). In the present study, the BAFs of Zn in the various fish tissues (except for *C. auratus auratus*) showed a small range (8.2–29 %) which would suggest that Zn was regulated to maintain a homeostatic status. The muscle BAFs of all metals for all three species at fishpond 1 and fish at fishpond 2 were similar to published results for *L. macrolepis* (Chen and Chen 1999) and *P. erythrinus* (Uluturhan and Kucuksezgin 2007), respectively.

Sediment from fishpond 2 contained higher levels of all heavy metals than fishpond 1, but this was not reflected in metal BAFs and concentrations in fish tissues among fish species. Higher Pb concentrations in liver, muscle and gills of three fish species at fishpond 1 were found compared with those at fishpond 1, suggesting that the metal levels of biologically non-essential elements, such as Pb and Cd, in the fish may increase with prolonged exposure (Usero et al. 1997). Furthermore, the BAFs of all metals in different tissues of *H. molitrix* (aged 2 years) at fishpond 1 were higher than those (aged 1 year) at fishpond 2, though heavy metal concentrations in sediments were lower than metal levels at fishpond 2. These results are consistent with the finding of Fernandes et al. (2007), suggesting a significant positive relationship between BAFs of metals and fish age. Moreover, the high BAFs of metals in fishpond 1 were likely due to the low sediment pH values (Table 1), which might cause the heavy metals to be more soluble and bioavailable (Adhikari et al. 2006). This pattern is probably directly related to the discharge of contaminants from the nearby historical mine operation (Zhuang et al. 2009b). Fishpond 2 is situated closer to a mud-retaining impoundment of Dabaoshan mine and received highly contaminated water (Fig. 1). The present studies indicate that the mining effluents increase metal levels in the aquatic system, and consumption of contaminated sediments and water originating from mining operations is an important exposure route that can result in metal accumulation in fish (Moiseenko and Kudryavtseva 2001; Borgmann et al. 2007; Schmitt et al. 2007) .

Human health risk from fish consumption

Heavy metals in fish can pose potential health risks to the fish as well as to humans who consume them (Moiseenko and Kudryavtseva 2001; Castro-González and Méndez-Armenta 2008). Although fish muscle tended to accumulate low concentrations of metals, it is important to compare

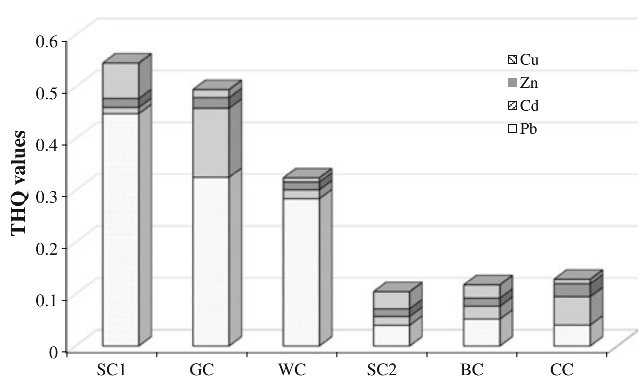

Fig. 4 Total target hazard quotients (*THQ*) of heavy metals (Pb, Cd, Zn, and Cu) via consumption of all selected fish species by local residents at Fandong village. The consumption rate is 33.5 $\mathrm{g\,day^{-1}}$. *SC1* silver carp (*H. molitrix*), *GC* grass carp (*C. idellus*), *WC* wuchang carp (*M. amblycephala*) at fishpond 1, *SC2* silver carp, *BC* bighead carp (*A. nobilis*), *CC* crucian carp (*C. auratus auratus*) at fishpond 2

these to known safe levels because muscle constitutes the greatest mass of the fish that is consumed. Table 4 shows the maximum permissible level (MPL) of metals in fish flesh prescribed by China and international standards (FAO and EC 2001 limits). The muscle Pb concentrations of *H. molitrix*, *C. idellus*, and *M. amblycephala* at fishpond 1 were 4–6.4 times higher than the national and FAO limit (0.5 $mgkg^{-1}$). Concentrations of Pb in the muscle (0.29–3.21 $mgkg^{-1}$ ww or 1.7–19 $mgkg^{-1}$ dw) of five fish species were above national and FAO MPL in 68 % of muscle samples, and above EU MPL in 95 % of analyzed samples. These results were higher than those reported in similar and different fish species (0.42–2.33 $mgkg^{-1}$ dw) from Taihu lake (Yu et al. 2012). Muscle Cd concentrations of *C. idellus* and *C. auratus auratus* also exceeded the legal limits (0.1 $mgkg^{-1}$); specifically, 28 % of Cd concentrations of muscle samples exceeded the prescribed national MPL. The mean levels of Zn and Cu were below the national and FAO MPL (50 and 20 $mgkg^{-1}$, respectively). Although the liver of *C. auratus auratus* (278 $mgkg^{-1}$ Zn) and *A. nobilis* (1,053 $mgkg^{-1}$ Cu) greatly exceeded the health limits, it is unlikely that this organ would be consumed.

Figure 4 shows the THQ of heavy metals calculated according to consumption of fish by the local residents in Fandong village. The estimated THQ for individual metals decreased in following sequence: Pb>Cd>Cu>Zn, with the exception of Cu>Cd in *H. molitrix.* THQ values of Pb (0.29–0.45) for three fish species were higher than comparable values for Pb via consumption of fish from Taihu lake (Yu et al. 2012) and Yangtze River (Yi et al. 2011) in the general population. All the total THQ values were less than 1 for all fish species, suggesting a relative absence of human health risk associated with intake of a single heavy metal via consumption of fish flesh alone. However, the THQ values exhibited different potential health risks for different fish species. The THQs of heavy metals through consumption of three fish species at fishpond 1 showed higher values than those at fishpond 2.

The present results have shown that consuming fish solely from the fishponds near the mine-affected area is not harmful to humans, but inhabitants should limit consumption of *C. auratus auratus*, *C. idellus*, *H. molitrix*, and *M. amblycephala* owing to the potential Pb and Cd exposure. Farmed fish is the primary meat consumption for the local residents' diet. Some local inhabitants, who consume more fish flesh and liver than average, and also eat contaminated locally grown foodcrops, breathe contaminated air, or drink contaminated water, might be exposed to a potential health risk from dietary heavy metals. Therefore, the selection of species of fish consumed, based on the different tissue concentrations of heavy metals, can be beneficial in diminishing the hazard to public health. In summary, this work provided a comprehensive status of heavy metals in fish from fishponds near Dabaoshan mine and its health risk assessment, which would be useful for local governments to refer to in regulating and limiting the environmental pollution surrounding the metal mine.

Conclusions

Heavy metal concentrations in the sediment from two fishponds near Dabaoshan mine were above the national guideline for sediment and posed an environmental risk. The Canonical Discriminant Analysis showed that high differentiation among the four tissues and fish species. The concentration of Pb and Cd in the muscle of some fish species exceeded the MPL of metals in fish flesh of the international and Chinese quality standards. Although the total THQ were less than one, risk assessments suggested that human health risk may be present owing to the potential Pb and Cd exposure from long-term consumption of *C. auratus auratus*, *C. idellus*, *H. molitrix*, and *M. amblycephala*.

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