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ORIGINAL ARTICLE

# Accumulation of heavy metals in wild commercial fish from the Baotou Urban Section of the Yellow River, China

**Changwei Lü · Jiang He · Qingyun Fan · Hongxi Xue**

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**Abstract** In this work we studied the accumulation of heavy metals in nine species of fish with different life and feeding habitats which are native and major commercial fish in the Baotou Urban Section of the Yellow River. The results showed that the concentration of heavy metals was significantly dependent on fish species; the pollution index of heavy metals in different species were ranked as *Hemiculter leucisclus* > *Carassius auratus auratus* > *Hemibarbus maculatus* > *Megalobrama amblycephala* > *Abbottina rivularis* > *Cyprinus carpio* > *Squaliobarbus curriculus* > *Perccottus glehni* > *Saurogobio dabryi*. Product–moment correlation coefficients among the metal pairs Pb–Zn, Cu–Cd, Cu–Zn, Cu–Pb, Pb–Cd, and Zn–Cd revealed there was no competitions between metals in each tissue. Correlations between heavy metal concentrations and fish length or weight indicated that accumulation of the heavy metals by the different fish species was related to their surrounding environments and their life and feeding habitats. According to the mean bioconcentration factors (BCFs), the heavy metal concentrations in these nine species were ranked Zn $\gg$ Cu > Cd $\approx$ Pb. In this work, the bioaccumulation factors (BAFs) were developed by using the sum of exchangeable and bound-to-carbonate heavy metals as Cs values. It was found that BAFs better reveal the accumulation characteristics of the heavy metals in the fish, which might provide an effective method for assessing bioaccumulation of heavy metals.

**Keywords** Heavy metals accumulation · Pollution index · Wild commercial fishes · The Baotou Urban Section

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## Introduction

Aquatic ecosystems are under permanent pressure from anthropogenic pollutants originating from various sources located in the catchment area or at distant places. Many pollutants, including heavy metals, are toxic to aquatic organisms and cause their lethal or sublethal deterioration. Fish are a major part of the human diet and numerous studies have been carried out on metal pollution in different species of edible fish (Kucuksezgin et al. 2002; Lewis et al. 2002; Prudente et al. 1997). The serious health consequences of mercury exposure in terms of neurocognitive effects were for the first time illustrated in 1953, when an epidemic of MeHg poisoning occurred in humans in villages around Minamata Bay as a result of consumption of fish (Amin-Zaki et al. 1974). Another outbreak of MeHg intoxication occurred in rural Iraq in 1971–1972 from seed grain treated with an Hg-based fungicide that was used for planting (Bakir et al. 1997; Eskanazi 1984; Takizawa and Kitamura 2001).

The Yellow River is the biggest sand transformation river in the world. The Baotou Urban Section is considered to be of bad environmental quality in the drainage basin of the Yellow River. In recent years, contamination accidents have frequently arisen in the Yellow River. In particular, a momentous problem occurred in the reach from the Baotou to Wanjia village in April 2004 because of discharge of paper-making effluent from the Wuliangsuhai Lake to the Yellow River, resulting in fish species being almost annihilated and even the living fish in the reach not being suitable for human use. However, few data have been published on heavy metal pollution of fish from the Baotou Urban Section.

Nine species of fish with different life and feeding habitats were selected in this work. The objectives of this study were:

1. To investigate accumulation of heavy metals in the selected fish species from the Baotou Urban Section in order to assess the health risk for humans and provide fundamental data for studying the accumulation characteristics of heavy metals in fishes from the Yellow River; and
2. To compare the accumulation of different heavy metals in different fish species in order to statistically examine the correlations among metal concentrations in fish tissue.

## Study area and methods

### Study area

The investigated reach was the Baotou Urban Section of the Yellow River. The study area is the most arid region of the Yellow River drainage area with, usually, a flow of approximately 100 $m^3$ $s^{-1}$ in the annual dry season from April to June. The annual average rainfall is approximately 200–350 mm with a maximum in August and little rain during the dry period, and the annual average evaporation is high, up to 2,000–2,200 mm.

The study area is heavily industrialized. In terms of pollution, a large variety of industries, primarily metallurgical, chemical, and paper-making, are responsible for a wide range of contaminant inputs, and the water and sediment quality of this section are largely affected by the Kundulun, Sidaosha, Xi, and Dong river tributaries because of industrial discharge. More than 275,000 tons of wastewater is discharged daily into the Baotou Urban Section through the several tributaries. According to the 2004 statistics, the Cu, Pb, Zn, and Cd content of discharges into the reach were 11.52, 28.84, 258.0, and 0.57 tons, respectively.

### Sampling and preservation

Sampling took place in April 2005; the location of sampling sites is given in Fig. 1. Site A, B, C and D, which are in stable conditions for depositing materials, were selected for water and sediment sampling. Fish samples were collected using sweep nets from the selected section which is approximately 72 km from Zhaojunfen to Dengkou (marked with filled triangle, Fig. 1) in the Baotou Urban Section of the Yellow River. The fish samples were randomly selected independently of their species, and sealed in different polyethylene plastic bags. After transport to the laboratory, the fish samples were stored at −20°C until analysis.

The suitability of the caught fish for study of heavy metal accumulation relates to their widespread distribution and ease of collection, their sedentary filter-feeding habits, and the concentration of pollutants in their tissues, which closely corresponds to levels in the environment in April. During sampling, the Yellow River was just thawing soon after a frozen period of approximately 5 months; it is therefore safe to say that the fish have spent most of their lives in this environment and have not received food from outside or been subject to any other type of external influence.

Thirty families and 176 species of fish have been recorded in the Yellow River, of which 138 species are freshwater fish. Ten families and 88 species are found in the middle reaches of the Yellow River, and 63 of the 88 species were *Cyprinidae* (Yang 1999). In this work, nine species of fish with different life and feeding habits were investigated: *Cyprinus carpio*, *Squaliobarbus curriculus*, *Carassius auratus auratus*, *Hemiculter leucisclus*, *Megalobrama amblycephala*, *Saurogobio dabryi*, *Perccottus glehni*, *Abbottina rivularis*, and *Hemibarbus maculatus*. Among the species investigated, eight were *Cyprinidae*, only *Perccottus glehni* was *Eleotridae*, which reflected that the major wild fishes were *Cyprinidae* in the middle reaches of the Yellow River. Except *Megalobrama amblycephala,* which was introduced from inshore aquaculture to the Yellow River in recent years, all the investigated species were the native varieties of the Yellow River, and *Cyprinus carpio, Carassius auratus auratus*, and *Squaliobarbus curriculus* were the major commercial species. In addition, although other species were very small, the local people also consumed these species after frying, which increases interest in the wild fishes. These fishes were chosen because they are common, are fished in large quantities, and are commercial species in China, particularly in the study area.

### Methods

Fish samples were unfrozen at room temperature, and their length and weight were recorded at the same time. They were dissected using stainless steel scalpels and Teflon forceps. The muscle, fin, gill, bone, skin, head, and viscera were removed and transferred to separate polypropylene vials. Subsequently, the samples were appropriately homogenized in a stainless-steel blender. Aliquots of approximately 2–10 g (wet weight) homogenized samples were ashed in porcelain crucibles on an adjustable electric hotplate until smoke-free, and then the samples were further ashed in a muffle furnace for 8 h at 500°C. When the samples were cold, nitric acid (0.5 mol $L^{-1}$) was added to dissolve the ashed samples. The digested solutions were passed through-0.45 μm pore-size filtration membranes before transfer to 25-ml glass flasks for analysis. Speciation analysis of the heavy metals (Cu, Pb, Zn, and Cd) in

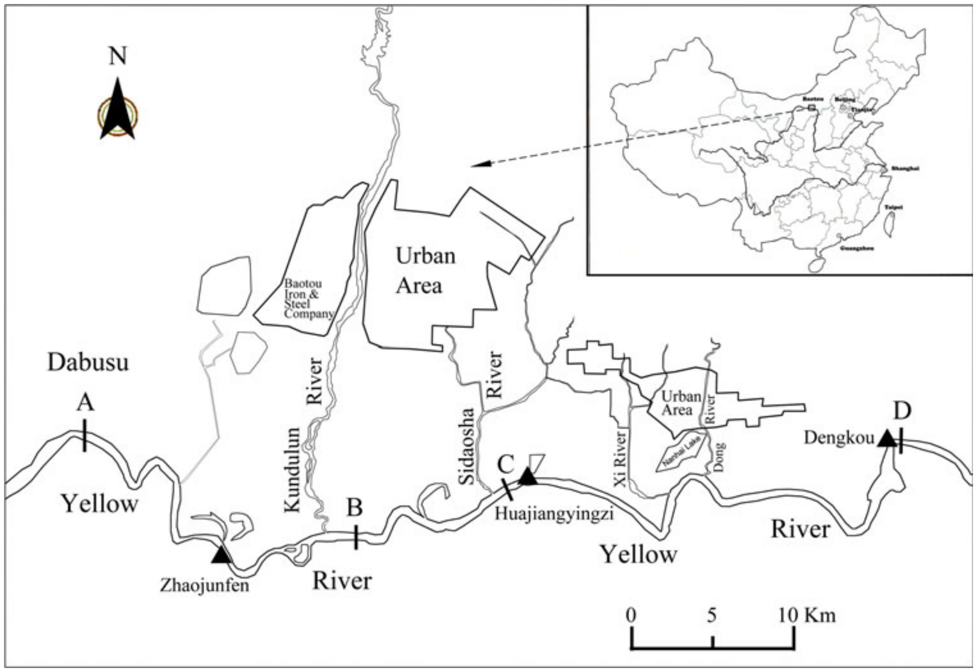


**Fig. 1** Locations of sampling points along the Yellow River

sediments was performed by the five-step sequential extraction technique of Tessier et al. (1979). The concentrations of Zn, Cd, Cu, and Pb in all the samples were determined by flame and graphite furnace AAS (Z-5000; Hitachi, Japan). Recoveries of Cu, Pb, Zn, and Cd were 96, 102, 93, and 97%, respectively, and the coefficients of variation were always <8%.

All the acids used in the experiments were guaranteed reagents; other chemical reagents were analytically pure, and water was double deionized.

## Results and discussion

### Metal levels in the fish muscle, and analysis of food safety

Zn and Cu are required by a wide variety of enzymes and other cell components of organisms and are essential elements. The recommended dietary allowance (RDA) for zinc is 15 mg $day^{-1}$ for men, 12 mg $day^{-1}$ for women, 10 mg $day^{-1}$ for children, and 5 mg $day^{-1}$ for infants (Agency for Toxic Substances and Disease Registry 1999). When 10–15 times the RDA is exceeded, it will harm human health. The dietary allowance for Cu recommended by the National Research Council (1999) is 1.5–3.0 mg for adults, 0.7–1.5 mg for children, and 0.4–0.7 mg for infants. Given children's daily food intake of 1 kg, maximum permissible concentrations of Zn and Cu are 100 and 15 μg $g^{-1}$ respectively. There are no Zn and Cu limits recommended by the Food and Drug Administration (FDA, USA). Permitted values of Cu and Zn are both 50 μg $g^{-1}$ according to the Chinese National Standards for tolerance limit of Cu and Zn in foods (GB15199-94, GB13106-91).

Pb and Cd are not essential elements for organisms. Permitted values of Pb and Cd strictly restricted by the EU are 0.2 and 0.05 μg $g^{-1}$, respectively. Daily intake of Pb recommended by the World Health Organization (1972) should not exceed 0.3 μg $g^{-1}$ (wet weight basis), and amounts of Pb and Cd permitted by the Chinese National Standards for tolerance limit of Pb and Cd in foods (GB14935-94, GB15201-94) are 0.5 and 0.1 μg $g^{-1}$ respectively.

The concentrations of the heavy metals analyzed in the body and muscle of the nine fish species are given in Table 1.

Zn concentrations in a total of 24 muscles and in the body of the investigated species were in the ranges 4.62–25.46 and 15.15–64.62 μg $g^{-1}$, with average values of 9.82 and 36.9 μg $g^{-1}$, respectively. According to the values mentioned above, Zn concentrations in the all muscles and the whole body of the nine selected species were much lower than the values permitted by the Chinese National Standards for tolerance limits of Zn in foods (GB13106-91); therefore, the muscle of the investigated fish was fit for human consumption.

In the United States Missouri, Zn concentrations in the muscle and whole body of sunfish from the Big River and Flat River Creek were in the ranges 7.6–29.8 and 23.6–173 μg $g^{-1}$, with averages of 15.3 and 49.5 μg $g^{-1}$ (Gale et al. 2004), respectively. These levels are slightly higher than those in the Baotou Urban Section.

**Table 1** Heavy metal concentrations in fish muscle and whole body (wet weight basis) (μg/g)

| | Family | Muscle/whole body | Cu | Pb | Zn | Cd |
|---|---|---|---|---|---|---|
| *Cyprinus carpio* | Cydrinidae | Muscle | 1.13 | 0.0217 | 9.34 | 0.0129 |
| | | Whole body | 1.32 | 0.0735 | 33.30 | 0.0133 |
| *Squaliobarbus curriculus* | Cydrinidae | Muscle | 0.64 | 0.0673 | 5.99 | 0.0147 |
| | | Whole body | 0.90 | 0.0939 | 18.21 | 0.0130 |
| *Carassius auratus auratus* | Cydrinidae | Muscle | 0.92 | 0.0849 | 12.83 | 0.0170 |
| | | Whole body | 1.25 | 0.1560 | 33.80 | 0.0321 |
| *Hemiculter leucisclus* | Cydrinidae | Muscle | 0.63 | 0.1981 | 16.65 | 0.0230 |
| | | Whole body | 1.23 | 0.2482 | 33.71 | 0.0476 |
| *Megalobrama amblycephala* | Cydrinidae | Muscle | 0.57 | 0.0714 | 6.95 | 0.0320 |
| | | Whole body | 1.21 | 0.1243 | 22.87 | 0.0417 |
| *Saurogobio dabryi* | Cydrinidae | Muscle | 0.73 | 0.0031 | 6.30 | 0.0068 |
| | | Whole body | 0.95 | 0.0593 | 18.17 | 0.0090 |
| *Perccottus glehni* | Eleotridae | Muscle | 0.50 | 0.0080 | 14.19 | 0.0056 |
| | | Whole body | 1.05 | 0.0123 | 26.22 | 0.0075 |
| *Abbottina rivularis (Basilewsky)* | Cydrinidae | Muscle | 0.83 | 0.0111 | 11.64 | 0.0094 |
| | | Whole body | 4.22 | 0.0209 | 33.80 | 0.0187 |
| *Hemibarbus maculatus* | Cydrinidae | Muscle | 0.66 | 0.0017 | 11.87 | 0.0095 |
| | | Whole body | 1.20 | 0.1214 | 39.98 | 0.0157 |
| Mean ± SD (muscle) | | $n = 24$ | 0.85 ± 0.71 | 0.052 ± 0.070 | 9.82 ± 4.6 | 0.015 ± 0.008 |
| Mean ± SD (whole body) | | $n = 24$ | 1.23 ± 1.04 | 0.139 ± 0.073 | 36.9 ± 7.8 | 0.024 ± 0.015 |
| Chinese National Standards | | | 50 | 0.5 | 50 | 0.1 |
| Standard code of China | | | GB15199-94 | GB14935-94 | GB13106-91 | GB15201-94 |
| EU standards for edible fish* | | | | 0.2 | | 0.05 |

* Commission Regulation (EC) No. 221/2002

Comparatively, Zn concentrations in lake freshwater fish in the Suzhou region (31.7 ± 8.9 μg $g^{-1}$, Dai et al. 1990), in the Heilongjiang reach of the Songhua River (1.1–5.7 μg $g^{-1}$, Yu 1994) and in the Chongqing reach of the Yangtze River of China (1.32 and 4.98 μg $g^{-1}$, respectively, He et al. 1998) were lower than those in the Baotou Urban Section. Based on this comparison, it was found that Zn concentrations in the muscle and whole body of fish from the Baotou Urban Section were higher than those in other rivers and lakes, and comparable with those of other studies carried out in polluted rivers, indicating that the Zn was obviously accumulated in the fish body because of the effect of heavy metal pollution in the Baotou Urban Section.

Cu concentrations in a total of 24 muscles and in the body of the investigated species were in the ranges 0.42–3.69 and 0.86–4.60 μg $g^{-1}$, with average values of 0.85 and 1.23 μg $g^{-1}$, respectively. Cu concentrations in the muscle of the nine selected species were in all cases much lower than levels permitted by the Chinese National Standards for tolerance limit of Cu in foods (GB15199-94), and near the RDA of United States ATSDR, indicating that the muscle of investigated fish was fit for human consumption.

In the Big River and Flat River Creek (Gale et al. 2004), Cu concentrations (0.002–1.07 μg $g^{-1}$, with an average of 0.309 μg $g^{-1}$) in the fish muscle of sucker only correspond to 36.4% of those in the Baotou Urban Section. Mean Cu concentrations (0.99 μg $g^{-1}$) in the whole body of bullhead in Devens reach of Nashua river were similar to those in the study area. In the freshwater lake in the Suzhou region of China (Dai et al. 1990), Cu concentrations (3.18 ± 0.57 μg $g^{-1}$) in the whole body were 2.58 times higher than those in the study area; Cu concentrations (1.162 μg $g^{-1}$) in the fish muscle in the Heilongjiang reach of the Songhua River (Yu 1994) were 1.37 times higher than those in the study area; Cu concentrations (0.48 μg $g^{-1}$) in the muscle of *Saurogobio dabryi* in the Chongqing reach of the Yangtze River (He et al. 1998) only correspond to 56.5% of those in the study area. As mentioned above, the Cu concentrations in the muscle and whole body were not high which indicated there were no obvious Cu accumulation and contamination in the Baotou Urban Section.

Pb concentrations in the muscle and whole body were in the ranges 0.00–0.33 and 0.013–0.325 μg $g^{-1}$ with average values of 0.052 and 0.139 μg $g^{-1}$, respectively, which were lower than the levels of the Chinese National

Standards for tolerance limit of Pb in foods (GB14935-94). The Pb concentration in the whole body of the *Hemiculter leucisclus* in the Baotou Urban Section exceeded the EU permitted value. According to the US Fish and Wildlife Service, the average whole body Pb concentration of 315 samples from 109 sites across the United States was 0.11 μg $g^{-1}$ with an maximum of 4.88 μg $g^{-1}$ (Schmitt and Brumbaugh 1990), which were very similar to those of the Baotou Urban Section. Compared with the Baotou Urban Section, Pb concentrations were higher in fish from the Devens reach of the Nashua River (0.59 μg $g^{-1}$) of the US, the Heilongjiang reach of the Songhua River (0.588 μg $g^{-1}$) (Yu 1994), the freshwater lake in the Suzhou region (1.5 ± 0.4 μg $g^{-1}$, Dai et al. 1990), and Wuhan City (0.114 μg $g^{-1}$, Qiao et al. 2007) of China. On the basis of the values mentioned above, Pb concentrations in the fish were at a basic natural level with no obvious accumulation in the Baotou Urban Section.

Generally, Cd is regarded as an easily accumulated pollutant in hydrobiota. Cd concentration ranges in a total of 24 muscles and the whole body of the nine investigated species were 0.006–0.032 and 0.008–0.049 μg $g^{-1}$ with average values of 0.015 and 0.024 μg $g^{-1}$ respectively, which were lower than the levels permitted by EU standards and Chinese National Standards for tolerance limit of Cd in foods (GB15201-94). Cd concentrations in the muscle and the whole body of sunfish in the Big River and Flat River Creek (Gale et al. 2004) were 0.016 and 0.239 μg $g^{-1}$ respectively. The levels in the muscle were very similar to those in the Baotou Urban Section, whereas the levels in the body were far higher than those in the Baotou Urban Section. The Cd concentrations in fish from the Devens reach of the Nashua river of US (0.15 μg $g^{-1}$), in freshwater lake fish in the Suzhou region (0.068 ± 0.043 μg $g^{-1}$, Dai et al. 1990), and in the Heilongjiang reach of the Songhua River of China (0.123 μg $g^{-1}$) (Yu 1994) were higher than those in the Baotou Urban Section. Accordingly, Cd concentrations in the fish bodies have no obviously accumulated trends in the study area.

Compared with the freshwater fish of other areas, Pb and Cd concentrations were at lower levels, Cu at moderate levels in the muscle and the whole body, and Zn was evidently enriched in the body because of the evident effect of environmental pollution in the study area. The research showed that the average Zn concentrations in the whole body of *Hemibarbus maculatus* and *Cyprinus carpio* exceeded the permissible level of the Chinese National Standards for tolerance limit of Zn in foods; Pb concentrations of the whole body in the *Hemiculter leucisclus* in the Baotou Urban Section exceeded the EU permissible level. Considering that Pb and Zn exceeded the permissible levels in the nonmuscle part, it is right to select muscle as much as possible for human consumption.

## Heavy metals accumulation in different fish species

### *Concentration differences of heavy metals in different fish species*

Differences between heavy metal concentrations in the investigated species may be related to fish habitat, mobility, and diet, or to other characteristic behavior. Generally, heavy metals were accumulated in the fish body mainly via direct exposure to metals in the water column and food chain in the water body, and biomagnification could enlarge the biotoxicity of the heavy metals. Cd was confirmed to be more readily enriched in the body via the food chain (Xu et al. 2006). The study showed that metal levels in the whole body in the Baotou Urban Section were ranked as follows: *Abbottina rivularis* > *Megalobrama amblycephala* > *Hemiculter leucisclus* > *Hemibarbus maculatus* > *Cyprinus carpio* > *Carassius auratus auratus* > *Perccottus glehni* > *Saurogobio dabryi* > *Squaliobarbus curriculus* for Cu, *Hemibarbus maculatus* > *Hemiculter leucisclus* > *Carassius auratus auratus* > *Megalobrama amblycephala* > *Cyprinus carpio* > *Squaliobarbus curriculus* > *Saurogobio dabryi* > *Abbottina rivularis* > *Perccottus glehni* for Pb, *Hemibarbus maculatus* > *Cyprinus carpio* > *Carassius auratus auratus* > *Hemiculter leucisclus* > *Abbottina rivularis* > *Megalobrama amblycephala* > *Perccottus glehni* > *Saurogobio dabryi* > *Squaliobarbus curriculus* for Zn, and *Hemiculter leucisclus* > *Megalobrama amblycephala* > *Carassius auratus auratus* > *Abbottina rivularis* > *Hemibarbus maculatus* > *Cyprinus carpio* > *Squaliobarbus curriculus* > *Saurogobio dabryi* > *Perccottus glehni* for Cd. This indicated that different fish species showed obvious differences in accumulation capacity for the heavy metals. A substantial amount of the heavy metals is likely to be adsorbed by sediment particles and might therefore constitute a risk especially to sediment-living and sediment-eating organisms. Accumulation of a contaminant in the aquatic environment is determined by its physical and chemical properties and its availability and persistence in water and the type of food chains exposed. Consequently, the life and feeding habits of fish can similarly affect heavy metal enrichment in the fish.

### *Assessment of heavy metal contamination in different fish species*

The pollution index method was used to assess the heavy metal accumulation in the nine species in this work. The comprehensive pollution index can be expressed as follows:

$$P_j = \sum_{i=1}^{n} P_{ij} \quad (1)$$

$$P_{ij} = \frac{C_{ij}}{C_{i0}} \quad (2)$$

where $P_j$ is the pollution integrated index of species $j$, $P_{ij}$ is the pollution index of pollutant $i$ for species $j$, $C_{ij}$ is the concentration of the pollutant $i$ for species $j$, $C_{io}$ is the evaluation standard of the pollutant $i$ and $n$ is the number of pollutants involved in the evaluation.

The results showed that the comprehensive accumulation indexes of heavy metals in different species were ranked *Hemiculter leucisclus* > *Carassius auratus auratus* > *Hemibarbus maculatus* > *Megalobrama amblycephala* > *Abbottina rivularis* > *Cyprinus carpio* > *Squaliobarbus curriculus* > *Perccottus glehni* > *Saurogobio dabryi* (Fig. 2). Studies have shown that heavy metals are strongly accumulated by the fish species inhabiting the bottom of lakes in the Suzhou region of China (Dai et al. 1990) and the Big River and Flat River Creek in the United States Missouri (Gale et al. 2004). Different from the results mentioned above, fish species inhabiting both the bottom and the upper parts of the water column concentrated heavy metals more readily than those inhabiting the middle-demersal water in the Baotou Urban Section. For example, the highest metal accumulation was found in *Hemiculter leucisclus* which inhabits the upper parts of the column. The heavy metal accumulation of fish species inhabiting different parts of the water column would be affected by breathing, food intake, direct exposure to metals, and suspended particulate matter in the aquatic environment. The Yellow River is world famous for its high suspended particulate matter. Relatively, the particle sizes of the suspended particulate matter (SPM) were very small and the heavy metal concentrations in the SPM were very high in the upper parts of the water column in the Baotou Urban Section. Accordingly, fish species such as *Hemiculter leucisclus*, which inhabit the upper parts of the water column, may have more chance of being contaminated by heavy metals. In addition, fish species such as *Hemibarbus maculates*, which inhabits the bottom and is exposed to the sediments polluted by heavy metals, because of sediment-living and sediment-eating (Fig. 2), may also accumulate much heavy metals. In terms of feeding habits, all investigated fish species were omnivorous. *Squaliobarbus curriculus* favors a herbivorous diet and *Perccottus glehni* favors a carnivorous diet; and the lowest heavy metal accumulations were found in these two fish species; this may be related to the high selectivity of their diet and less consumption of organic debris from the urban wastewater.

*Accumulation of heavy metals in fish tissues*

The results showed that significant differences of the heavy metal concentrations were found in the different tissues (Table 2; Figs. 3, 4, 5, 6). Generally, the lowest amounts of the heavy metals were found in the muscle among all fish species studied, indicating that it was safe for human consumption. The highest concentrations of Cu and Cd were found in the viscera of *Cyprinus carpio, Squaliobarbus curriculus, Carassius auratus auratus, Megalobrama amblycephala, Perccottus glehni, Abbottina rivularis*, and *Hemibarbus maculates* followed by *Hemiculter leucisclus* and *Saurogobio dabryi*, indicating that Cu and Cd were mainly taken up in food by all the fish species analyzed. The highest concentrations of Pb and Zn were found in the gills and fins of *Cyprinus carpio* and *Carassius auratus auratus*, indicating that Pb and Zn accumulation were closely related to breathing, food intake, and direct exposure to metals in the water column. Lower amounts of Pb were found in the skin and muscle of all the fish species studied, revealing that Pb was mainly accumulated by breathing and food intake, and not by direct exposure to metals in the water column. Higher Pb concentrations were found in the fins and bones, implying Pb probably had the potential to be enriched in the bones.

The results showed (Fig. 6) that concentrations of Cu in the different organs in the nine fish species studied were ranked viscera > fin > gill > bone > head > muscle > skin; Pb as: fin > gill > bone > viscera > skin > head > muscle; Zn as: fin > gill > head > bone > liver > skin > muscle; and Cd as: viscera > gill > muscle > fin > bone > head > skin, indicating that the different organs or tissues had different selectivity for heavy metals. Generally, the highest concentrations of heavy metals were found in the viscera, gills, and fins and the lowest in the skin and

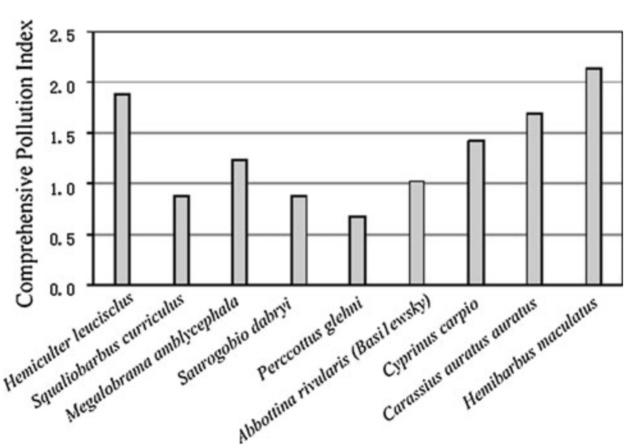


**Fig. 2** The heavy meals pollution index of commercial fish in the Yellow River

**Table 2** Order of heavy metal concentrations in different tissues of the nine species fish

| | Cu | Pb | Zn | Cd |
|---|---|---|---|---|
| *Cyprinus carpio* | viscera > gill > fin > muscle > bone, skin > head | gill > fin > bone > viscera > head > skin > muscle | gill > fin > viscera > head > bone > skin > muscle | viscera > fin > skin > bone > muscle > gill > head |
| *Squaliobarbus curriculus* | viscera > gill > bone > whole body > fin > muscle > head > skin | fin > gill > head > bone > muscle > viscera > whole body > skin | fin > viscera, gill, head, bone > whole body > skin > muscle | viscera > muscle > fin > whole body > bone > head > gill > skin |
| *Carassius auratus auratus* | viscera > fin > bone > muscle > gill > head > skin | fin > gill > viscera > bone > head > muscle > skin | fin > gill > head > viscera > bone > skin > muscle | viscera > gill > muscle > fin > skin > bone > head |
| *Hemiculter leucisclus* | viscera > gill > fin > head > skin > whole body > muscle > bone | gill > viscera > fin > muscle > head > whole body > skin > bone | Gill > fin > head > viscera > skin > bone > muscle > whole body | gill > viscera > whole body > muscle > head > skin > fin > bone |
| *Megalobrama amblycephala* | viscera > fin > bone > skin > gill > head > whole body > muscle | fin > viscera > gill > head > bone > muscle > whole body > skin | fin > head > bone > gill > viscera > whole body > skin > muscle | viscera > muscle > whole body > gill > head > fin > bone > skin |
| *Saurogobio dabryi* | gill > fin > viscera > head > muscle > bone > skin > whole body | fin > bone > head > skin > gill > viscera > whole body > muscle | fin > bone > head > gill > skin > viscera > whole body > muscle | viscera > bone > fin > skin > head > whole body > gill > muscle |
| *Perccottus glehni* | viscera > head > whole body > muscle | head > viscera > whole body > muscle | head > viscera > whole body > muscle | viscera > head > whole body > muscle |
| *Abbottina rivularis (Basilewsky)* | viscera > head > muscle | head > viscera > muscle | head > viscera > muscle | viscera > muscle, head |
| *Hemibarbus maculatus* | viscera > fin > bone > head > gill > skin > muscle | fin > bone > gill > skin > head > viscera > muscle | fin > gill > bone > head, viscera > skin > muscle | viscera > bone > fin > gill > skin > head > muscle |

muscle. The highest concentrations of Cu and Cd were found in the viscera, whereas Pb and Zn were highest in the fins, gills, and skeletons, which can be explained by the different affinity of the heavy metals for organs or tissue. In terms of accumulation routes, it could be deduced that the metals were mainly concentrated by the gills which could transport metals to other organs and tissues in the blood circulation; the metals in food were also assimilated by alimentary canal and then transferred to the blood and liver. The lower concentrations of the metals in the skin indicated there was little accumulation of the metals via permeable exchange between the fish body surface and the water, indicating that concentrations of dissolved metals were low in the water environment. The lowest mean metal concentrations found in the muscles may be related to the muscle being the extremity of heavy metals migration.

Site competition and metallothionein (MT) induction are the major mechanisms accumulating metals in fish bodies. MT, with a low-molecular-weight (6,000–7,000 Da), could selectively bind the metals (Marafante 1976; Roesijadi 1992). It is notable that MT (divided into MTI and MT2 subtypes) is rich in dicysteine (20 of 60 amino acids) and cystine (Dunn et al. 1987). Site competition between Cd and Cu and for both Zn and Pb was found in the gills of *Carassius auratus auratus* (Zhou et al. 2002). Because Cd and Zn bound with the gills more strongly than Cu and Pb, Cu and Pb concentrations were reduced in the gills. Accumulation of heavy metals in the liver may be mainly related to metallothionein (MT) induction. Pb and Cd as non-essential elements can stimulate the liver and strongly activate MT genes transcription and expression. Accordingly, heavy metals were more enriched with increasing the MT genes in the liver. Therefore, the order of accumulation liver > gill > muscle was obtained for Cu and Pb. In this work, the accumulation of Cu by the fish species studied was basically in agreement with the above order. But for Pb, higher accumulation was found in the gill, with the order fin > gill > bone > viscera > skin > head > muscle. This can be explained by the fact that the dissolved heavy metal concentrations were lower in the water because it was mainly adsorbed by the suspended particulate matter; therefore, uptake of the heavy metals depended more on the gill micro-environment from the suspended particulate matter.

## The correlation between metal levels in fish body and fish length and weight

Significant negative correlation between fish age (and weight) and Cd concentrations, and significant positive correlation between age (and weight) and Cu, Pb, and Zn concentrations were found in the Tilapia of the sabal channel, Al-Menoufiya province, Egypt (Authman 2008).

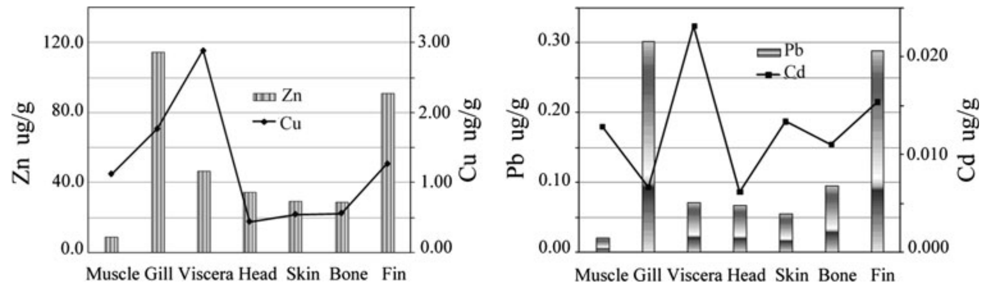


**Fig. 3** Heavy metal distribution in organs of *Cyprinus carpio* in the Baotou Section

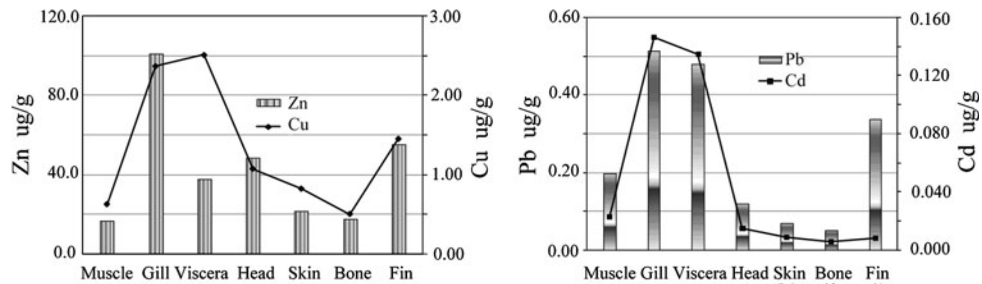


**Fig. 4** Heavy metal distribution in organs of *Hemiculter leucisclus* in the Baotou Section

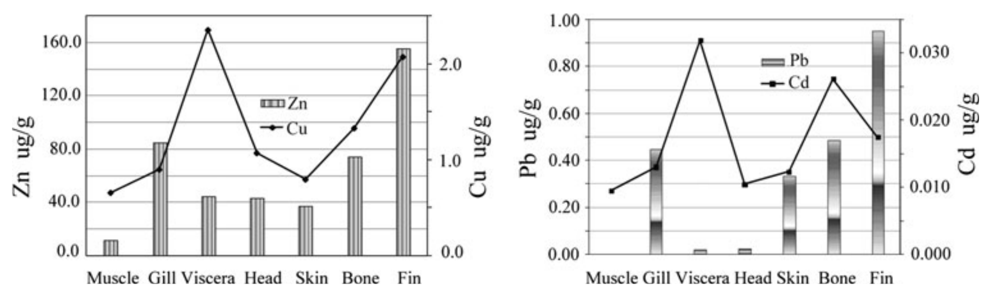


**Fig. 5** Heavy metal distribution in organs of *Hemibarbus maculatus* in the Baotou Section

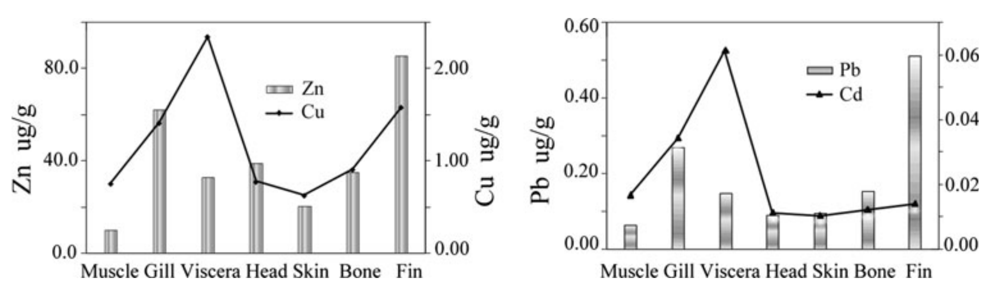


**Fig. 6** Heavy metal distribution in the organs of seven species economic fish in the Baotou Section

Studies (Sun and Jeng 1998) have shown that the Zn accumulation in juvenile fish increased with age, reached a peak in 130 days, then gradually decreased and tended to a constant. The results indicate body concentrations of accumulated metals vary enormously across metals and fish species with changes of fish age in different environments.

To investigate the accumulation of heavy metals in fish, Yellow River *Cyprinus carpio*, which are the most representative fish species in this study area, were divided into six grades with the weight ranges of 8–502 g, and *Squaliobarbus curriculus* into four grades with the weight ranges of 0.5–210 g according to the weight and the numbers of the fish caught. The *Carassius auratus auratus,*

**Table 3** Grades of fish weight and length in the Yellow River

| Grade | Item | *Cyprinus carpio* | *Squaliobarbus curriculus* | *Carassius auratus auratus* | *Hemiculter leucisclus* | *Megalobrama amblycephala* | *Saurogobio dabryi* |
|---|---|---|---|---|---|---|---|
| 1 | Weight (g) | 398–502 | 192–210 | 9–28 | 20–35 | 8.8–24.1 | 18–25 |
| | Average weight (g) | 468 | 200 | 13.9 | 24.1 | 15.1 | 19.35 |
| | Length (mm) | 302–256 | 257–264 | 89–125 | 142–168 | 110–142 | 122–134 |
| | Average length (mm) | 328 | 260 | 98.8 | 146.3 | 124.7 | 129.5 |
| | *n* | 3 | 3 | 14 | 6 | 9 | 5 |
| 2 | Weight (g) | 210–323 | 156–175 | 4–9 | 9.8–17 | 5.4–8.4 | 7.9–14 |
| | Average weight (g) | 286 | 167 | 7.5 | 13.3 | 6.74 | 9.8 |
| | Length (mm) | 242–296 | 238–255 | 70–90 | 115–133 | 88–98 | 101–109 |
| | Average length (mm) | 273 | 248 | 78 | 123.7 | 93.4 | 105.3 |
| | *n* | 3 | 3 | 12 | 9 | 5 | 11 |
| 3 | Weight (g) | 72–103 | 9–19 | 1.4–4 | 1.2–2.6 | 0.9–2.5 | 2.4–3.9 |
| | Average weight (g) | 80 | 13.2 | 2.6 | 1.73 | 1.7 | 2.97 |
| | Length (mm) | 182–196 | 105–130 | 51–66 | 52–66 | 45–60 | 62–73 |
| | Average length (mm) | 185 | 118 | 57.8 | 58.1 | 52 | 66.6 |
| | *n* | 4 | 9 | 21 | 10 | 15 | 15 |
| 4 | Weight (g) | 52–70 | 0.5–3.6 | | | | |
| | Average weight (g) | 63 | 1.7 | | | | |
| | Length (mm) | 170–180 | 40–70 | | | | |
| | Average length (mm) | 177 | 52 | | | | |
| | *n* | 4 | 13 | | | | |
| 5 | Weight (g) | 25–50 | | | | | |
| | Average weight (g) | 41 | | | | | |
| | Length (mm) | 135–160 | | | | | |
| | Average length (mm) | 149 | | | | | |
| | *n* | 5 | | | | | |
| 6 | Weight (g) | 8–18 | | | | | |
| | Average weight (g) | 12 | | | | | |
| | Length (mm) | 88–99 | | | | | |
| | Average length (mm) | 92 | | | | | |
| | *n* | 14 | | | | | |

*Hemiculter leucisclus, Megalobrama amblycephala*, and *Saurogobio dabryi* were all small-sized fish species with the body weight ranges of 0.9–28 g and were divided into three grades (Table 3). Generally, the weight of the fish caught was low, which may be relate to long-term over-fishing.

As can be seen in Table 4, metal levels accumulating in tissues varied in the different organs of *Cyprinus carpio*, indicating different absorption mechanisms. No significant correlations were found between fish weight (and length) and metal concentrations in the body of *Cyprinus carpio*. However, there was a trend of increasing Cu and Zn with increasing fish weight and length. In contrast, Pb and Cd accumulating in the body decreased with increasing fish weight and length. Because metal concentrations in the aquatic environment have not yet reached a dangerous level, the ability to actively absorb essential metals and resist non-essential metals increased synchronously with the growth of fish. In terms of specific organs, significant correlations were found between fish weight and Pb in muscle and bone, Zn in the gills, and Cu in viscera. The correlations between fish length and metal concentrations in the organs were basically similar to those of the weight; there was a significant correlation between Cu concentrations in the organs and the size of the individual fish, with the exception of viscera. These results indicate that Pb was easily accumulated in the muscle and bone of *Cyprinus carpio*, with potential ecological risks as a non-essential toxic metal.

As can be seen in Table 5, the Cu, Zn, and Cd content of the whole body evidently decreased with increasing weight

**Table 4** Correlations between fish weight (and length) and heavy metals in *Cyprinus carpio* tissues

| | Item | Tissue | Length | Cu | Pb | Zn | Cd |
|---|---|---|---|---|---|---|---|
| Weight | Pearson correlation | Whole body | 0.959** | 0.706 | −0.230 | 0.526 | −0.614 |
| | Sig. (two-tailed) | | 0.002 | 0.117 | 0.661 | 0.283 | 0.194 |
| Length | Pearson correlation | | 1 | 0.641 | −0.196 | 0.383 | −0.589 |
| | Sig. (two-tailed) | | | 0.170 | 0.710 | 0.453 | 0.219 |
| Weight | Pearson correlation | Muscle | 0.959** | 0.734 | 0.975** | 0.342 | 0.565 |
| | Sig. (two-tailed) | | 0.002 | 0.096 | 0.001 | 0.507 | 0.242 |
| Length | Pearson correlation | | 1 | 0.535 | 0.887** | 0.226 | 0.372 |
| | Sig. (two-tailed) | | | 0.274 | 0.018 | 0.666 | 0.468 |
| Weight | Pearson correlation | Gill | 0.959** | −0.144 | −0.225 | 0.959** | −0.418 |
| | Sig. (two-tailed) | | 0.002 | 0.786 | 0.668 | 0.003 | 0.410 |
| Length | Pearson correlation | | 1 | −0.072 | −0.095 | 0.972** | −0.228 |
| | Sig. (two-tailed) | | | 0.891 | 0.858 | 0.001 | 0.664 |
| Weight | Pearson correlation | Viscera | 0.959** | 0.825* | 0.697 | 0.735 | −0.508 |
| | Sig. (two-tailed) | | 0.002 | 0.043 | 0.124 | 0.096 | 0.303 |
| Length | Pearson correlation | | 1 | 0.663 | 0.630 | 0.692 | −0.495 |
| | Sig. (two-tailed) | | | 0.151 | 0.180 | 0.127 | 0.318 |
| Weight | Pearson correlation | Skin | 0.959** | 0.128 | −0.345 | 0.623 | −0.408 |
| | Sig. (two-tailed) | | 0.002 | 0.810 | 0.502 | 0.186 | 0.423 |
| Length | Pearson correlation | | 1 | 0.097 | −0.590 | 0.577 | −0.383 |
| | Sig. (two-tailed) | | | 0.855 | 0.218 | 0.231 | 0.453 |
| Weight | Pearson correlation | Bone | 0.959** | 0.222 | 0.938** | 0.450 | −0.561 |
| | Sig. (two-tailed) | | 0.002 | 0.673 | 0.006 | 0.371 | 0.246 |
| Length | Pearson correlation | | 1 | 0.308 | 0.893* | 0.200 | −0.660 |
| | Sig. (two-tailed) | | | 0.553 | 0.016 | 0.704 | 0.154 |
| Weight | Pearson correlation | Fin | 0.959** | −0.389 | −0.309 | −0.535 | −0.376 |
| | Sig. (two-tailed) | | 0.002 | 0.446 | 0.551 | 0.275 | 0.462 |
| Length | Pearson correlation | | 1 | −0.358 | −0.551 | −0.661 | −0.394 |
| | Sig. (two-tailed) | | | 0.486 | 0.257 | 0.153 | 0.439 |

$N = 6$

** Correlation is significant at the 0.01 level (two-tailed)

* Correlation is significant at the 0.05 level (two-tailed)

of *Squaliobarbus curriculus*. For Pb, however, there was no correlation. This indicated that body concentrations of accumulated metals were decreased with increasing growth of *Squaliobarbus curriculus*, a herbivorous fish species living near the surface of the water.

In contrast with *Cyprinus carpio*, body concentrations of accumulated Cu and Zn in *Carassius auratus* decreased with increasing weight, whereas Pb and Cd concentrations increased with increasing weight (Table 6). Accumulated amounts of essential and non-essential metals decreased and increased, respectively, with increasing weight, indicating that *Carassius auratus*, an omnivorous fish species living near the bottom, could be badly affected by accumulated metals. Accumulated amounts of metals in each tissue of *Carassius auratus* all increased with increasing weight. There were significant positive correlations between weight and the Pb and Cd content of the viscera, and there seemed to be significant negative correlations between weight and Pb content of the muscle and Cu content of the bone.

*Carassius auratus auratus* inhabit the bottom, close to sediments where they burrow and feed. This resulted in accumulation of metals by *Carassius auratus auratus* because of its feeding habits. The negative correlations between fish weight and Pb content of the muscle showed that amounts of Pb accumulated by *Carassius auratus auratus* were still low.

For metals accumulated by *Hemiculter leucisclus* there was a trend of increasing body concentrations with increasing weight, indicating that *Hemiculter leucisclus* are exposed to the highest heavy metal contamination among the nine fish species studied. *Hemiculter leucisclus* is a physically agile and omnivorous small fish species inhabiting the upper parts of the water column, and with the

**Table 5** Correlations between fish weight and heavy metals in *Squaliobarbus curriculus* tissues

| | Items | Tissues | Cu | Pb | Zn | Cd |
|---|---|---|---|---|---|---|
| Weight | Pearson correlation | Whole body | −0.621 | 0.091 | −0.937 | −0.750 |
| | Sig. (two-tailed) | | 0.379 | 0.909 | 0.063 | 0.250 |
| Weight | Pearson correlation | Muscle | −0.265 | 0.785 | −0.424 | 0.614 |
| | Sig. (two-tailed) | | 0.735 | 0.215 | 0.576 | 0.386 |
| Weight | Pearson correlation | Gill | −0.217 | 0.216 | 0.127 | −0.429 |
| | Sig. (two-tailed) | | 0.783 | 0.784 | 0.873 | 0.571 |
| Weight | Pearson correlation | Viscera | 0.349 | −0.354 | 0.605 | −0.705 |
| | Sig. (two-tailed) | | 0.651 | 0.646 | 0.395 | 0.295 |
| Weight | Pearson correlation | Bone | −0.645 | −0.366 | −0.981* | −0.348 |
| | Sig. (two-tailed) | | 0.355 | 0.634 | 0.019 | 0.652 |

$N = 4$

* Correlation is significant at the 0.05 level (two-tailed)

peculiarity of accumulating heavy metals by feeding on floating organic debris. There was a significant negative correlation and a better negative correlation between body weight and Cu content of muscle and bone, respectively, whereas the Pb and Cd content of the viscera seemed to be significant positively correlated with the body weight.

For metals accumulated by *Megalobrama amblycephala* there was a trend of decreasing body and tissue concentrations with increasing weight, with the exception of Pb. This indicated this fish species had the ability to resist heavy metal contamination with growth.

There were positive correlations between fish weight and accumulated metals in the *Saurogobio dabryi*. *Saurogobio dabryi* is a small fish which inhabits the middle-demersal water. Its diet consists mainly of aquatic animals, so it is less exposed to sediment-associated contamination. As a result, tissue concentrations of accumulated metals in this species were the lowest in all species studied.

## Heavy metal bioaccumulation and migration in the Baotou Urban Section

### *Correlations between heavy metals in the fish*

Natural waters are contaminated with many heavy metals (Gischler 2005), so intake of one heavy metal by fish is affected by other metals. With the exception of *Perccottus glehni* and *Abbottina rivularis*, for seven tissues (muscle, gill, viscera, head, skin, bones, fins) of each of the seven fish species studied (a total of 49 samples), the relationship between tissues and metal concentrations were investigated by bivariate Pearson correlation analysis (SPSS 13.0 software). The product–moment correlation coefficients and significance test results are given in Table 7.

Significant positive correlations were obtained between the metal pairs Pb–Zn, Cu–Cd, Cu–Zn, and Cu–Pb with Pearson correlation coefficients of 0.819 ($p < 0.001$), 0.608 ($p < 0.001$), 0.425 ($p < 0.002$), and 0.364 ($p < 0.01$), respectively. However, there were no significant correlations between Pb and Cd in the tissues, or between Zn and Cd. Positive correlations imply there is no competition between the metals, and significant positive correlations indicate there were synergisms, with a linear relationship between the metals.

The product–moment correlation coefficients and their significance test results are given in Table 8. As can be seen from Table 8, there were significant negative correlations between the metal content of each tissue of the fish species studied, indicating no competition between the metals in each tissue. Significant positive correlations were found between Cd–Pb, Cd–Zn, and Cd–Cu in the bones and heads, Cd–Zn and Cd–Pb in the fins and viscera, and Zn-Cu in the head and viscera, and Zn-Pb in the head, muscle, bone, and skin. Irrespective of the species, metal concentrations in the tissues measured in this study all showed a poor correlation between Pb and Cu concentrations. Bone, head, and fins mainly consisting of skeleton were the extremity of metal migration with less physiological function. Thus the metal concentrations accumulated in these tissues were mainly controlled by the biochemical properties of the metals and the skeleton. Generally, the proportion and rate of the metal storage and excretion were stable. Therefore, whatever the species, there were strong correlations between the metal content of these tissues. As the major organs of uptake, storage, and transfer of metals, viscera could take up and accumulate a specific proportion of metals whether essential Cu and Zn or non-essential Pb and Cd. There were, therefore, significant correlations between the metal contents of viscera.

**Table 6** Correlations between fish weight and heavy metals in tissues of *Carassius auratus auratus, Hemiculter leucisclus, Megalobrama amblycephala*, and *Saurogobio dabryi*

| | Items | Species | Tissues | Cu | Pb | Zn | Cd |
|---|---|---|---|---|---|---|---|
| Weight | Pearson correlation | *Carassius auratus auratus* | Whole body | −0.892 | 0.807 | −0.582 | 0.986 |
| | Sig. (two-tailed) | | | 0.298 | 0.402 | 0.605 | 0.106 |
| Weight | Pearson correlation | *Carassius auratus auratus* | Muscle | −0.753 | −0.995 | −0.687 | 0.432 |
| | Sig. (two-tailed) | | | 0.457 | 0.067 | 0.518 | 0.715 |
| Weight | Pearson correlation | *Carassius auratus auratus* | Gill | −0.789 | 0.612 | 0.392 | 0.417 |
| | Sig. (two-tailed) | | | 0.421 | 0.581 | 0.744 | 0.726 |
| Weight | Pearson correlation | *Carassius auratus auratus* | Viscera | −0.788 | 0.965 | −0.855 | 0.978 |
| | Sig. (two-tailed) | | | 0.422 | 0.170 | 0.348 | 0.134 |
| Weight | Pearson correlation | *Carassius auratus auratus* | Bone | −0.990 | −0.189 | −0.218 | −0.903 |
| | Sig. (two-tailed) | | | 0.090 | 0.879 | 0.860 | 0.283 |
| Weight | Pearson correlation | *Hemiculter leucisclus* | Whole body | 0.958 | 0.800 | 0.978 | 0.941 |
| | Sig. (two-tailed) | | | 0.185 | 0.410 | 0.135 | 0.219 |
| Weight | Pearson correlation | *Hemiculter leucisclus* | Muscle | −0.998* | 0.854 | 0.512 | −0.037 |
| | Sig. (two-tailed) | | | 0.041 | 0.348 | 0.658 | 0.976 |
| Weight | Pearson correlation | *Hemiculter leucisclus* | Gill | 0.780 | 0.465 | 0.932 | 0.955 |
| | Sig. (two-tailed) | | | 0.430 | 0.692 | 0.236 | 0.192 |
| Weight | Pearson correlation | *Hemiculter leucisclus* | Viscera | 0.989 | 0.139 | 0.577 | 0.816 |
| | Sig. (two-tailed) | | | 0.094 | 0.911 | 0.608 | 0.392 |
| Weight | Pearson correlation | *Megalobrama amblycephala* | Whole body | −0.989 | 0.260 | −0.907 | −0.724 |
| | Sig. (two-tailed) | | | 0.095 | 0.833 | 0.277 | 0.485 |
| Weight | Pearson correlation | *Megalobrama amblycephala* | Muscle | −0.786 | 0.671 | −0.733 | −0.928 |
| | Sig. (two-tailed) | | | 0.424 | 0.532 | 0.476 | 0.243 |
| Weight | Pearson correlation | *Megalobrama amblycephala* | Gill | 0.093 | 0.766 | −0.897 | −0.912 |
| | Sig. (two-tailed) | | | 0.941 | 0.445 | 0.292 | 0.269 |
| Weight | Pearson correlation | *Megalobrama amblycephala* | Viscera | −0.970 | −0.962 | −0.847 | −0.978 |
| | Sig. (two-tailed) | | | 0.155 | 0.177 | 0.357 | 0.132 |
| Weight | Pearson correlation | *Saurogobio dabryi* | Whole body | 0.867 | 0.189 | 0.981 | 0.939 |
| | Sig. (two-tailed) | | | 0.332 | 0.879 | 0.123 | 0.223 |
| Weight | Pearson correlation | *Saurogobio dabryi* | Muscle | 0.862 | −0.811 | −0.811 | 0.275 |
| | Sig. (two-tailed) | | | 0.339 | 0.398 | 0.398 | 0.823 |
| Weight | Pearson correlation | *Saurogobio dabryi* | Gill | 1.000** | −0.028 | −0.488 | 0.553 |
| | Sig. (two-tailed) | | | 0.007 | 0.982 | 0.675 | 0.627 |
| Weight | Pearson correlation | *Saurogobio dabryi* | Viscera | 0.711 | 0.213 | 0.805 | 0.644 |
| | Sig. (two-tailed) | | | 0.496 | 0.864 | 0.405 | 0.554 |

$N = 3$

* Correlation is significant at the 0.05 level (two-tailed)

** Correlation is significant at the 0.01 level (two-tailed)

The a previous study (Zhou et al. 2002) showed there was adsorption site competition between Cu and Cd in gills when Cu and Cd concentrations reached subacute toxicity levels of 100 and 10 μg $L^{-1}$, respectively, and negative and positive correlations between Cu and Cd were observed in the gills and in the viscera and brain respectively. In our survey there were significant positive correlations between the Cu and Cd content of the tissues as a whole (Figs. 7, 8, 9, 10, 11, 12); however, no significant correlations were found between pairs of metals in the gills and viscera, with the exception of the head (Table 8). Cu and Cd concentrations, only 1.88 and 0.50 μg $L^{-1}$, respectively, in filtered water from the study area, were too low to be effective competition in the gill.

There were significant differences in bonding strength between MT and metals, with the order ranked as Cu > Cd > Pb > Zn, in which Cu is 100 times higher than Cd. Generation of MT needed endogenous or exogenetic induction processes. Metals have the ability to induce MT expression and production in organisms, and induction

**Table 7** Correlations of heavy metals in seven species of fish

| | Pb | Zn | Cd |
|---|---|---|---|
| Cu | | | |
| Pearson correlation | 0.364* | 0.425** | 0.608** |
| Sig. (two-tailed) | 0.010 | 0.002 | 0.000 |
| Pb | | | |
| Pearson correlation | 1 | 0.819** | 0.281 |
| Sig. (two-tailed) | | 0.000 | 0.051 |
| Zn | | | |
| Pearson correlation | | 1 | 0.152 |
| Sig. (two-tailed) | | | 0.298 |

$N = 46$

* Correlation is significant at the 0.05 level (two-tailed)

** Correlation is significant at the 0.01 level (two-tailed)

ability can be ordered as Zn > Cd > Pb > Cu. The significant positive correlation between Cu and Cd and both Pb and Zn in each tissue of the fish species studied could be explained by the fact that, in the same tissues, induction of MT by Zn and Cd was stronger than that by Pb and Cu; this could induce and produce amounts of MT corresponding to concentrations of Zn and Cd and, as a result, intake of Pb and Cu were enhanced proportionally.

### *Bioconcentration factors for heavy metals in different fish species*

Accumulation of a contaminant by different organisms is very different, and is strongly affected by its physical and chemical properties, by its availability and persistence in water, and by the type of food chain involved. Bioconcentration is the process by which living organisms, especially those living in water, can collect and concentrate chemicals from the surrounding environment. It includes the effect on an organism's internal concentration as a result of the organism taking up a chemical via the respiratory surface and skin (uptake), moving it internally (distribution), changing it (metabolism), and returning it to the environment (elimination). Bioconcentration factors (BCF) are usually used to describe the accumulation of chemicals in organisms, primarily aquatic, that live in contaminated environments. According to EPA guidelines, the BCF is defined as the ratio of chemical concentration in the organism to that in the surrounding water. Bioconcentration occurs by uptake and retention of a substance from water only, through gill membranes or other external body surfaces (USEPA, 2000). The BCF can be expressed as follows:

$$\text{BCFs} = C_t/C_w \quad (3)$$

where $C_t$ is the particular heavy metal concentration in the fish body (μg $g^{-1}$) and $C_w$ is the dissolved concentration of the heavy metal in the water.

**Table 8** Correlations of heavy metals in each organ of seven species fish

| | Items | Tissues | Pb | Zn | Cd | *n* |
|---|---|---|---|---|---|---|
| Cu | Pearson correlation | | 0.470 | 0.257 | 0.390 | |
| | Sig. (two-tailed) | | 0.057 | 0.319 | 0.121 | |
| Pb | Pearson correlation | Gill | | 0.181 | 0.178 | |
| | Sig. (two-tailed) | | | 0.488 | 0.493 | 17 |
| Zn | Pearson correlation | | | | 0.152 | |
| | Sig. (two-tailed) | | | | 0.560 | |
| Cu | Pearson correlation | | 0.075 | 0.606** | −0.025 | |
| | Sig. (two-tailed) | | 0.776 | 0.010 | 0.923 | |
| Pb | Pearson correlation | Viscera | | 0.146 | 0.684** | |
| | Sig. (two-tailed) | | | 0.576 | 0.002 | 17 |
| Zn | Pearson correlation | | | | −0.057 | |
| | Sig. (two-tailed) | | | | 0.828 | |
| Cu | Pearson correlation | | 0.045 | 0.177 | −0.155 | |
| | Sig. (two-tailed) | | 0.836 | 0.408 | 0.468 | |
| Pb | Pearson correlation | Muscle | | 0.628** | 0.176 | |
| | Sig. (two-tailed) | | | 0.001 | 0.410 | 24 |
| Zn | Pearson correlation | | | | −0.117 | |
| | Sig. (two-tailed) | | | | 0.587 | |
| Cu | Pearson correlation | | 0.202 | 0.720** | 0.599** | |
| | Sig. (two-tailed) | | 0.343 | 0.000 | 0.002 | |
| Pb | Pearson correlation | Head | | 0.414* | 0.423* | 24 |
| | Sig. (two-tailed) | | | 0.044 | 0.039 | |
| Zn | Pearson correlation | | | | 0.606** | |
| | Sig. (two-tailed) | | | | 0.002 | |
| Cu | Pearson correlation | | 0.132 | **0.427** | 0.127 | |
| | Sig. (two-tailed) | | 0.603 | **0.077** | 0.614 | |
| Pb | Pearson correlation | Skin | | 0.334 | 0.020 | 24 |
| | Sig. (two-tailed) | | | 0.175 | 0.938 | |
| Zn | Pearson correlation | | | | 0.392 | |
| | Sig. (two-tailed) | | | | 0.108 | |
| Cu | Pearson correlation | | 0.175 | **0.441** | 0.455* | |
| | Sig. (two-tailed) | | 0.460 | **0.052** | 0.044 | |
| Pb | Pearson correlation | Bone | | 0.520* | 0.541* | 20 |
| | Sig. (two-tailed) | | | 0.019 | 0.014 | |
| Zn | Pearson correlation | | | | 0.810** | |
| | Sig. (two-tailed) | | | | 0.000 | |
| Cu | Pearson correlation | | −0.123 | 0.247 | 0.139 | |
| | Sig. (two-tailed) | | 0.626 | 0.324 | 0.583 | |
| Pb | Pearson correlation | Fin | | 0.480* | 0.020 | |
| | Sig. (two-tailed) | | | 0.044 | 0.937 | 18 |
| Zn | Pearson correlation | | | | 0.677** | |
| | Sig. (two-tailed) | | | | 0.002 | |

* Correlation is significant at the 0.05 level (two-tailed)

** Correlation is significant at the 0.01 level (two-tailed)

Bioconcentration factors were calculated on the basis of the mean concentrations of heavy metal in the filtered

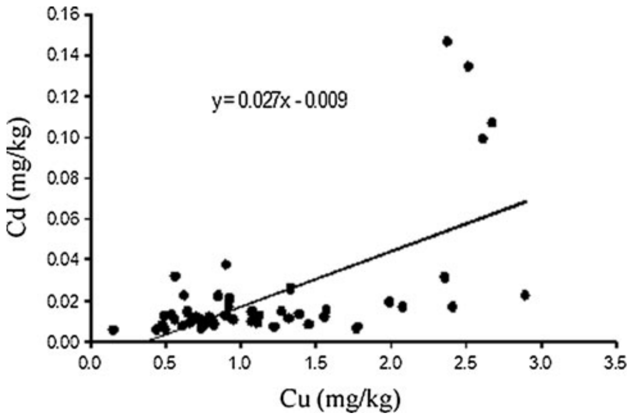


**Fig. 7** Correlation between Cu and Cd in the organs of seven fish species

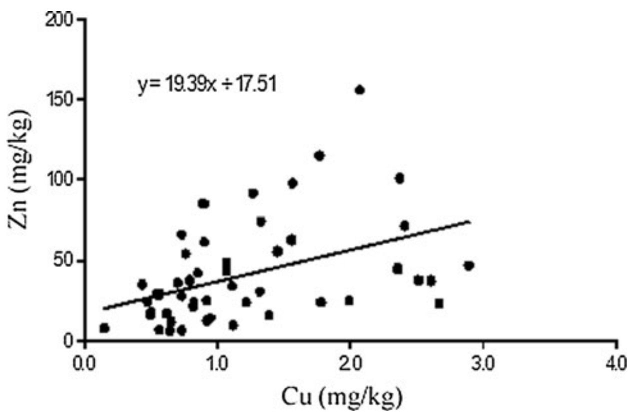


**Fig. 8** Correlation between Cu and Zn in the organs of seven fish species

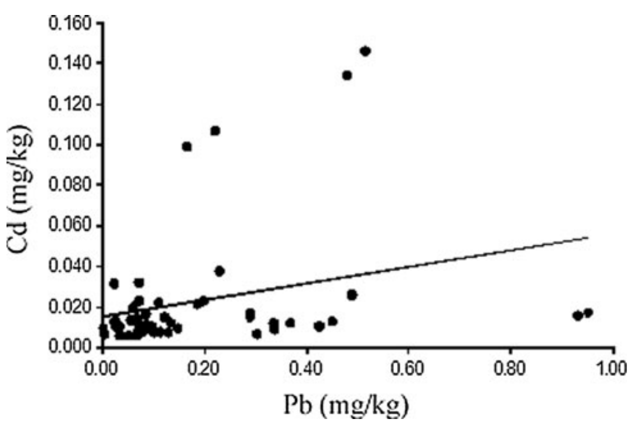


**Fig. 9** Correlation between Pb and Cd in the organs of seven fish species

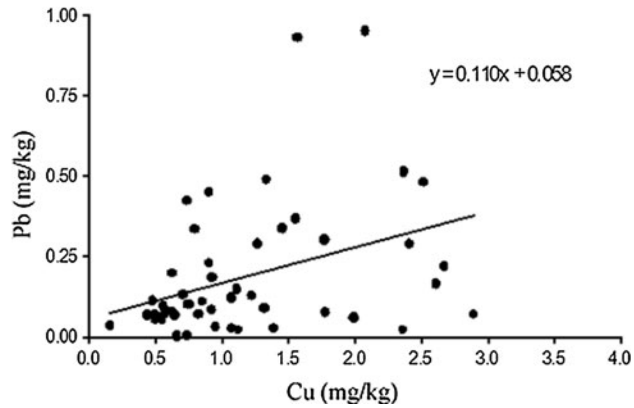


**Fig. 10** Correlation between Cu and Pb in the organs of seven fish species

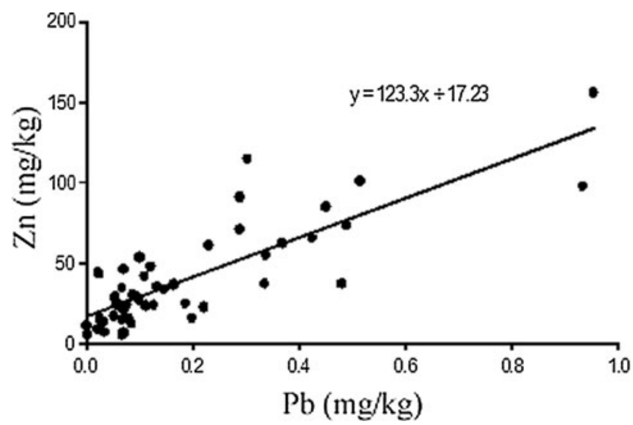


**Fig. 11** Correlation between Pb and Zn in the organs of seven fish species

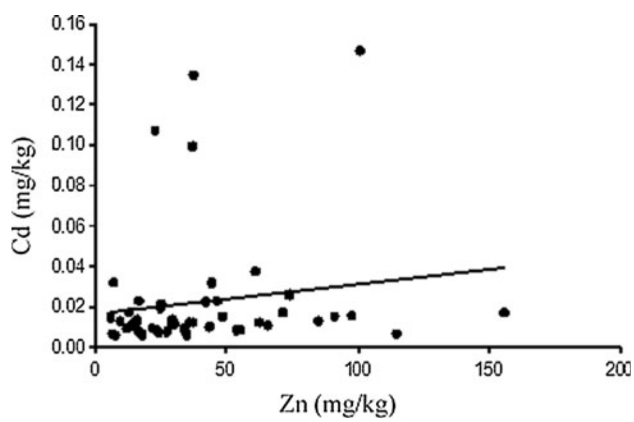


**Fig. 12** Correlation between Zn and Cd in the organs of seven fish species

water in the low water season from sites A, B, C,and D in the Baotou Urban Section (Table 9).

Significantly different BCFs for different heavy metals were found in the fish species studied. The mean values of BCFs for Zn reached orders of magnitude of $10^4$ whereas those for Pb and Cd were only 38 and 45, respectively (Table 10). According to the mean BCFs, the heavy metal concentrations in the investigated fish species were ranked Zn $\gg$ Cu $>$ Cd $\approx$ Pb, which was completely different from the sequence of adsorption capacities of the four

**Table 9** Average concentrations of heavy metals in overlying water and filtered water from the Baotou Section

| Heavy metals (μg $L^{-1}$) | Cu | Pb | Zn | Cd |
|---|---|---|---|---|
| Overlying water | 53.923 | 28.915 | 151.024 | 4.335 |
| Filtrated water | 1.877 | 2.68 | 2.825 | 0.496 |

**Table 10** Bioconcentration factors for the major commercial fish in the Baotou Section

| Species | Cu | Pb | Zn | Cd |
|---|---|---|---|---|
| *Cyprinus carpio* | 705 | 27 | 11,786 | 27 |
| *Squaliobarbus curriculus* | 479 | 35 | 6,448 | 26 |
| *Carassius auratus auratus* | 665 | 58 | 11,965 | 65 |
| *Hemiculter leucisclus* | 653 | 93 | 11,933 | 96 |
| *Megalobrama amblycephala* | 646 | 46 | 8,096 | 84 |
| *Saurogobio dabryi* | 507 | 22 | 6,431 | 18 |
| *Perccottus glehni* | 560 | 5 | 9,280 | 15 |
| *Abbottina rivularis (Basi1ewsky)* | 2,248 | 8 | 11,963 | 38 |
| *Hemibarbus maculatus* | 641 | 45 | 14,152 | 32 |
| Mean | 789 | 38 | 10,228 | 45 |

heavy metals (Pb > Cu ≫ Zn > Cd) (Fan et al. 2007). The sequence of BCFs revealed the different affinity of the different heavy metals for the fish. Among the four heavy metals, Zn and Cu play a crucial role in biological function in organisms, whereas Pb and Cd were non-essential for life. Fish could uptake and store essential elements, and eliminate toxic contamination in the process of the exchange interaction between the fish body and the surrounding environment. Generally, accumulation of heavy metals in fish bodies is controlled by their biochemical properties and physiological processes controlling taken up, accumulated, and excreted heavy metals. Toxicity does not depend on total accumulated metal concentration but is related to a threshold concentration of internal metabolically available metal. Toxicity ensues when the rate of metal uptake from all sources exceeds the combined rates of detoxification and excretion (if present) of the metal concerned.

Differences between accumulation of heavy metals were observed in the species investigated. For example, Zn and Cu were readily accumulated in *Hemibarbus maculatus* and *Abbottina rivularis* respectively; Pb and Cd were more accumulated in *Hemiculter leucisclus*, whereas Pb and Cd were most strongly discharged by *Perccottus glehni* (Table 10). These observations comprehensively reflected differences resulting from the living environment, feeding habits, and physiological function of fish.

Among the four metals, the concentrations and BCFs of Zn were highest in the investigated fish species. The reasons may be twofold:

1. As an essential element, Zn can be active taken up by the organisms which resulted in the Zn accumulation in the fish; and
2. It may be mainly because of the alkaline environment of the water in the studied area, in which Zn could be hydrolyzed into a soluble complex, increasing the concentration of dissolved Zn in the water.

Certainly, the gill micro-environments could also be conducive to Zn uptake from suspended particulate matter. In this work, concentrations of the four heavy metals measured in the gills in all investigated fish species were in all cases considerably higher than those of the other tissues, indicating that the metals were strongly taken up by the gills, and scant competition between the four metals. However, significantly different concentrations of the four metals were observed in the viscera. The highest concentrations of Cu and Cd were found in the viscera in all the fish species investigated, and the concentrations of Pb and Zn were lower than those of Cu and Cd. In contrast, the concentrations of Pb and Zn in the fins were higher than those of Cu and Cd. This revealed that the internal environment in the fish was propitious to transfer, storage, and excretion of Pb.

*Application and development of the bioaccumulation factors*

Heavy metals can be removed from the water column by sedimentation to the bottom sediments. Generally, heavy metals mainly in the dissolved form can be accumulated by aquatic organism by exchange reactions at the sediment–water interface (Croteau and Luoma 2005). Certainly, aquatic organisms can also accumulate heavy metals via food intake and direct exposure to metals in the water column. Amounts of suspended particulates in the Yellow River are very high, and can significantly affect absorption of the heavy metals by fish. Previous work indicated that Cu accumulation in Yellow River *Cyprinus carpio* and *Carassius auratus auratus* was markedly higher in the turbid water than in the fresh water, and there was a significant correlation between Cu concentrations in the fish body and those in the secondary phase of suspended particulate matter (Li et al. 1996). Previous studies also found that the effect of Cu on fish was about one order of magnitude lower in sediments than in water. $CO_2$ and ammonia nitrogen, discharged from the microenvironment of the fish gill through respiration, can affect the pH of the water flowing through the gills (Long et al. 2002). Concentrations of heavy metals in sediments were 2–4 orders of magnitudes higher than those of dissolved heavy metals in water in the Yellow River (Table 11). The pH of the Yellow River was approximately 8.0. Under such conditions, acidification and organic complexation co-exist in the micro-environment of *Cyprinus carpio* gills, which promotes dissolution of the heavy metals. In addition, wherever fish live, they always swallow large amounts of suspended matter and absorbed heavy metals from sediments, which pass through the digestive system.

Bioaccumulation is a process by which living organisms, especially those living in water, can collect and concentrate chemicals both directly from the surrounding environment (i.e. bioconcentration) and indirectly from their food. In order to thoroughly interpret the process of accumulation of heavy metals in fish, the bioaccumulation factor (BAF) was introduced in this work. BAF is defined as the ratio of the concentration of a chemical inside an organism to the concentration in the surrounding environment. It can be expressed as follows:

$$\mathrm{BAF_s} = C_t / C_s \tag{4}$$

where $C_t$ is a particular heavy metal concentration in fish tissues (μg $g^{-1}$) and $C_s$ is the concentration of the heavy metal in surface sediments (μg $g^{-1}$).

Heavy metals in the primary phase (residual form) are not involved in re-equilibrium distribution in the sediment–water system, and artificial pollution is mainly accumulated in the secondary phase (bio-available form) in sediments. Therefore, percentage heavy metal content of the secondary phase not only indicates trends of transformation of heavy metal forms in sediments, but also determines whether or not the heavy metals remobilize and migrate easily. Generally, bioaccumulation of heavy metals from sediments in fish is determined by its bioavailability. Dissolved and exchangeable forms have higher bioavailability; the bound-to-carbonate form which can be dissolved in the weak reduction and oxidation environment has also some bioavailability. Metals bound to Fe–Mn oxides and to organic matter are hardly absorbed by fish; and the residual form has no bioavailability (Chen 2003). Considering the results mentioned above, BAFs were calculated using different heavy metal forms in surface sediments as Cs values in this work (Table 11).

Using the concentrations of heavy metals in the secondary phase as Cs values, the BAFs of heavy metals in fish bodies were ranked Zn > Cu > Cd > Pb. BAFs of Zn reached 1.44, indicating that the Zn concentration was basically keeping in an equilibrium state between the fish body and sediments with a slight trend to enrichment in the fish body (Wang et al. 2008). Compared with the concentration sequence of the heavy metals in the secondary phase (Zn > Pb > Cu > Cd), Pb decreased substantially in the orders of the BAFs. The BAFs of Pb, Cu, and Cd were much less than unity, showing that the rate of excretion of metals exceeded the rate of uptake of the metals by the fish body.

The BAFs were calculated by using the concentrations of heavy metals in the secondary phase, because Cs values may be relatively small because the fractions of heavy metals with low bioavailability were very high in the secondary phase. When the sum of the exchangeable and bound-to-carbonate heavy metals were used as Cs values, the BAFs of Zn would reach as high as 4.467, indicating that Zn as an essential element can be strongly selectively absorbed by the fish. Based on the acute water quality criteria (WQC-acute) and chronic water quality criteria (WQC-chronic) recommended by the United States Environmental Protection Agency (USEPA), the concentration of Zn was partly higher than the water quality criteria (WQC) in filtered water in a high-water period. Zn from industrial discharge draining into the Yellow River was mainly adsorbed by the sediments. After adsorption, Zn, for the most part, was transformed into the exchangeable form and the carbonate-bound form (Fan et al. 2007). Zn can be hydrolyzed into multi-hydroxyl complexes

**Table 11** Bioaccumulation factors of fish in the Baotou Section

| | Cu | Pb | Zn | Cd |
|---|---|---|---|---|
| Heavy metal concentration (μg $g^{-1}$)[a] | 23.53 | 14.96 | 62.37 | 0.238 |
| Heavy metal concentration in the secondary phase (μg $g^{-1}$)* | 4.20 | 6.45 | 25.6 | 0.187 |
| Total concentration of exchangeable and carbonate bound forms (μg $g^{-1}$) | 1.29 | 1.00 | 8.26 | 0.101 |
| Partition coefficient of sediment–water system (KOC) | 12,536 | 5,582 | 22,078 | 480 |
| $\mathrm{BAF_{Sed}}$ | 0.052 | 0.009 | 0.592 | 0.101 |
| $\mathrm{BAF_{Sec}}$ | 0.293 | 0.022 | 1.44 | 0.128 |
| $\mathrm{BAF_{exc\text{-}Car}}$ | 0.953 | 0.139 | 4.467 | 0.238 |

$BAF_{Sed}$ BAFs calculated by using the concentrations of heavy metals in the sediments as Cs values, $BAF_{Sec}$ BAFs calculated by using the concentrations of heavy metals in the secondary phase as Cs values, $BAF_{exc\text{-}Car}$ BAFs calculated by using the total concentration of exchangeable and bound-to-carbonate forms as Cs values

[a] Average concentration of heavy metals in surface sediments from the Baotou Section of the Yellow River in dry season in 2004

($Zn(OH)_n^{(n-2)}$) under the slightly alkaline conditions in the Yellow River (pH 8.0); $Zn^{2+}$ can, furthermore, combine with amino acids and organic acids to produce soluble complexes in the aquatic environment, which causes Zn mobility from sediments to water (Fan et al. 2008). In addition, acidification and organic complexation co-exist in the micro-environment of the fish gill under the slightly alkaline conditions, which favors dissolution of the heavy metals. Therefore the Zn bioaccumulation in the fish from the study area can be interpreted as the combined actions of the factors mentioned above. The BAFs of Cu was 0.953, showing that the Cu concentration was basically in equilibrium between the fish body and sediments. The BAFs of Cd and Pb were 0.238 and 0.139 respectively, indicating the fish had strong ability to excrete non-essential elements. The studies found that the BAFs calculated by using the sum of the exchangeable and the bound-to-carbonate heavy metals as Cs values, can better indicate essential features of accumulated heavy metals in fish, which might provide an effective method for assessing bioaccumulation of heavy metals.

## Conclusions

These results showed that the fish species investigated had obvious differences in accumulation capacity for the heavy metals, and the levels of heavy metals accumulated by different species were ranked *Hemiculter leucisclus* > *Carassius auratus auratus* > *Hemibarbus maculatus* > *Megalobrama amblycephala* > *Abbottina rivularis* > *Cyprinus carpio* > *Squaliobarbus curriculus* > *Perccottus glehni* > *Saurogobio dabryi*. Considering that Pb and Zn exceeded permissible levels in the nonmuscle part, it was right to select muscle as much as possible for human consumption.

The different organs or tissues had different selectivity for heavy metals with the orders viscera > fin > gill > bone > head > muscle > skin for Cu, fin > gill > bone > viscera > skin > head > muscle for Pb, fin > gill > head > bone > liver > skin > muscle for Zn, and viscera > gill > muscle > fin > bone > head > skin for Cd.

The product–moment correlation coefficients among the metal pairs Pb–Zn, Cu–Cd, Cu–Zn, Cu–Pb, Pb–Cd, and Zn–Cd revealed there was no competition between metals in each tissue. The correlations between fish length (and weight) and heavy metals in the fish body indicated that accumulation of heavy metals by the fish species investigated was related to their surrounding environments and their life and feeding habitats.

According to the mean bioconcentration factors (BCFs), the heavy metal concentrations in the fish species investigated were ranked Zn $\gg$ Cu > Cd $\approx$ Pb. In this work, bioaccumulation factors (BAFs) were introduced and developed. The studies found that BAFs calculated by using the sum of exchangeable and the bound-to-carbonate heavy metals as Cs values can better indicate essential features of accumulated heavy metals in fish, which might provide an effective method for assessing bioaccumulation of heavy metals.

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