DISTRIBUTION OF HEAVY METALS (Pb, Zn, Cu, Cd AND Cr) FORM THE SOURCE OF THE PEARL RIVER, CHINA

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Abstract. The present paper has a research on the distribution and bioaccumulation of heavy metals (Pb, Zn, Cu, Cd and Cr) in the water, sediments, and three endemic fish species from the Huashan Reservoir, source of the Pearl River. The results showed that the water of Huashan Reservoir was under the grade II standard for most of the heavy metals according to the national environmental quality standard for surface water (GB3838-2002) launched by the State Environmental Protection Administration of China, and the metal concentrations of most surface sediments have exceeded the background values of the local soil in Yunnan Province. Furthermore, the Pb, Zn, Cu, Cd and Cr content in the sediment cores increased abruptly around early 1970s. Notably, most metals in all collected fish in this study didn't exceed the safety thresholds according to the national standards. Finally, the results found that the concentrations of heavy metals in the muscles of three fishes were all safe for human consumption, and the mean concentration in the fish organs followed the sequence of liver>gill>muscle.
Keywords: *Huashan Reservoir, heavy metals, water sediment, endemic fish*

Introduction

Heavy metals are normal constituents of the environment and widely present in aquatic ecosystems on a global scale. The heavy metal pollutions of rivers and reservoirs mainly come from the sewage discharge (Frascareli et al., 2018; Lan et al., 2019). Besides, geochemical structure, mining activity, metal smelting, industrial wastes, incineration of garbage and urban sewage discharge create potential sources of heavy metal pollution in the water bodies, too (Kumar et al., 2019; Kostka and Leśniak, 2020; Zhou et al., 2020). Heavy metals are deposited, assimilated or incorporated in water, sediments which can't be degraded by aquatic animals due to their chemical properties (Sobhanardakani et al., 2018; Debnath et al., 2021). Heavy metals will enter and accumulate in the food chain and they are non-biodegradable, persistent and potentially accumulated in organisms, causing extremely harmful to human bodies (Li et al., 2014; Isangedighi and David, 2019). Once above bioavailable threshold levels, they become toxic to human bodies (Ali et al., 2019; Singh et al., 2020).

Despite many municipal sewage treatments were established, water bodies and sediments are continuously being loaded with a large number of heavy metals. Especially the external physicochemical conditions might affect the enrichment of heavy metals in the sediments (Tian et al., 2020; Miranda et al., 2021). Sediments are significant sinks of heavy metals in the aquatic environment, but the heavy metals will release from sediments to the water bodies with the environment changed, leading the sediments as a monitor of the aquatic ecosystems

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(Al-Edresy et al., 2019; Ayodele et al., 2021). Sediment cores can provide an archive of environmental changes and show temporal and spatial differences in the concentrations of different heavy metals (Liu, R. et al., 2019; Liu, H. et al., 2022). Determining heavy metal content in water or sediments only can not provide information on heavy metal bioaccumulation or biomagnification. So clarifying the concentrations of heavy metal in sediment cores can provide a valuable historical record of heavy metal contamination.

Fish often accumulate large amounts of heavy metals from the water. Fish is not only long-living and absorb a variety of pollutants over time, but also normally occupy high positions in aquatic trophic webs so that they can be used as a biomonitor of heavy metal contamination, too (Kumar et al., 2020; Łuczyńska et al., 2020; Abu Shnaf et al., 2021). Fish optimally reflect the consequences of heavy metal pollution in the water (Adams et al., 1992; Merciai et al., 2014; Rajeshkumar and Li, 2018). Heavy metals can be classified as toxic (e.g., lead, cadmium and chromium) or essential (e.g., copper, zinc) for living organisms, but essential metals are toxic with a higher concentration (Munoz-Olivas and Camara, 2001). For this reason, to evaluate the potential risk to human health of fish consumption, determining the content of heavy metals in fish is extremely necessary (Buffle and DeVitre, 1993; Xie et al., 2020).

The study of heavy metal accumulation in fish tissues (muscle, liver and gills) is therefore interesting in assessing pollutions in natural water bodies. These tissues in fish were chosen because of that (1) the muscle was selected for its importance in case of fish consumption by humans; (2) liver is a crucial organ in the metabolism and storage of metals (Miller et al., 1992); (3) the gills reflect the metal levels in the water since they are the primary sites of gas exchange, acid-base regulation and ion transfer (Salem et al., 2014).

Pearl River is the third largest river in China, derived from southern Maxiong Mountain in Qujing, with an elevation of 1998 m, and then flows through the Huashan Reservoir. The Huashan Reservoir was finished in 1958, and the capacity of the reservoir was 80 million cubic meters. Nanpan River, the first stream upriver from the Pearl River, will cutoff if the Huashan Reservoir dries up. The local people have developed the fish farm in this reservoir; the *Cyprinus carpio*, *Carassius auratus* and *Anabarilius alburnops* can be found here easily. But there are many large chemical plants around the Huashan Reservoir. The annual production value of the industrial parks is nearly 50 billion. So there may be some heavy metal pollution in the reservoir. This area is important not only for the local people but also for the whole Pearl River basin. However, no research has been conducted on the distribution and behavior of metals in this area. In addition, the potential health risk should be concerned for intaking the endemic fish for local people. In a word, the line of study is lacking, specifically in the source of Pearl River.

The present study indicated Lead (Pb), Zinc (Zn), Cuprum (Cu), Cadmium (Cd) and Chromium (Cr) concentrations in water, sediments and some endemic fish (*Cyprinus carpio*, *Carassius auratus* and *Anabarilius alburnops*) in water of Hushan Reservoir. It should be noted that these fish species are considered an essential part of the diet in this region.

Material and methods

Collection of water and sediment samples

Water samples and sediment core samples were collected from 8 sites across the reservoir in June 2019. The coordinates of sampling were recorded with a global position system (*Table 1, Figure 1*). Water samples were collected with 4 L amber glass bottles. Nitric acid (1% by volume) was immediately added into the samples to suppress the metals binding with the container wall. Sediment core samples were collected up to a depth of 110 cm by a sampling

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vessel with a stainless steel gravity corer (*Figure 2*). The core was sectioned into twenty-two and finished at 5 cm intervals with a pre-cleaned stainless steel knife. All of the sectioned sediment core samples were placed into the labeled and sealed plastic pack, respectively. Both water and sediment core samples were placed into ice-packed coolers and transported to the laboratory as soon as possible. Water samples were refrigerated at 4°C until analysis, while sediment core samples were frozen at -35°C for further analysis.

Table 1. *GPS sites of water samplings and core samples in Huashan Reservoir*

Location	X (Longitude)	Y (Latitude)
C1	103.9158	25.7895
C2	103.9181	25.7826
C3	103.9210	25.7769
C4	103.9212	25.7710
C5	103.9024	25.7670
C6	103.9110	25.7674
C7	103.9314	25.7690
C8	103.9387	25.7755

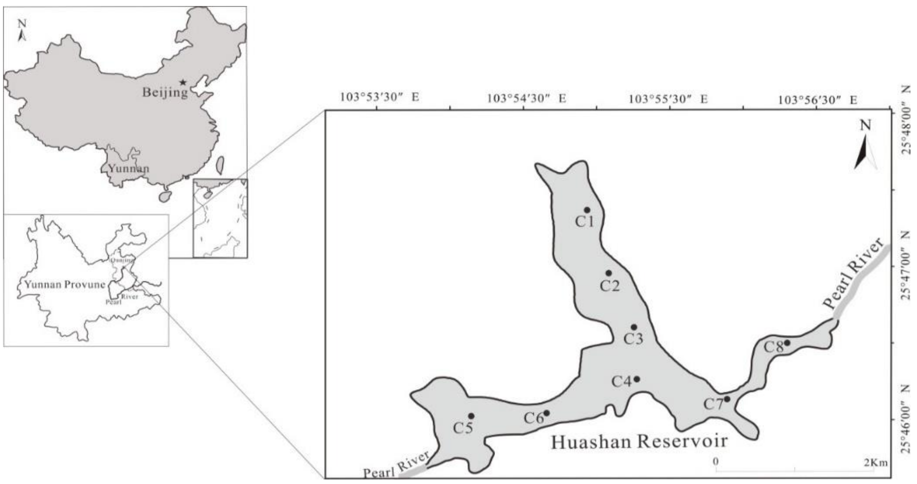

Figure 1. *Water and sediment core sampling sites in the Huashan Reservoir*

Collection of fish samples

Fish samples were collected from local fishermen across the reservoir, after they had been interviewed to ensure that the species had been caught in the area of interest for this study. Fish species were selected for analysis basing on several considerations (Keith et al., 2001) and considering the availability in the food chain from sampling sites, including their size (weight), migratory behavior and placement. As the fish species were meant to represent an area within a reservoir, fewer migratory species were preferred (Liu et al., 2011). Fish species analyzed in this paper include carp (*Cyprinus carpio,* body length 14.0-28.3 cm and body weight 98.0-507.5 g), crucian carp (*Carassius auratus,* body length 9.5-15.6 cm and body weight 56.2-211.0 g) and silvery minnow (*Anabarilius alburnops,* body length 5.3-6.8 cm and body weight 15.4-116.0 g), which were common in the reservoir and placed in the same position in the food chain. A total of 102 specimens, representing 3 species, were collected from six sites. Fish was immediately placed in coolers with ice and carried to the laboratory for sample preparation. All

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the equipment used for sample collection, transportation and preparation were free from contamination. The data of analyzed fish from each site were presented in *Table 2*.

Table 2. *Data of analyzed fish from Hushan Reservoir*

Species	Sampling sites					
	Huashan Town (F1)	The estuary of Nanpan River (F2)	Around the area of China Xuantian Grade I Road (F3)	Industrial Park (F4)	The East of Huashan Reservoir (F5)	The East of Huanshan Town (F6)
carp	5	6	7	4	7	6
crucian carp	7	5	3	5	3	4
silvery minnow	8	9	5	7	6	5

Chemicals and apparatus

All solvents in this study were of pure analytical grade or pure chromatographic grade. The standard stock solutions (1,000 μg ml^{-1}) of Pb, Zn, Cu, Cd and Cr were used. Solutions for standard curve preparation were made by appropriate dilution prior to use. All the plastic containers and glassware were soaked in dilute nitric acid (1+9) and rinsed with distilled water before use.

Microwave-assisted extraction was performed by ETHOS 1 advanced microwave extraction system (Milestone, Italy) equipped with a 12-sample tray and temperature control system. A flame/graphite atomic absorption spectrometer (AAFS, Varian Instruments AA240; Varian, America) was used for sample analysis in this study.

Sample preparation and analysis

Water samples were taken on-site and immediately measured for pH using Microwave-assisted extraction equipment (Milestone, Italy). Water samples were filtered through Millipore 0.45 μm glass fiber filters (Billerica, MA, USA) to remove algae, zooplankton, and suspended particles and then stored at 0-4 ºC. After that 15 ml water samples were digested with 2 ml of concentrated HNO_3 (65%) and 1 ml H_2O_2 (30%) at 180ºC for 10 min. A blank digestion was carried out in the same way.

Sediment samples were freeze-dried and passed through a 1 mm clean plastic sieve to remove shell fragments. Sieved sediments were ground with an agate mortar until all particles passing a 100-mesh nylon sieve (pore diameter: 0.147 mm). For the total content determination of heavy metals in sediments, our previous report about microwave-assisted digestion (MAD) procedures with some modifications was adopted (Li et al., 2014). Firstly, 0.2 g sediment samples were digested with 4 ml HNO_3 (65%), 2 ml H_2O_2 (30%) and 1 ml HF (40%) at 200 ºC for 5 min. It took 26 minutes to accomplish the set program process. A blank digestion process was carried out in the same way. After cooling, the supernatant was separated from the solid phase by filtration and then diluted into a colorimetric cylinder until the requisite volume arrived with double deionized water (Milli-Q Millipore 18.2 M cm^{-1} resistivity) (Liu et al., 2012). Eight sediment samples were subjected to three technical replications. The dating of the sediment samples was extrapolated utilizing a 137Cs chronology, which refers to the magnitude of 137 Cs activity having two peaks at all core sampling points. This procedure provides the possibility of calculating sedimentation rates from 1963-1986 and 1986 to the present (Xue et al., 2007).

Total nitrogen (TN) and total phosphorus (TP) was measured using potassium persulfate digestion-UV spectrophotometric method (GB11894-89, GB11893-89). An oxidising agent is

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added to the water, and after the oxidation is completed, the oxidised solution is subjected to an atomic absorption spectrometer for colorimetric measurement of total nitrogen and total phosphorus.

For the determination of heavy metals, after the samples were collected, the water samples were firstly digested with a combination of HNO_3-H_2O_2 acid system and elevated temperature; For the sediment, a certain amount of sediment was first taken, wrapped in aluminium foil and placed in an oven and dried at 105ºC. After drying, the sediment was grounded and passed through a 100 mesh sieve, and the soil samples were retained by the quadratic method. The sediment sample was weighed to 0.1 g and subjected to microwave digestion using a combined HNO_3-H_2O_2 acid system and elevated temperature. The water and sediment were determined using atomic absorption for Pb, Zn, Cu, Cd and Cr.

Fish was killed in a lethal dose of anesthetic (MS-222) and dissected with a clean scalpel blade to separate the tissues from the bones. Muscles of some individuals were dissected, pooled, homogenized and freeze-dried (Eyela FDU-1200, Japan) for four days. Each organ tissue was homogenized and kept separately. Due to their small size (< 12 cm), they only separate muscles of silvery minnows and internal organs. After lyophilization, the samples were ground to powder, sieved to1 mm, and then stored in the sealed plastic pack at room temperature until digestion. 1 g dry fish samples were digested with 6 ml HNO_3 (65%) and 2 ml H_2O_2 (30%) in a microwave digestion system and diluted to 10 ml with double deionized water (Milli-Q Millipore 18.2 M cm^{-1} resistivity) (Liu et al., 2012). The digestion conditions for the microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively. A blank digest was carried out the same way (Tuzen, 2009).

Pb, Zn, Cu Cd and Cr levels in the water sediments, and fish tissues were measured by a flame/graphite atomic absorption spectrometer (AAFS, Varian Instruments AA240, Varian America). All the samples were analyzed as soon as possible.

Statistical analysis

All statistical analyses were conducted by IBM SPSS (Statistical Product and Service Solutions) Statistics, 5 Version 20.0. One-way analysis of variance (ANOVA) was implemented to test the differences between all sites for each water, sediment and fish. The relationships between metal concentrations and other water chemistry variables were explored with Spearman's rank correlation analysis (rho). A one-way ANOVA also compared differences in mean metal concentrations between different species, tissues and locations. Multiple comparisons were conducted using Tukey's Honestly Significant Difference test (HSD) by the program of ANOVA. Differences were considered significant if $P<0.05$, and all data were expressed as means ± standard error.

Results

Water and surface sediment

The concentrations heavy metals in water from the Huashan Reservoir were shown in *Table 3*. The concentrations of Pb, Zn, Cu, Cd and Cr in water were 14.33 ± 0.60-46.31 ± 2.07 μg L^{-1} (mean, 32.59 μg L^{-1}), 214.78 ± 1.51-491.72 ± 3.50 μg L^{-1} (mean, 370.23 μg L^{-1}), 84.15 ± 1.75-126.36 ± 2.54 μg L^{-1} (mean, 105.32 μg L^{-1}), 1.02 ± 0.22-3.22 ± 0.12 μg L^{-1} (mean, 1.94 μg L^{-1}) and 86.72 ± 5.28-127.83 ± 2.90 μg L^{-1} (mean, 112.29 μg L^{-1}), respectively. The heavy metal concentrations in water have a big difference in different locations (ANOVA, $p<0.001$).

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Table 3. *Water quality and mean heavy metal concentrations (µg L^{-1} ± standard deviation) at each sampling site surveyed in Huashan Reservoir. Grade II standards of the environmental quality standards for surface water in China (GB3838-2002) was also included. The letters (a, b, c, d, e, f) group sites by heavy metal, considered homogenous at $p<0.05$*

Location	C1	C2	C3	C4	C5	C6	C7	C8	Environmental quality standard (Grade II)
Water depth(m)	4.56	5.20	4.80	5.80	5.10	4.00	5.10	3.60	-
Temperature(°C)	22.5	22.0	22.1	21.9	22.0	22.7	22.5	22.3	-
pH	7.79	7.67	7.74	7.87	7.83	8.04	8.01	7.85	6-9
Total phosphorus(mg L^{-1})	0.243	0.171	0.208	0.203	0.178	0.216	0.208	0.176	≤0.025
Total nitrogen(mg L^{-1})	2.26	2.56	2.66	2.64	2.64	3.17	2.67	2.47	≤0.5
Pb(µg L^{-1})	36.58±2.03^{ab}	20.96±1.84^{c}	46.31±2.07^{d}	42.84±1.82^{bd}	44.85±3.50^{d}	33.62±3.13^{a}	14.33±0.60^{e}	21.22±1.62^{c}	≤10
Zn(µg L^{-1})	466.77±4.86^{a}	491.72±3.50^{b}	355.92±3.43^{c}	316.48±3.41^{d}	384.02±4.07^{e}	345.22±4.08^{f}	214.78±1.51^{g}	386.97±1.56^{e}	≤1000
Cu(µg L^{-1})	93.20±1.88^{a}	105.28±5.20^{b}	84.15±1.75^{c}	125.34±3.06^{d}	107.20±1.83^{b}	100.43±4.94^{ab}	100.58±0.88^{ab}	126.36±2.54^{d}	≤1000
Cd(µg L^{-1})	2.78±0.09^{ab}	3.22±0.12^{b}	1.62±0.09^{c}	2.54±0.34^{a}	1.56±0.23^{c}	1.45±0.05^{cd}	1.02±0.22^{d}	1.36±0.13^{cd}	≤5
Cr(µg L^{-1})	105.73±0.85^{a}	127.83±2.90^{b}	115.89±3.46^{c}	113.48±2.75^{ac}	115.26±3.98^{ac}	118.25±2.18^{bc}	86.72±5.28^{d}	115.19±3.87^{ac}	≤50

Table 4. *Surface sediment mean heavy metal concentrations (mg kg^{-1} dw ± standard deviation) at 8 sites surveyed in Huashan Reservoir. Heavy metal background values in soils from Yunnan Province (State Environmental Protection Agency Administration of China, 1990) was also included. The letters (A, B, C, D, E, F) group sites by environmental variable, considered homogenous at $p < 0.05$*

Location	C1	C2	C3	C4	C5	C6	C7	C8	Background value
Pb(mg kg^{-1})	75.03±4.42^{A}	96.18±3.39^{B}	98.10±4.19^{B}	111.76±7.51^{BC}	112.13±7.05^{BC}	100.90±8.69^{BC}	119.13±6.36^{CD}	135.37±8.01^{D}	26.2
Zn(mg kg^{-1})	210.18±6.02^{A}	225.04±3.27^{A}	165.39±5.59^{B}	172.42±6.71^{B}	190.09±9.87^{C}	189.66±5.51^{C}	157.67±8.55^{B}	171.80±5.71^{B}	88.4
Cu(mg kg^{-1})	118.26±2.16^{AD}	104.96±5.00^{ABC}	120.73±3.96^{D}	115.46±5.06^{ABD}	193.30±6.12^{E}	102.09±7.10^{BC}	99.97±8.05^{C}	86.59±5.71^{F}	35.1
Cd(mg kg^{-1})	2.21±0.09^{ABC}	2.54±0.08^{BC}	2.09±0.14^{ABD}	2.29±0.14^{ABC}	2.33±0.24^{ABC}	2.58±0.08^{C}	1.68±0.31^{D}	1.86±0.09^{AD}	0.28
Cr(mg kg^{-1}))	134.39±5.16^{A}	148.80±3.68^{B}	132.68±4.06^{AC}	122.62±5.42^{ACD}	127.00±6.08^{AC}	123.78±4.34^{ACD}	110.51±9.45^{D}	119.70±10.65^{CD}	58.6

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Compared to all sites, the highest values of Zn, Cd and Cr were observed at site C2 ($p<0.05$), and the highest values of Cu were observed at site C8 ($p<0.05$). Total phosphorus concentration was also positively related to total nitrogen concentration in water ($r=0.808$, $p=0.015$). In addition, pH was some negatively related to all metal concentrations in water ($r<-0.454$, $p<0.258$), with the exception of Cu ($r=0.147$, $p=0.05$) and Pb ($r=-0.039$, $p=0.928$).

The heavy metal concentrations of surface sediments from the Huashan Reservoir were shown in *Table 4*. The concentrations of Pb, Zn, Cu, Cd and Cr in surface sediments were 75.03 ± 4.42-135.37 ± 8.01 mg kg^{-1} (mean, 106.07 mg kg^{-1}), 157.67 ± 8.55-225.04 ± 3.27 mg kg^{-1} (mean, 185.28 mg kg^{-1}), 86.59 ± 5.71-193.30 ± 6.12 mg kg^{-1} (mean, 117.67 mg kg^{-1}), 1.68 ± 0.31-2.54 ± 0.08 mg kg^{-1} (mean, 2.13 mg kg^{-1}) and 110.51 ± 9.45-148.80 ± 3.68 mg kg^{-1} (mean, 127.43 mg kg^{-1}), respectively. The heavy metal concentrations in the surface sediments also varied significantly at different locations (ANOVA, $p<0.001$). The highest concentration of Zn, Cd and Cr was observed at site C2, which was one of the closest sites near the industrial park. The concentrations of Zn, Cd and Cr in surface sediment were higher than other sites.

The correlation coefficients between heavy metals in water and surface sediments were shown in *Table 5*. A significant positive correlation (0.873) of Zn was found between the water and sediments. And significant positive correlations (0.872) between Zn level in the water and Cr level in the sediments. Cd content of water showed significant positive relationships with Zn and Cr content in surface sediments with correlation coefficients 0.778 and 0.800, respectively. Furthermore, the Cr level in the water correlated positively with Cr (0.759) and Cd (0.742) in surface sediments of the same site.

Table 5. *Pearson's correlation coefficient (r) between heavy metals level in water (µg L^{-1}) and sediment (mg kg^{-1} dw) samples collected from all sites (n = 8)*

		Water				
		Pb	Zn	Cu	Cd	Cr
Sediment	Pb	-0.364	-0.526	0.683	-0.619	-0.155
	Zn	-0.023	0.873**	-0.129	0.778*	0.554
	Cu	0.627	-0.114	-0.141	-0.026	0.110
	Cd	0.403	0.562	-0.072	0.562	0.759*
	Cr	0.193	0.872**	-0.307	0.800*	0.716*

* Correlation is significant at the 0.05 level (2-tailed), ** Correlation is significant at the 0.01 level (2-tailed)

Sediment cores

The vertical distribution patterns for Pb, Zn, Cu, Cd and Cr in the sediment cores from the reservoir were shown in *Figure 2*. Overall, the mean metal concentrations approximately equaled the background levels in the local soils from 30 to 110 cm depth. The metal concentrations in sediment cores markedly increased from 10 to 30 cm depth and placidly increased from 10 cm depth to the surface.

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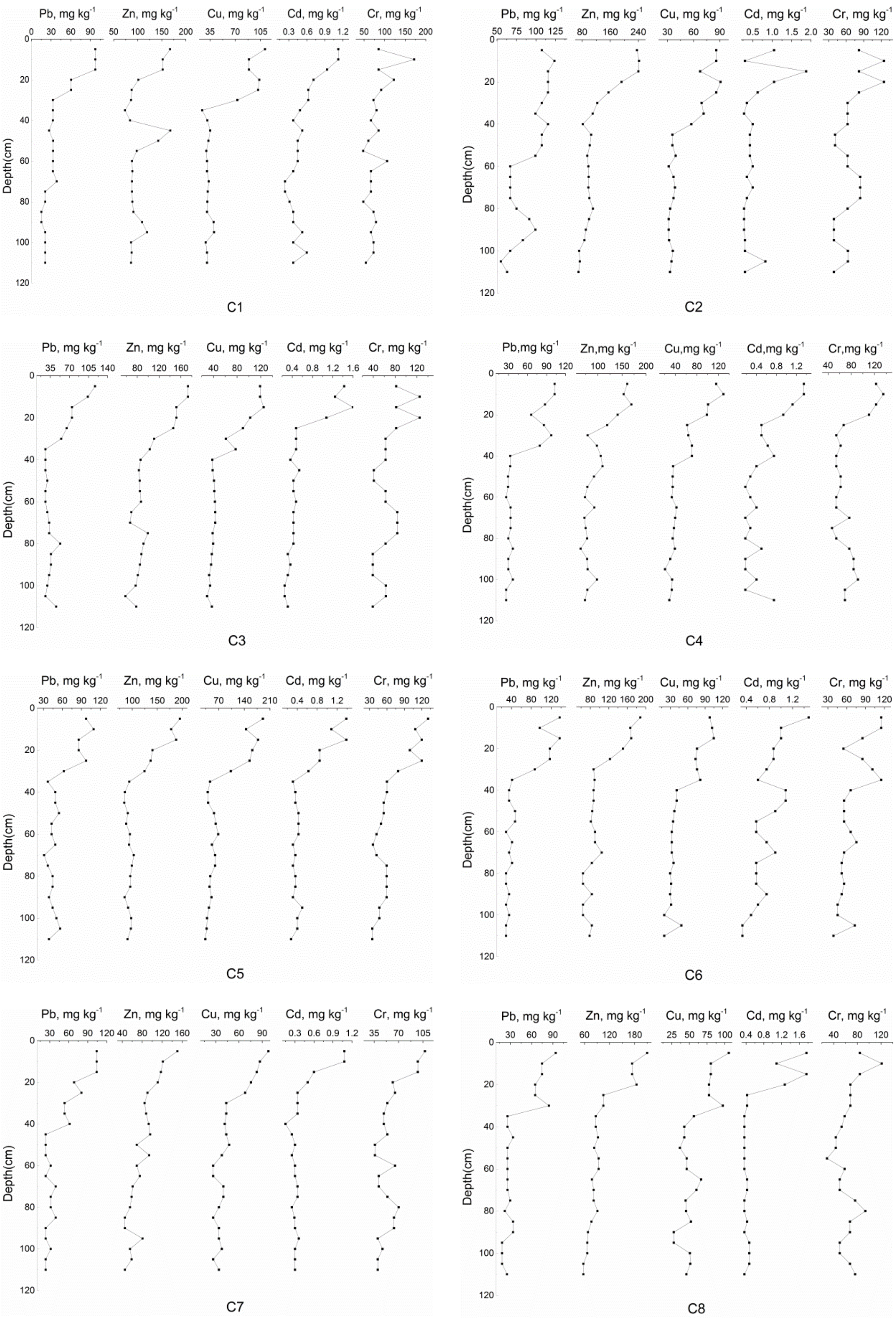

Figure 2. *The concentration of heavy metals changed with depth in sediment cores*

Fish

The concentrations of all the metals differed significantly between different locations (ANOVA, F5, 12<12.761, p<0.01), tissues (ANOVA, F2, 51>7.410, p<0.01) and significantly negative between species. The concentrations of heavy metals in fish muscle

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samples from Hushan Reservior were shown in *Figure 3*. All metal concentrations were determined on a dry weight basis. For all sampling sites, the mean concentrations of Pb, Zn, Cu, Cd and Cr in muscle samples were 0.10-0.78 mg kg^{-1}, 21.79-67.87 mg kg^{-1}, 0.48-1.47 mg kg^{-1}, 0.03-0.16 mg kg^{-1} and 0.13-0.94 mg kg^{-1}, respectively. Compared to all the sites F1, F2, F3, F4, F5 and F6, shown in *Table 2*), the three fish species at site F4 had a higher concentration of Pb, Zn, Cu, Cd and Cr ($p<0.05$) except the concentrations of Pb in crucian carp, which was the closest site to the industrial park. Similarly, concentrations of Pb, Zn and Cu were much higher ($p<0.05$) at F1 and F4 sites, and concentrations of Cd were much higher ($p<0.05$) at F4 and F6 sites comparing to the other sites.

For all sampling sites, organs (liver and gill) from the same species (carp and crucian carp) were anatomized and pooled to determine Pb, Zn, Cu, Cd and Cr concentrations.

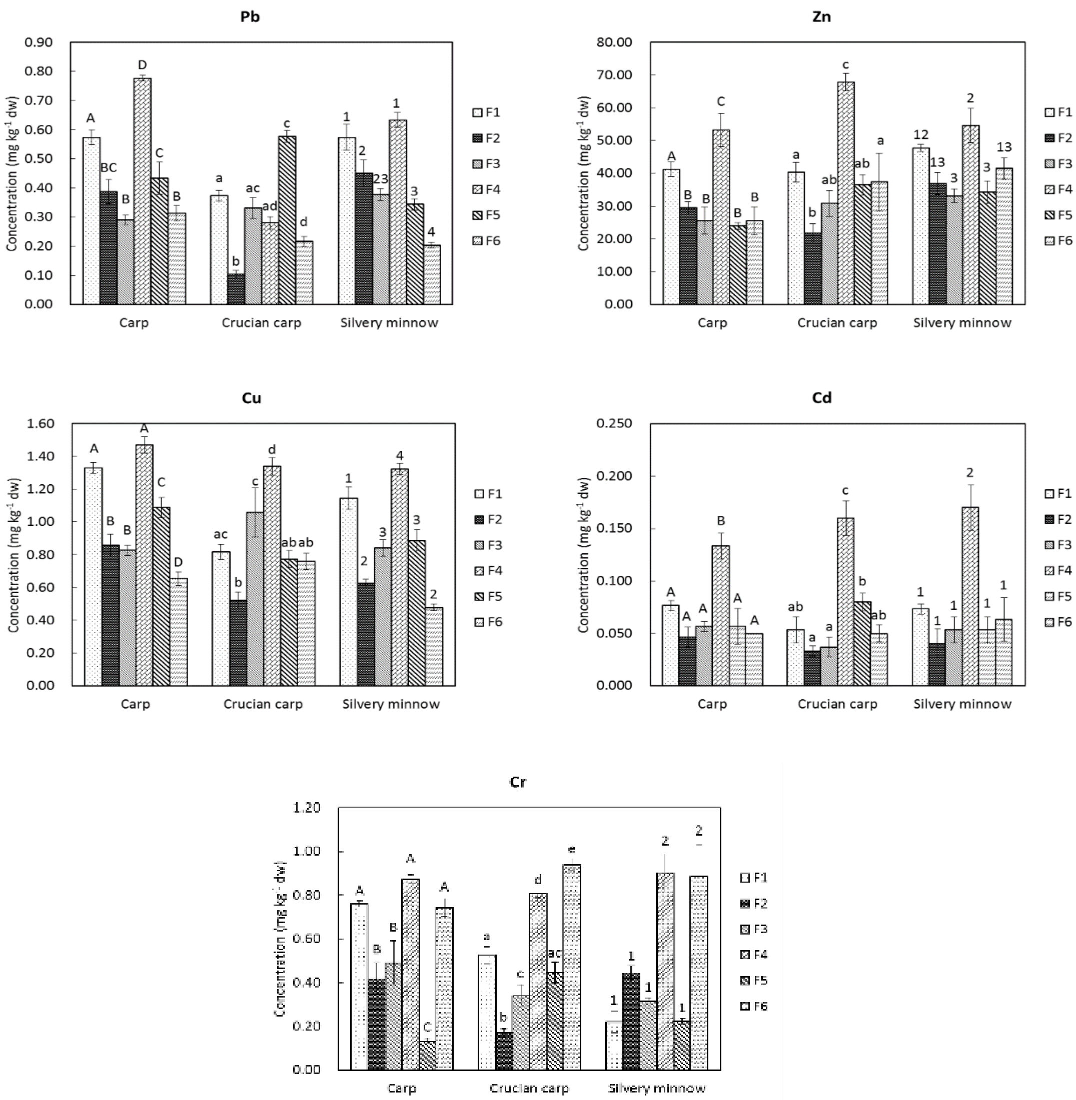

Figure 3. *Concentrations of Pb, Zn, Cu, Cd and Cr in fish muscle samples collected from Huashan Reservoir. The different letters (A, B, C, D) represent significant differences (p<0.05) between different sites for carp. The different letters (a, b, c, d) represent significant differences (p<0.05) between sites for crucian carp. The different numbers (1, 2, 3, 4) represent significant differences (p<0.05) between sites for silvery minnow*

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Specifically, carp had the highest mean values of Pb (1.63 ± 0.32 mg kg^{-1}), Zn (85.67 ± 7.70 mg kg^{-1}), Cu (1.97 ± 0.42 mg kg^{-1}), Cd (0.20 ± 0.05 mg kg^{-1}) and Cr (1.09 ± 0.54 mg kg^{-1}) and crucian carp had the highest mean values of Pb (1.35 ± 0.45 mg kg^{-1}), Zn (68.68 ± 21.23 mg kg^{-1}), Cu (1.41 ± 0.35 mg kg^{-1}), Cd (0.16 ± 0.03 mg kg^{-1}) and Cr (0.98 ± 0.43 mg kg^{-1}) in liver. According to the national food safety standard (GB 2762-2012). The Pb, Cd Cr Zn and Cu values of threshold established were 0.5 mg kg^{-1} ww, 0.1 mg kg^{-1} ww 2.0 mg kg^{-1} ww, 100 mg kg^{-1} ww and 10 mg kg^{-1} ww, respectively. This illustrated that the metal concentrations of Pb, Zn, Cu, Cd and Cr in all fish species collected from the reservoir didn’t exceed those standards by the Ministry of Health of the People's Republic of China. The present levels observed in fish species were safe for human consumption from this reservoir.

Discussion

Water and surface sediment analysis

Based on the national environmental quality standard for surface water (GB3838-2002) launched by the State Environmental Protection Administration of China, the results showed that the content of metals in water was under the grade II standards except for Pb and Cr. The highest concentrations for Zn, Cd and Cr occurred closest to the industrial park, and the highest concentration of Cu occurred closest to the Huashan town, which is also adjacent to a major industrial park. This high concentration of heavy metals maybe due to the urban runoff, sewage outfallsand and wastewater discharges. In addition, there were many industries near those sampling sites. The presence of some industrial resources such as phosphorus chemical industry, machinery, and steel smelting in this area may directly or indirectly contaminated the reservoir. The average value of pH was 7.85, indicating a weak alkaline environment. In this pH condition, minimal metal would be bound and not be released from the sediment (Atkinson et al., 2007). The average values of total nitrogen(TN) and total phosphorus(TP) were 2.63 mg/L and 0.200 mg/L, which were the grade V standards based on the national environmental quality standard for surface water (GB3838-2002). This pollution of TN and TP may also come from domestic sewage and chemical plants.

The metal concentrations of most surface sediments had exceeded the background values of local soils. The contamination of this area with heavy metals was caused by the higher population densities of urbanization and industrialization. It was apparent that the sediments with higher metal concentrations were influenced by anthropogenic discharge. The heavy metal concentrations in the sediments were higher in the reservoir because humic substances present in sediments creating metal complexes.

Therefore, heavy metals of Cd, Zn and Cr in waters and surface sediments may come from similar sources. The primary source of heavy metals was anthropogenic activities and weathering of bedrocks. Sediments act as the most important sink of metals in the aquatic environment. Some metals may interact with organic matter in the water and settle down, causing the precipitation of metals in the sediments (Gupta et al., 2009; Debnath et al., 2021). The detected positive correlation of each metal between the water and the sediment supported this argument.

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Sediment cores analysis

Because the sediment deposition and burial rates were characterized, concentrations within each sediment slice can be characterized on a temporal basis. The chronology of the sediment samples was inferred according to the 137Cs method (Xue et al., 2007; Abbasi, 2019). The 5-10 cm and 25-30 cm of cores layers referred to the 2000s and 1970s, respectively. The historical changes of heavy metals were relatively small before the 1970s. Pb, Zn, Cu, Cd and Cr concentrations increased abruptly around early 1970s. It was apparent that the Huashan Reservoir was more polluted with anthropogenic source metals from the 1970s. During this period, the heavy metal pollution was also caused by urbanization and industrialization in Huashan Town. In addition, the results showed that the concentrations of these metals tended to remain unchanged from the 2000s to now. This phenomenon may be due to the environment administered engineering with the Qujing government from 2003.

Fish analysis

It can be seen from the figures that the concentrations of Pb, Zn, Cu, Cd and Cr in fish muscle samples were in agreement with some other research (Tuzen, 2009; Xie et al., 2020) and concentrations of Cd were in agreement with these reported by Canli and Atli (2003). Similarly, the mean concentrations of Pb and Zn observed in the current study might be considered comparable with those reported in the muscle of Cyprinidae by Yang et al. (2014). In addition, the Pb, Cu and Cr concentrations detected in fish muscle samples in our study were lower than the data reported by Chale (2002). The Zn concentrations found in muscle samples resemble to the data from the paper finished by Merciai et al. (2014), who reported that similar concentrations ranged from 32.91 to 114.2 mg kg^{-1} in fish collected from the Llobregat River, which flows into the Mediterranean Sea.

The lowest and highest Pb levels in fish muscles were found as 0.10 ± 0.01 mg kg^{-1} in crucian carp at site F2 and 0.78 ± 0.01 mg kg^{-1} in carp at site F4, respectively. Pb is known to induce increase of blood pressure and cardiovascular disease in adults and reduce children's intellectual performance and cognitive development. Zn (21.79-67.87 mg kg^{-1}) and Cu (0.48-1.47 mg kg^{-1}) concentrations were comparatively high in muscles of all species studied during the present investigation. However, Zn and Cu in analyzed fish samples were lower than limits. Zn and Cu are usually essential elements, but it can cause adverse health problems under very high intake, such as liver and kidney damage (Ikem and Egiebor, 2005; Attar, 2020). Cd (0.03-0.16 mg kg^{-1}) concentrations were comparatively low in muscles for all species studied during the present investigation. Compared to all sites, the three fish species at site F4 had 2-3 times higher concentrations of Cd. These results are in accordance with the higher concentrations of Cd in surface sediment in this site. To some degree, industrial effluents contribute to the Cd pollution in this area, which was the closest site to the industrial park. Cr is an essential mineral in humans and has been related to carbohydrate, lipid and protein metabolism (Biswas et al., 2012). The lowest and highest Cr levels in fish muscles of species were found as 0.13 ± 0.01 mg kg^{-1} in carp and 0.89 ± 0.15 mg kg^{-1} in a silvery minnow.

As the results obtained in our study, the mean concentrations of metal were comparatively higher in the livers, while the lowest concentration was obtained in the edible muscles. For the most part, the higher concentrations of the studied metals were found in the gills of carp, crucian carp and silvery minnow collected from the Huashan Reservoir. Overall, the mean concentration in fish organs followed the sequence of

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liver>gill>muscle. For the tissues, the liver was confirmed as the best metal depository for all elements determined (Çoğun et al., 2006; Sattari et al., 2020). The adsorption of metals into the gill surface could also be an important influence on the total metal levels of the gill (Heath, 1995).

Conclusion

This study may increase our knowledge of the geochemistry of water, sediment and some fish of the Huashan Reservoir, a part of the Pearl River source. The results showed that the water and sediment samples of Huashan Reservoir were polluted by a certain extent, especially from the waste water of industrial parks. From the results, we concluded that concentrations of Pb, Zn, Cu, Cd and Cr increased abruptly from around early 1970s. This study fills a gap by providing information on heavy metal concentrations in different fish species from the Huashan Reservoir. Fortunately, metal concentrations found in edible parts of carp, crucian carp and silvery minnow were not heavily burdened based on the samples collected. Metal quantities were higher in liver and gills than that in muscle. The liver was confirmed as the best metal depository for all elements determined. However, fish livers were very seldom consumed in the area.

Further work is necessary to decide on the form of storage of metals in the liver of the studied fish species. Proper management is needed to sustain the quality of this lake for the coming generations. Therefore, we need to investigate the levels and spatial variations of heavy metals in water, sediment and fish and to provide baseline information on the pollution situation in this basin. The information could contribute to the knowledge and rational management of this region in the future.

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