Science of the Total Environment 672 (2019) 883–892

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Spatial and interspecies differences in concentrations of eight trace elements in wild freshwater fishes at different trophic levels from middle and eastern China

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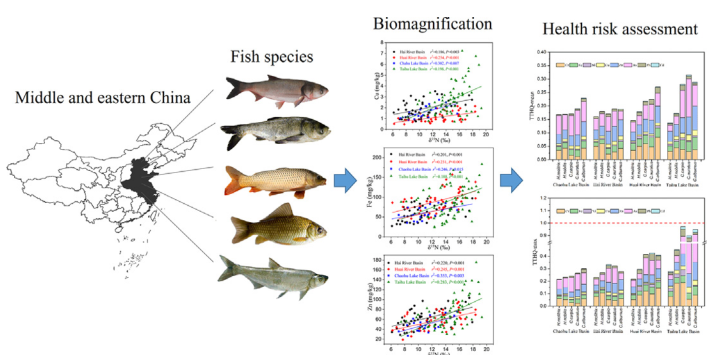
HIGHLIGHTS

- A large scale investigation of trace element concentrations in freshwater wild fish was conducted.
- Spatial differences of trace element concentrations in fishes were found.
- Concentrations of trace elements in fish varied greatly among species.
- Biomagnification of Cu, Fe and Zn among trophic levels were observed.
- Risks to health of humans posed by consumption of fish were estimated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 January 2019
Received in revised form 7 March 2019
Accepted 9 March 2019
Available online 11 March 2019

Editor: Henner Hollert

Keywords:
Trace elements
Freshwater wild fish
Biomagnification
Stable isotope ratios
Risk assessment

ABSTRACT

There have been numerous studies on concentrations of trace elements in aquatic ecosystems, but few have been conducted at a large spatial scale. This study collected 410 samples of five wild freshwater fishes at different trophic levels from middle and eastern China. Concentrations of eight trace elements, chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), lead (Pb) and cadmium (Cd) and stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) were determined in dorsal muscle of fishes. Spatially, concentrations of trace elements were least in fishes from the Hai River Basin, while those in fishes from the Taihu Lake Basin were greatest. The carnivorous topmouth culter and omnivorous common carp and crucian carp accumulated greater amounts of trace elements than did the planktivorous silver carp and bighead carp. Trophic biomagnification was for Cu, Fe and Zn, but not for Cr, Ni, As, Pb and Cd. Concentrations of As in 15 muscle samples (3.7%) from Taihu Lake Basin exceeded the guidelines (1.0 mg/kg, wet mass) provided by FAO/WHO (2014), while the total target hazard quotient (TTHQ) values were <1.0, indicating no obvious non-carcinogenic risks to humans that consume those fishes. However, people who consume larger amounts of fish products, or people who are vulnerable, such as pregnant

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https://doi.org/10.1016/j.scitotenv.2019.03.134

women, children and people with poor health, might be at greater risk. Also, exposure to trace metals through other routes cannot be ignored. Accumulations of trace elements in Chinese freshwater fishes were affected by both geographical conditions and human activities.

1. Introduction

In recent years, accelerating industrialization and urbanization have resulted in accumulation of some trace elements in aquatic environments in China (Zhang et al., 2010; Fu et al., 2013). Trace elements often come from a variety of point sources, including discharges of industrial and domestic sewages, mining and smelting activities, and non-point sources such as combustion of coal (Zhao et al., 2014; Ma et al., 2015). Due to their accumulation in water and sediment, fishes at higher trophic levels in aquatic ecosystems can accumulate trace elements to detrimental concentrations (Voigt et al., 2015; Fang et al., 2019). Consumption of fishes contaminated with greater concentrations of trace metals can pose risks to health of humans (Zhong et al., 2018; Zeng et al., 2019).

China, has the largest aquaculture industry in the world and has a full production capacity of 45,469,000 tons, which accounts for 61.6% of the global total fisheries production (73,783,700 tons) in 2014 (FAO, 2016). Fish is rich in nutrition, and contains abundant omega-3 fatty acids, which can help decrease risks of some cancer and cardiovascular diseases (Storelli, 2008). However, some trace elements, due to their persistence, can be accumulated in water and sediment. Because they lack the ability to escape from contaminated aquatic environments, native fishes can suffer sublethal effects or death (Ofukany et al., 2014). In view of the toxicity of some trace elements to fishes, they have been widely employed as sensitive indicators of trace elements in aquatic ecosystem (Muiruri et al., 2013). It is of importance to note that trace elements at higher concentrations can cause toxicity to some fishes as well as affecting higher trophic organisms, including humans that consume contaminated fish (Hao et al., 2013; Wang et al., 2013a; Avigliano et al., 2015). Hence, estimation of trace elements in edible portions of fishes is vital for assessment of their potential risks to ultimate consumers, including human beings (Qian et al., 2010; Islam et al., 2014; Gu et al., 2015).

Previous researches have reported concentrations of trace elements in individual bodies of water, such lakes, rivers or reservoirs (Leung et al., 2014; Guo et al., 2016; Liu et al., 2018c). However, little is known about their spatial patterns at larger geographic scales. Also, there have been several studies of relationships between concentrations of trace elements in fish muscle and their feeding habits to determine whether or not there is biomagnification of trace elements in various fishes (Wei et al., 2014; Yi et al., 2017; Jiang et al., 2018). Previously, determination of trophic levels occupied by fishes have mostly been based on food items in their diets, or gut contents of captured fishes. However, previously digested food was seldom considered. Ratios of stable isotopes in fishes are dependent not only on current consumed food, but also on food consumed during earlier life stages.

In this study, for the first time, a large-scale study of accumulation of trace elements by wild, freshwater fishes was conducted in middle and eastern China. Concentrations of eight trace elements chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), lead (Pb) and cadmium (Cd) and stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$), were determined in edible muscle of five commercial freshwater fishes. The objectives of this study were to: (1) examine whether there are any spatial or interspecific differences in concentrations of the trace elements among fishes; (2) test if there is biomagnification of trace elements in fish species by the stable isotope method ($\delta^{13}C$, $\delta^{15}N$) and (3) assess whether consumption of these fishes pose risks to health of humans.

2. Materials and methods

2.1. Study area and sampling locations

The study was conducted in middle and eastern China (Fig. 1) including six provinces: Hebei, Shandong, Anhui, Jiangsu, Henan and Zhejiang. Also, this area can be divided into four watersheds (Hai River Basin, Huai River Basin, Chaohu Lake Basin and Taihu Lake Basin). Each watershed has several smaller water bodies, including lakes, rivers and reservoirs (Table 1). For example, Gehu Lake, Duihekou Reservoir and Tiaoxi River are included in the Taihu Lake Basin.

From July to September of 2016, a total of 410 individuals were captured by local fisherfolk by use of fyke nets. These fishes belong to five different fish species, silver carp (*Hypophthalmichthys molitrix*), bighead carp (*Hypophthalmichthys nobilis*), common carp (*Cyprinus carpio*), crucian carp (*Carassius auratus*), and topmouth culter (*Culter alburnus*), which are frequently consumed by local residents. Body lengths of silver carp, bighead carp, common carp, crucian carp, and topmouth culter were approximately 40, 40, 20, 20, and 15 cm, respectively. Information of fishes and sampling locations are listed in Table 1. After capture, fish were washed carefully with tap water, and then with deionized water. Dorsal muscle, without skin or backbone, was immediately placed in plastic bags and stored at −20 °C. Wet muscles were freeze dried until constant mass. Dried muscle samples were ground, homogenized and then kept in clean corning centrifuge tube before analysis.

2.2. Quantification of trace elements

All reagents (67% HNO_3 and 30% H_2O_2 were purchased from Suzhou Crystal Clear Chemical Co., Ltd., China) and were of ultra-pure grade in this study. 0.3 ± 0.01 g of dried muscle samples were weighed in a polytetrafluoroethylene (PTFE) container, and then kept for 60 min at 100 °C for preheating after 7 mL HNO_3 and 2 mL H_2O_2 were added. Afterwards, samples were digested by use of a Microwave System as follows: 20 min to 190 °C, 30 min at 190 °C, and then cooling to room temperature. In order to eliminate excess nitric acid, after digestion, the solution was held at 140 °C for about 2 h until the total volume was <1 mL. Solutions were diluted to 20 mL with ultra-pure water produced by Milli-Q Reference (Millipore SAS, 67120 Molsheim, France). A blank digestion was also implemented at the same time in the same way. If necessary, digestates were filtered. Concentrations of eight trace elements (Cr, Fe, Ni, Cu, Zn, As, Pb and Cd) were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher Scientific, iCAP Qc).

During analysis, In and Rh were added as internal standards. External calibration curves ($r^2 > 0.999$; 8 points) were developed for each element quantified and additional curves were developed as well as instrumental and procedural blanks. Accuracy of results were reported as means of replicate quantifications and every tenth sample was analyzed 3 times (relative deviation < 5%). Standard reference material GBW08573 (*Pseudosciaena crocea*) was applied to verify methods of quantification of trace elements. Results were in good agreement with certified values. Recoveries, based on spiked samples for elements, ranged from 86.3 to 113.5%. Limits of detections (LOD) for the eight trace elements, measured values and recovery of standard reference material are given in Table S1.

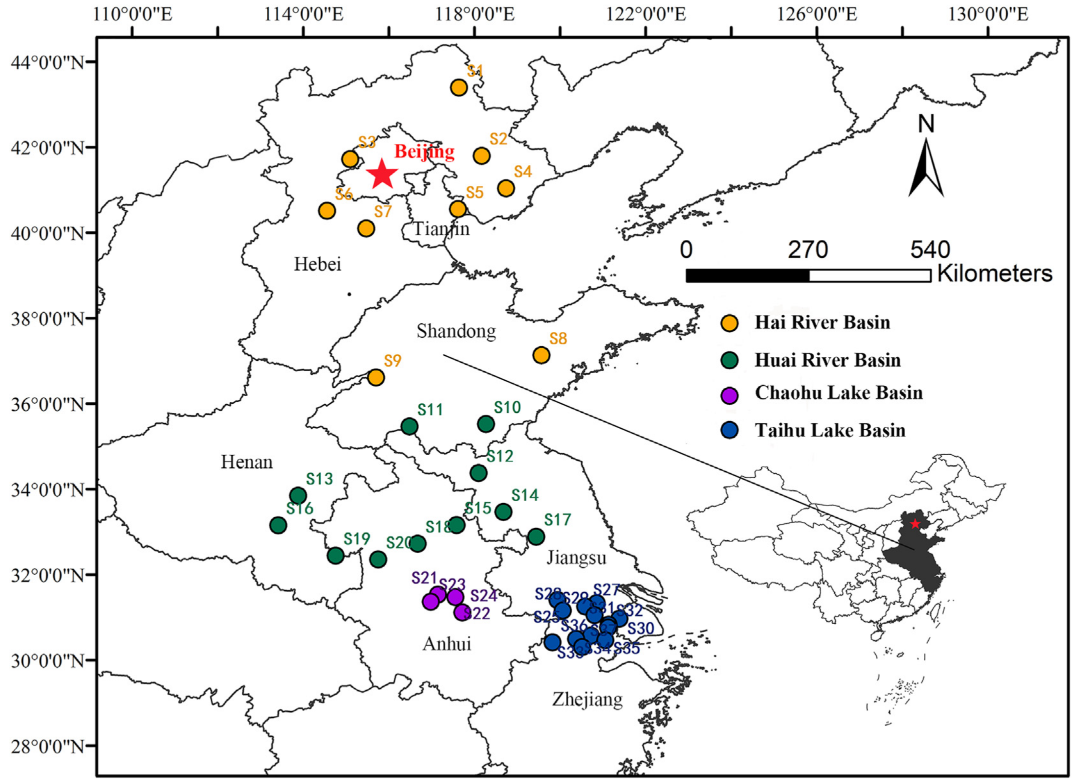

Fig. 1. Study area and sampling locations. Circles represent sampling locations.

2.3. Stable isotope analysis

After roasting at 60 °C to constant mass, homogenized samples were ground into powder with a pestle and a mortar. An ultra-microbalance (Sartorius MSA3.6P-000-DM Cubis Micro Balance) was used to weigh 3 mg of muscle into 6 × 9 mm tin capsules. Stable isotopes were then analyzed with Delta Plus (Thermo Scientific, Waltham, MA, USA) continuous flow isotope ratio mass spectrometer (CF-IRMS) connected to a Carlo Erba NA2500 elemental analyzer. International standards (atmospheric nitrogen for nitrogen; Pee Dee Belemnite for carbon) were used as reference materials. Fish muscles (analyzed for many times previously, analytical precision were <0.2‰ and <0.3‰ for δ^{13}C and δ^{15}N, respectively) with known isotopic composition were used as an internal standard. δ^{13}C and δ^{15}N were employed to exhibit the isotopic compositions of samples (Eqs. (1) and (2)).

$$\delta^{13}C(‰) = \left[\left(\frac{R_{sample}}{R_{standard}} - 1\right)\right] \times 10^3 \quad (1)$$

$$\delta^{15}N(‰) = \left[\left(\frac{R_{sample}}{R_{standard}} - 1\right)\right] \times 10^3 \quad (2)$$

where R is the ratio $^{15}N/^{14}N$ or $^{13}C/^{12}C$, the $R_{standard}$ values were relative to Pee Dee Belemnite for δ^{13}C and atmospheric nitrogen (N_2) for δ^{15}N.

Table 1
Descriptive information for sampling sites with fish species collected from middle and eastern China.

Watershed	Sites	Water bodies	Fish	N
Hai River Basin	S1–S11	Gongmiao Reservoir (S1), Panjiakou Reservoir (S2), Guanting Reservoir (S3), Luan River (S4), Jiyun Canal (S5), Angezhuang Reservoir (S6), Baiyangdian (S7), Xiashan Reservoir (S8), Dongpinghu Lake (S9), Yi River (S10), Dushanhu Lake (S11)	silver carp (*Hypophthalmichthys molitrix*)	13
			bighead carp (*Hypophthalmichthys nobilis*)	11
			common carp (*Cyprinus carpio*)	24
			crucian carp (*Carassius auratus*)	23
			topmouthculter (*Culter alburnus*)	20
Huai River Basin	S12–S20	Luomahu Lake (S12), Shaying River (S3), Hongzehu Lake (S14), Xin River (S15), Suyahu Lake (S16), Gaoyouhu Lake (S17), Gaotanghu Lake (S18), Huai River (S19), Chengxihu Lake (S20)	silver carp (*Hypophthalmichthys molitrix*)	18
			bighead carp (*Hypophthalmichthys nobilis*)	18
			common carp (*Cyprinus carpio*)	22
			crucian carp (*Carassius auratus*)	22
			topmouthculter (*Culter alburnus*)	20
Chaohu Lake Basin	S21–S24	Chaohu Lake (S21), Yuxi River (S22), Hangbu River (S23), Huangpihu Lake (S24),	silver carp (*Hypophthalmichthys molitrix*)	10
			bighead carp (*Hypophthalmichthys nobilis*)	11
			common carp (*Cyprinus carpio*)	12
			crucian carp (*Carassius auratus*)	12
			topmouthculter (*Culter alburnus*)	12
Taihu Lake Basin	S25–S37	Gehu Lake (S25), Caohu Lake (S26), Gonghuwan (S27), Dongjiu Lake (S28), Xukou River (S29), Dianshanhu Lake (S30), Sanbaidang Lake (S31), Fenhu Lake (S32), Shenzhuangyang Lake (S33), Dongtiaoxi River (S34), Jinghang Canal (S35), Xitiaoxi River (S36), Duihekou Reservoir (S37)	silver carp (*Hypophthalmichthys molitrix*)	28
			bighead carp (*Hypophthalmichthys nobilis*)	32
			common carp (*Cyprinus carpio*)	32
			crucian carp (*Carassius auratus*)	35
			topmouthculter (*Culter alburnus*)	35

2.4. Assessment of risk to health of humans

Results of a previous study (Chen et al., 1992) indicated that non-essential trace elements can cause adverse effects, even at trace concentrations. Furthermore, the dose makes the poison, and the essential trace elements can affect health when exposures exceed critical thresholds (Zeng et al., 2019). Concentrations of trace elements in fishes caught from several areas of China were measured to determine risks to health of humans, through consumption of contaminated fishes. Estimated daily ingestion (EDI) was employed to calculate human health risk to native inhabitants from common wild fish consumption (Eqs. (3)–(5)).

$$\mathrm{EDI}_i = \frac{C_i \times DC}{BW} \quad (3)$$

$$\mathrm{THQ}_i = \frac{EDI_i}{RfD_i} \times 10^{-3} \quad (4)$$

$$\mathrm{TTHQ} = \sum_i^n THQ_i \quad (5)$$

where EDI_i (μg/kg/day) is the estimated daily intake of trace element *i*, C_i (mg/kg wet mass) is the mean concentration of trace element *i* in fish, DC is daily consumption of fish (71 g/day/person) as recorded by the Food and Agricultural Organization (2008), BW is the mean adult body weight of Chinese (58.1 kg) (Gu et al., 2006), THQ is the target hazard quotient, TTHQ is the total target hazard quotient, THQ_i is the target hazard quotient for trace element *i*, $\mathrm{RfD_i}$ (mg/kg bm/day) is the oral reference dose (RfD) of individual trace element *i*. RfDs (mg/kg/day) of various trace elements used to calculate THQ and TTHQ values were obtained from the United States Environmental Protection Agency: 3×10^{-3} (Cr), 7×10^{-1} (Fe), 2×10^{-2} (Ni), 4×10^{-2} (Cu), 3×10^{-1} (Zn), 3×10^{-4} (As), 4×10^{-3} (Pb), 1×10^{-3} (Cd) (USEPA, 2013, 2017).

2.5. Statistical analyses

Statistical analyses were accomplished by use of SPSS version 18.0 for windows. Origin 8.0 and Arcgis 10.2 were used to plot the graphs. All data were tested for normality and homogeneity of variance and non-normal data were Log10(x) transformed and then one-way analysis of variance (ANOVA) and Duncan's Multiple Comparison test was employed to determine the significant differences ($p < 0.05$) of concentrations of individual elements among fishes and locations.

3. Results and discussion

3.1. Spatial distribution of trace elements in muscles of fishes

Mean concentrations and ranges of eight trace elements in dorsal muscle of fishes collected from middle and eastern China are summarized in Table S2. Mean concentrations in muscles of fishes ranged from 8.3 μg/kg, dry mass (Cd) to 79.9 mg/kg, dry mass (Fe) with an order of increasing concentrations of: Cd < Pb < Ni ≈ Cr < As<Cu < Zn < Fe. This tendency was not always identical among locations. In this study, taking into account that the wet to dry mass ratio is approximately 5 (water content of 80%) (Wei et al., 2014), the mean concentrations of non-essential trace elements Pb, As and Cd (0.16, 0.61 and 0.008 mg/kg, dm, respectively) in dorsal muscle of fishes were much less than threshold values (2.0, 1.0, and 1.0 mg/kg), wet mass for Pb, As, and Cd, respectively, suggested by FAO/WHO (2014). However, concentrations of As in 15 of 410 (3.7%) samples of common carp and crucian carp from Taihu Lake Basin were greater than the guideline (1.0 mg/kg, wm, equivalently to 5.0 mg/kg, dm) provided by FAO/WHO (2014). Concentrations of As were several times greater than those of fishes from the Yangtze and Heilongjiang rivers observed in previous studies (Yi and Zhang, 2012; Jiang et al., 2016). Chemical forms of As determine its mobility and toxic potency (Ma et al., 2017), and among its various forms, inorganic, especially arsenite (AsIII) is the most toxic, and is classified as a Group 1 human carcinogen (IARC, 2012). Since long-term exposure to small doses of inorganic As could result in carcinogenesis and other harmful effects to humans (Chen et al., 1992), more attention should be paid to inorganic As in fishes of the Taihu Lake Basin. Cu and Zn are essential nutrients for humans, but they can affect health if their intakes exceed critical thresholds (Demirezen and Uruc, 2006). Relatively great concentrations of Cu resulted in severe stress in the liver of the large yellow croaker (Zeng et al., 2019).

Concentrations of trace elements in fishes from the four basins are shown in Fig. 2. Concentrations of Cu, Zn and Cd in fish muscle were greater in the Taihu Lake Basin than in the other basins, and concentrations of Fe and Pb in fish muscle were greater in Huai River and Taihu Lake Basins than in the other two basins. Concentrations of Cr in muscle was greatest in fishes from the Huai River Basin. In the present study, concentrations of Fe in muscle of fishes was the greatest (40.6–134.9 mg/kg, dm) among trace elements studied, also greater than those (22.4–42.7 mg/kg, dm) in muscle of fishes from the Xiang River, China (Jia et al., 2018), but less than concentrations (771–2051 mg/kg, dm) in fishes from the Yellow River Estuary (Liu et al., 2018a) (Table 2). Concentrations of Zn in *C. auratus* observed during the present study (50.2–81.4 mg/kg, dm) were comparable to those observed in the same species (mean: 53.4 mg/kg, dm) from the Xiang River during a previous study (Jia et al., 2018). Concentrations of Ni in *H. molitrix* in this study (0.28–0.59 mg/kg dm) were less than those (0.68–2.81 mg/kg, dm) in the same species from the Yellow River Estuary (Liu et al., 2018a), but exhibited comparable values (mean: 0.65 mg/kg, dm) in the same species from Taihu Lake (Tao et al., 2012). Concentrations of copper (0.68–3.59 mg Cu/kg, dm) observed during the present study were comparable with those (1.52–3.39 mg/kg dm) in fishes from the Xiang River (Jia et al., 2018). Similar results were observed for concentrations of Cr, reported previously (Tao et al., 2012; Jiang et al., 2018) where it was reported that concentrations of Cr ranged from 0.62 to 0.99 mg/kg dm, and from 0.58 to 1.03 mg/kg dm, respectively. For non-essential trace elements, like As concentrations in *C. auratus* observed during the present study (0.71–1.13 mg/kg dm) were greater than those (mean: 0.384 mg/kg dm) in the same species from the Xiang River (Jia et al., 2018). Concentrations of Pb in *H. nobilis* in the present study (0.035–0.189 mg/kg dm) were less than those (mean: 2.305 mg/kg dm) in the same species from Taihu Lake (Tao et al., 2012). Concentrations of Cd in *C. alburnus* observed during the study, results of which are reported here (0.005–0.014 mg/kg dm) were comparable to those (mean: 0.008 mg/kg dm)

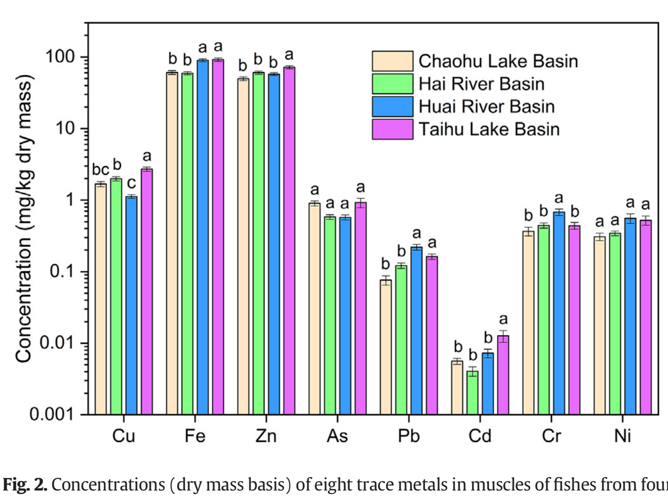

Fig. 2. Concentrations (dry mass basis) of eight trace metals in muscles of fishes from four basins. Different letters above the bars indicate significant differences ($p < 0.05$) identified by Duncan's Multiple Comparison test. All values were expressed as the mean ± standard error (SE).

Table 2
Comparison of trace element concentrations (dry mass basis) in fish muscles between this and previous studies.

Water bodies	Country	Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	References
		0.15-1.02	40.6-135.0	0.208-0.866	0.68-3.59	42.1-108.1	0.289-1.13	0.035-0.348	0.002-0.017	Present study
Tai Lake	China	0.62-0.99	NA	0.34-0.65	1.34-5.22	49.7-126.3	NA	0.43-2.31	0.01-0.37	Tao et al. (2012)
Tai Lake	China	0.08-0.092	NA	NA	0.03-0.097	NA	NA	0.06-0.087	0.023-0.042	Rajeshkumar et al. (2018)
Tai Lake	China	2.96-3.94	NA	5.04-5.41	1.92-3.72	63.3-367	2.10-3.31	19.4-20.13	1.24-1.58	Fu et al. (2013)
Xiang River	China	0.36-1.22	22.4-42.7	0.078-0.178	1.52-3.39	24.4-53.4	0.384-1.09	0.108-0.230	0.017-0.048	Jia et al. (2018)
Poyang Lake	China	0.186-0.291	NA	0.017-0.114	0.096-0.703	2.99-14.50	0.010-0.084	0.014-0.084	0.0009-0.009	Wei et al. (2014)
Caizi Lake	China	0.582-1.031	NA	NA	0.540-0.90	13.81-60.83	0.246-0.537	0.102-0.201	0.007-0.011	Jiang et al. (2018)
Yellow River	China	0.68-1.29	771-2,051	0.88-1.74	3.55-6.43	43.83-79.77	NA	0.48-1.0	NA	Liu et al. (2018a)
Jinjiang River	China	2.14-20.20	NA	0.17-5.14	1.78-5.18	38.7-101	0.06-0.97	0.14-0.69	0.001-0.02	Liu et al. (2018b)
Plitvice Lake	Croatia	NA	NA	NA	0.5	4.8	NA	0.08	0.01	Vukosav et al. (2014)[a]
Beyşehir Lake	Turkey	9.9-24.4	2.0-14.0	0.91-4.0	1.1-2.7	8.2-23.8	NA	1.6-5.2	2.1-4.0	Özparlak et al. (2012)
San Roque Lake	Argentina	0.04-3.32	10-59	0.2-1.04	0.08-0.86	52-62	2.6-7.9	0.01-0.07	< 0.02	Monferran et al. (2016)
Chascomus Lake	Argentina	1.75-2.23	25.5-52.1	0.84-1.04	0.95-1.35	20.8-23.1	0.13-0.27	0.37-1.30	< 0.01	Schenone et al. (2014)
Tshangalele Lake	Congo	0.08-0.49*	30-197.55*	0.09-0.35*	1.38-88.1*	27.4-122.9*	0.1-0.41*	0.03-0.56*	0.01-0.66*	Squadrone et al. (2016)
Indus River	Pakistan	0.002-0.96	NA	0.03-1.21	0.06-0.68	0.08-3.48	0.05-2.50	0.07-5.93	0.08-1.48	Nawab et al. (2018)

Data are expressed as range (from mean minimum to mean maximum). *: Data are expressed as range (from median minimum to median maximum).
[a] : Date are expressed as average (wet mass basis). NA: data not available.

in the same species from Caizi Lake (Jiang et al., 2018). To evaluate concentrations of trace elements in aquatic ecosystems, concentrations of trace elements in fishes in middle and eastern China in the present study were compared with those of fishes from other water bodies in the world (Table 2). Concentrations of trace elements in dorsal muscle of fishes varied among geographical regions and species with different diets. In general, concentrations of trace elements in muscle of fishes and their risks to health of humans were relatively small in middle and eastern China.

Spatial distributions of concentrations of trace elements in muscle of fishes from middle and eastern China are shown in Fig. 3. Geographically, distributions of concentrations of Cu and Zn in fishes were similar, with greater concentrations mainly in the northeast (Hebei Province) and southern regions, such as south of Jiangsu Province and Zhejiang Province, while the other greater concentrations were more evenly distributed. The greater concentrations of Cu and Zn might be attributed to intense development of industry (Lin et al., 2008; Wang et al., 2013b), such as iron-steel and electroplating factories in these areas. Greater concentrations of Cu and Zn could also be attributed to emissions from traffic associated with industrial activity and application of excessive amounts of chemical fertilizers (Rodriguez et al., 2008; Lv et al., 2013). Alternatively, greater concentrations of Cr were observed in the middle part of our study area. Similarly, concentrations of Fe, Ni, Pb, As and Cd in fish muscle increased from northern (Hebei Province) to southern (Zhejiang Province) regions in the present study. However, since there were fewer lakes and rivers in northern areas, most samples of fishes were collected from reservoirs where contamination was generally less. Many industrial parks were located in the northwest region, while there was more intensive agriculture in the central regions studied. Because Pb can be volatilized, deposition from air that was released during combustion of fuels in vehicles and industries was likely a wide-spread source of Pb (Meng et al., 2008; Wu et al., 2008).

3.2. Concentrations of trace elements among fishes

Detailed information on concentrations of trace elements in muscle of fishes are given in Table S2. Significant differences in accumulations of trace elements were observed among fishes. Greatest concentrations of Fe, Cu, Zn and Cr were observed in *C. alburnus*, while those of As and Cd were observed in *C. auratus*. Greatest concentrations of Pb were observed in *C. carpio*, while those of Ni were observed in *H. nobilis*. Least concentrations of Fe, Cu, Zn and Cd were observed in *H. molitrix*, while those of Pb and As were observed in *H. nobilis*. Least concentrations of Ni and Cr were observed in *C. carpio* and *C. auratus* respectively. These results indicate that carnivorous fishes, such as *C. alburnus* or omnivorous fishes living close to the sediment, such as *C. auratus* and *C. carpio* accumulated greater amounts of trace elements than did planktivorous fishes, such as *H. molitrix* and *H. nobilis*.

Concentrations of Cr by *C. alburnus* were significantly greater than those in other fishes. Concentrations of Fe were significantly ($p < 0.05$) greater in *C. alburnus* than in other fishes. Concentrations of Fe were greater ($p < 0.05$) in the omnivorous *C. auratus* and *C. carpio* than in the planktivorous fishes. Concentrations of Zn and Cu were significantly ($p < 0.05$) different between species except between *H. nobilis* and *H. molitrix*. The order of increasing concentrations was *H. nobilis* and *H. molitrix* < *C. carpio* < *C. auratus* < *C. alburnus*. Concentrations of Pb were significantly ($p < 0.05$) less in planktivorous fishes than in *C. auratus* or *C. carpio.* Concentrations of As were greatest ($p < 0.05$) in *C. auratus*, while those of As were significantly ($p < 0.05$) greater in *C. carpio* than in planktivorous fishes. Concentrations of Ni and Cd were not significantly different among fishes (Fig. 4).

Accumulation of trace elements by fishes can be affected by a lot of factors, such as type of element, trophic level, preferred habitat, diet, location and physical and chemical characteristics of water (Oost et al., 2003; Morgano et al., 2011; Weber et al., 2013). Generally, omnivorous fishes accumulated greater concentrations of trace elements than did carnivorous fishes (Yousafzai et al., 2010). However, the results of the study presented here, indicate that piscivorous fishes and demersal omnivorous fishes tended to accumulate greater concentrations of trace elements than did pelagic planktivorous fishes. Generally, the decreasing order of concentrations was carnivorous > omnivorous > planktivorous. Results of several other studies also showed that trace elements can be magnified along food chains (Has-Schön et al., 2006; Peakall and Burger, 2003). In the present study, although both *C. auratus* and *C. carpio* were grouped into omnivorous fishes, concentrations of several trace elements, including, Cu, Zn and As were significantly ($p < 0.05$) greater in *C. auratus* than in *C. carpio*, which is consistent with previously reported results (Kalyoncu et al., 2012). This might be attributed to the relatively slower growth rate and smaller effects of growth dilution of *C. auratus*.

3.3. Relationships between concentrations of trace elements and stable isotope ($\delta^{15}N$) values

Ratio of stable isotopes (^{13}C and ^{15}N) are widely used to study the structure of food webs, sources of food and apparent trophic level status of species (Peterson and Fry, 1987; Xu and Xie, 2004; Yuille et al., 2012).

In this study, values for δ^{13}C ranged from −32.32‰ to −20.07‰, and values for δ^{15}N ranged from 6.14‰ to 19.31‰. Wide ranges of δ^{13}C and δ^{15}N values were observed among the four basins, which is possibly due to spatial differences of isotopes. For instance, some areas might be dominated by autochthonous production of phytoplankton while others are dominated by allochthanous inputs of plant-based materials from terrestrial ecosystems (Riedl et al., 2018).

Relationships between concentrations of trace metal and δ^{15}N values of fish muscle were displayed in Fig. 5. Concentrations of Fe, Cu and Zn exhibited significantly positive relationships with values of δ^{15}N, which indicated their trophic magnification (biomagnification) along the food chain. No such relations were found for the other trace elements. Biomagnification of Zn by fishes was also observed in the Yellow River Estuary, China and laboratory studies (Zhang and Wang, 2007; Liu et al., 2018a), while no biomagnification of Zn was observed in the Daliao River and Liaodong Bay, China (Guo et al., 2016). This is due to different concentrations of Zn in various water bodies. In field studies of fishes, biomagnification of Zn only occurred in uncontaminated water bodies where prey contained generally <105 μg Zn/g, dm (Campbell et al., 2005; Cardwell et al., 2013). Results of a previous study also showed that Cu was biomagnified through the food chain (Jara-Marini et al., 2009). For biomagnifications of Zn, Cu and Fe, a

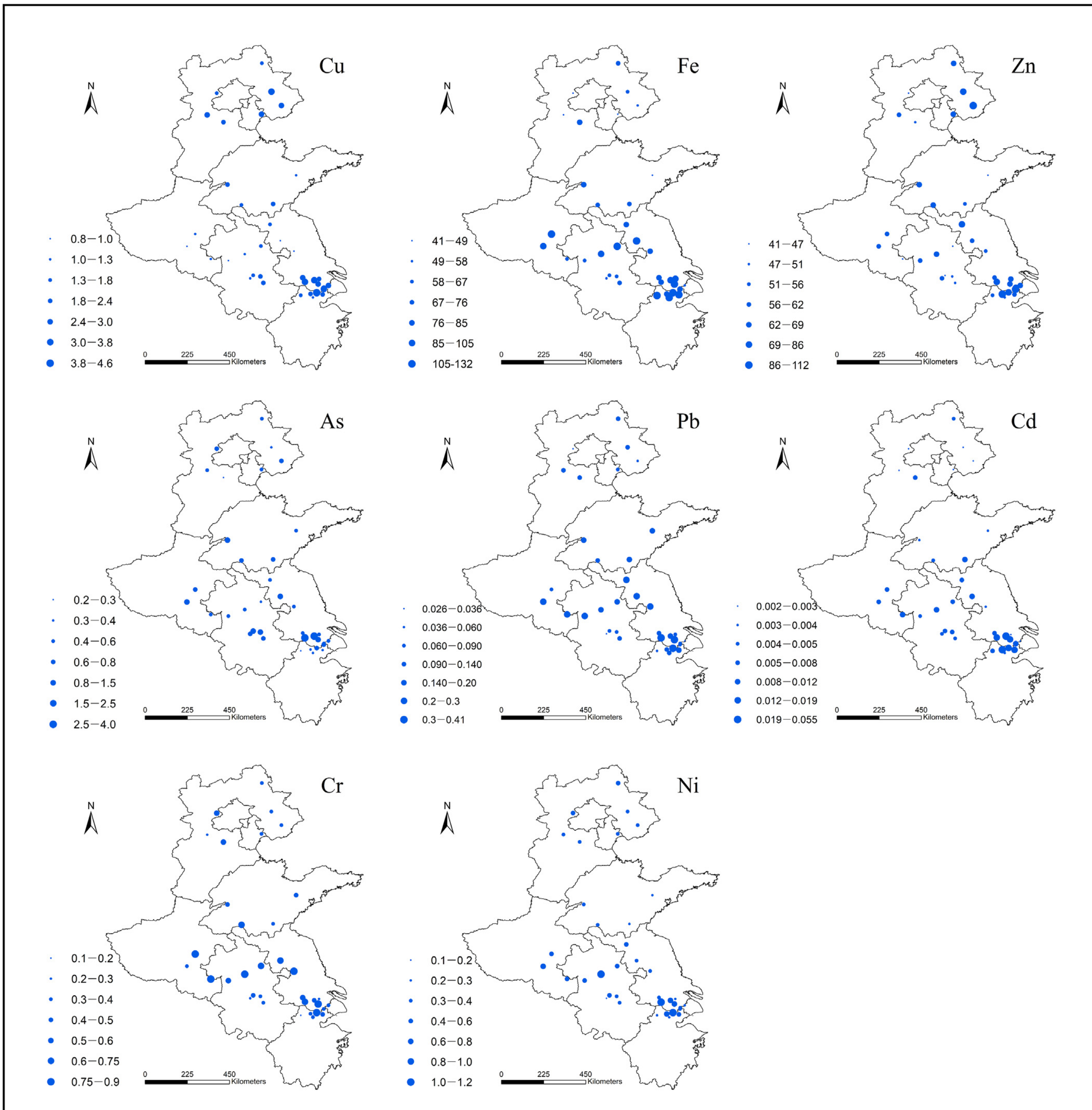

Fig. 3. Spatial distribution of concentrations (mg/kg, dry mass) of eight trace metals in fish muscles from middle and eastern China.

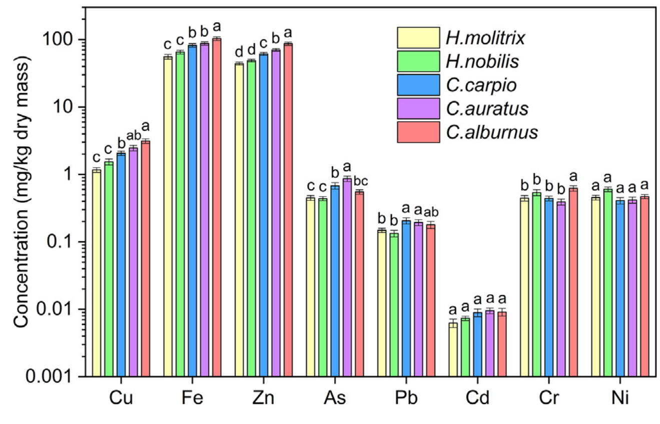

Fig. 4. Concentrations (mg/kg, dry mass) of metals in muscle of five fishes. Different letters above the bars indicate significant differences ($p < 0.05$) identified by Duncan's Multiple Comparison test. All values were expressed as mean ± standard error (SE).

possible explanation is that they are essential elements and their uptake, accumulation, and excretion by fish are homeostatically regulated (Zhang et al., 2010; Cardwell et al., 2013). In fact, this is the first study to report that Fe can be biomagnified in fish along the food chain.

3.4. Assessment of risk to health of humans

Worldwide, more and more attention is being paid to issues of food safety (Wong, 2017). Due to rapid industrialization and sometimes lax environmental monitoring programs, particularly in the context of wildlife that is consumed by humans, contamination of the environment by trace metals is a topic of broad concern. Monitoring of concentrations of trace elements in fish muscle can provide information on risks to health of humans posed by contaminants from this route of exposure. Fishes collected in this study are commonly consumed by native residents. Hence, it is of great importance to assess risks to health of humans due to chronic exposure of trace elements from fish consumption. The target hazard quotient (THQ) and total target hazard quotient (TTHQ) were used to evaluate non-carcinogenic risk to human health. THQs were calculated by mean and maximum concentrations of each trace element (Fig. 6). Results indicated that THQ values for individual trace elements varied among fishes, with an increasing order of Cd < Ni < Pb < Cu < Fe < Cr < Zn < As. When TTHQ (sum of THQs) of an individual element is <1.0, non-carcinogenic risk is *di minimis*, otherwise, it indicates greater risk. In the present study, non-carcinogenic risks posed by trace elements through consumption fish muscle was greater in Taihu Lake Basin than that in the other three basins. Based on either THQ-mean or THQ-max, the value of TTHQ was <1.0, which indicated

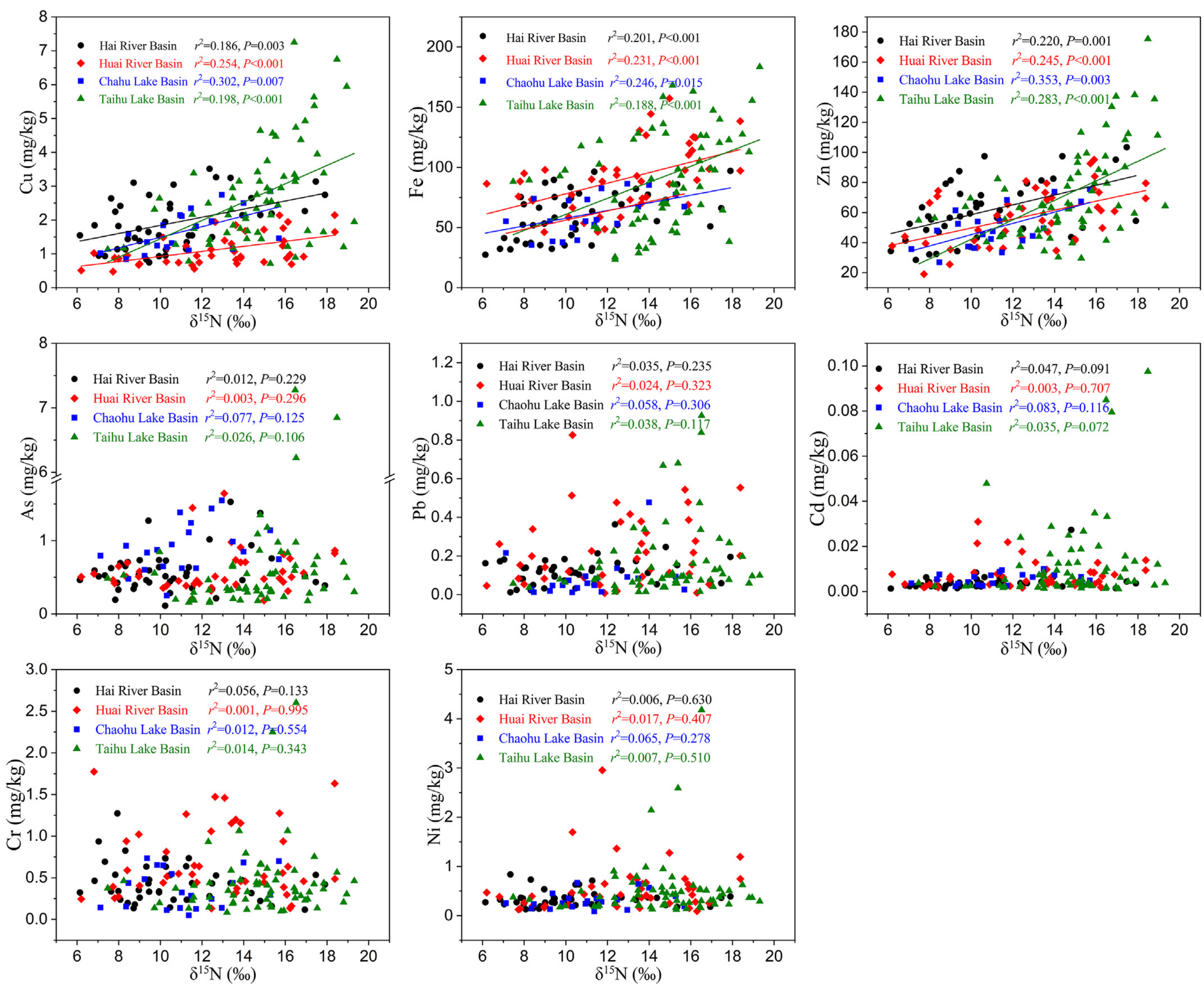

Fig. 5. Relationships between trace element concentrations (expressed as mg/kg, dry mass) and δ^{15}N values in freshwater wild fish from middle and eastern China.

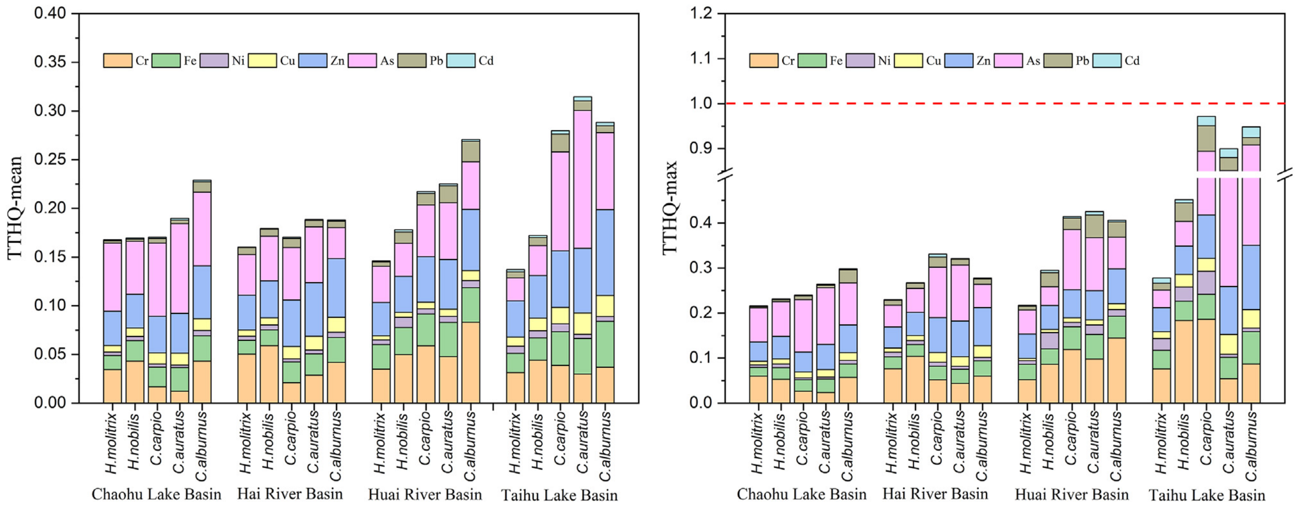

Fig. 6. Contributions to TTHQ for the trace elements via consumption of five fishes collected from middle and eastern China among different basin, TTHQ-mean: averaged target hazard quotients; THQ-max: maximum target hazard quotients. 10% of the total As (represent inorganic As) was used to calculate THQs (USFDA, 1993).

de minimis risks of non-carcinogenic effects to consumers. However, consumption of fish by particular groups of people, like fisherfolk, is greater than that of ordinary people. For people living in Taihu Lake Basin, the threshold of consumption of fish is 297.9 g/person/day, which is calculated by average of TTHQ-means of different fishes. For Chaohu Lake Basin, Huai River Basin and Hai River Basin, the threshold is 383.4, 342.4 and 400.5 g/person/day, respectively. Also, it should be noted that humans are exposed to trace elements not only by fish consumption, but also by several other routes, including drinking water. The impacts of trace elements contamination on health of vulnerable populations, such as pregnant women, children and people with poor physical fitness, also need to be carefully evaluated. Furthermore, complex interactions among the mixture components made it difficult to accurately assess actual risks to health (Wilbur et al., 2004; Huang et al., 2008).

4. Conclusions

In this study, 410 samples of five commercial fishes were collected from middle and eastern China, and eight trace elements (Cr, Fe, Ni, Cu, Zn, As, Pb and Cd) in dorsal muscle of fishes were analyzed for their possible biomagnification along the food chain. There were geographic differences in contents of these trace elements, probably due to different geochemical background values and/or human activities like industrial and agriculture inputs. Carnivorous and omnivorous fishes accumulated significantly greater concentrations of metals than did planktivorous fishes. Results of regression analyses between concentrations of trace elements and $\delta^{15}N$ in fish muscle revealed that only Fe, Cu and Zn could be biomagnified through food chain. TTHQ values suggested that trace elements in muscle of fish were at a safe level, and that non-carcinogenic health risk posed by these elements through fish consumption was *de minimis*. However, regular monitoring of trace elements contamination in fishes especially from intensive industrial and/or agricultural areas is needed.

Acknowledgements

This study was supported by the Major Science and Technology Program for Water Pollution Control and Treatment (2017ZX07203-004), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB31040000), and the Foundation Research Project of Qinghai Province (2018-ZJ-709). Prof. Giesy was supported by the “High Level Foreign Experts” program (#GDT20143200016) funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences. He was also supported by the Canada Research Chair program and a Distinguished Visiting Professorship in the School of Biological Sciences of the University of Hong Kong and the Department of Environmental Sciences at Baylor University.

We would like to express our sincere thanks to Dr. Henner Hollert and four anonymous reviewers for their critical and valuable comments which greatly improved the manuscript. Thanks are also given to Weizhen Zhang, Ting Shi, Yeke Wang, and Jia Zhang, for their help during the sampling.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.03.134.

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Supporting Information

Spatial and interspecies differences in concentrations of eight trace elements in wild freshwater fishes at different trophic levels from middle and eastern China

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Table S1. Limit of detection (LOD, mg/kg, dry mass) of the eight trace elements, and recovery of certified reference material GBW08573.

	Cr	Fe	Ni	Cu	Zn	As	Pb	Cd
LOD	0.087	0.191	0.008	0.132	0.185	0.011	0.006	0.001
Certified values	0.43	23.9 ± 3.4	1.50 ± 0.21	1.36 ± 0.13	28.8 ± 1.4	5.08 ± 0.39	0.81 ± 0.03	0.015
Measured values	0.45 ± 0.07	23.0 ± 3.2	1.34 ± 0.13	1.42 ± 0.14	31.4 ± 2.3	5.00 ± 0.55	0.91 ± 0.05	0.014 ± 0.02
Recovery (%)	104.7	96.2	89.3	104.4	109.0	98.4	112.3	93.3

Data are expressed as the mean ± standard deviation (SD). Certified reference material GBW08573 is detected for eight times (n = 8), and units of eight trace elements are all mg/kg, dry mass.

Table S2. Trace element concentrations (dry mass basis) and δ^{13}C and δ^{15}N values in fish species from middle and eastern China.

Watersheds	Fish species		Cr (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Pb (mg/kg)	Cd (μg/kg)	δ^{13}C (‰)	δ^{15}N (‰)
Hai River Basin	*Hypophthalmichthys molitrix*	Mean±SE	0.62±0.09	40.57±7.20	0.35±0.10	1.03±0.12	43.92±5.27	0.51±0.02	0.118±0.024	2.28±0.36	-25.79±0.26	7.92±0.54
		Range	0.32-0.94	27.36-75.33	0.23-0.84	0.75-1.55	28.49-57.37	0.46-0.60	0.012-0.181	1.28-3.74	-26.65to-24.83	6.14-9.46
	Hypophthalmichthys nobilis	Mean±SE	0.72±0.17	46.32±7.82	0.42±0.08	1.20±0.17	46.41±5.99	0.56±0.04	0.118±0.030	3.02±0.42	-25.06±0.20	8.65±0.64
		Range	0.33-1.27	32.36-74.36	0.25-0.73	0.93-1.85	32.47-63.48	0.43-0.65	0.024-0.184	2.16-4.36	-25.37to-24.27	6.84-10.25
	Cyprinus carpio	Mean±SE	0.26±0.04	61.32±4.66	0.25±0.05	2.09±0.23	58.54±5.62	0.66±0.10	0.151±0.026	5.22±2.24	-24.45±0.36	10.75±0.88
		Range	0.12-0.63	36.36-87.24	0.13-0.71	1.12-3.52	32.17-95.21	0.28-1.38	0.050-0.363	1.35-27.32	-26.93to-22.32	7.98-16.94
	Carassius auratus	Mean±SE	0.35±0.03	62.79±5.66	0.32±0.03	2.33±0.21	67.36±5.23	0.71±0.12	0.107±0.018	3.48±0.36	-24.44±0.35	10.60±0.80
		Range	0.16-0.54	35.45-89.62	0.18-0.54	1.55-3.47	45.37-97.47	0.19-1.53	0.024-0.214	2.19-6.25	-26.36to-21.98	7.64-15.35
	Culter alburnus	Mean±SE	0.51±0.05	73.21±6.04	0.44±0.04	2.52±0.29	74.01±6.16	0.39±0.05	0.108±0.018	5.10±0.60	-23.40±0.41	13.02±0.97
		Range	0.24-0.74	48.32-97.09	0.36-0.64	1.49-4.26	49.32-103.47	0.11-0.64	0.033-0.195	3.37-8.36	-25.37to-21.37	10.23-17.9
Huai River Basin	*Hypophthalmichthys molitrix*	Mean±SE	0.43±0.05	72.32±7.28	0.40±0.07	0.68±0.05	42.08±5.27	0.46±0.05	0.071±0.014	4.27±0.78	-28.08±0.85	9.86±0.89
		Range	0.25-0.64	46.45-98.02	0.13-0.65	0.48-0.86	19.01-66.47	0.21-0.65	0.008-0.142	1.79-7.65	-32.32to-24.39	6.20-13.67
	Hypophthalmichthys nobilis	Mean±SE	0.61±0.12	79.56±6.39	0.87±0.35	0.83±0.06	45.38±4.67	0.42±0.02	0.189±0.068	9.62±3.18	-26.99±0.63	11.29±0.79
		Range	0.13-1.06	46.24-97.96	0.14-2.96	0.56-1.13	25.51-65.37	0.32-0.51	0.019-0.513	1.58-21.84	-29.85to-23.77	7.80-14.98
	Cyprinus carpio	Mean±SE	0.72±0.16	93.36±9.67	0.44±0.07	1.11±0.11	57.35±4.64	0.65±0.14	0.193±0.038	7.53±1.14	-25.86±0.59	12.97±0.88
		Range	0.16-1.46	58.63-144.41	0.09-0.79	0.69-1.68	34.68-76.47	0.36-1.64	0.009-0.417	2.94-12.86	-27.55to-22.57	8.37-16.30
	Carassius auratus	Mean±SE	0.59±0.12	100.77±10.23	0.51±0.16	1.21±0.12	62.62±4.27	0.72±0.12	0.283±0.079	7.70±3.04	-25.04±0.60	13.47±0.89
		Range	0.14-1.20	66.51-157.44	0.16-1.70	0.88-1.85	41.46-79.48	0.18-1.45	0.048-0.826	1.78-30.90	-26.93to-22.06	8.41-16.88
	Culter alburnus	Mean±SE	1.02±0.18	101.72±8.58	0.60±0.10	1.69±0.13	77.21±5.01	0.60±0.06	0.348±0.053	7.12±1.18	-24.21±0.54	15.64±0.74
		Range	0.39-1.77	58.47-138.50	0.15-1.20	1.02-2.15	44.02-95.16	0.31-0.86	0.108-0.554	3.22-13.87	-25.98to-22.01	11.81-18.38
Chaohu Lake Basin	*Hypophthalmichthys molitrix*	Mean±SE	0.42±0.16	41.71±4.56	0.28±0.07	1.12±0.12	43.35±4.08	0.86±0.03	0.039±0.005	4.15±0.42	-30.08±0.37	8.67±0.60
		Range	0.14-0.74	35.38-55.23	0.14-0.45	0.84-1.35	35.64-52.47	0.79-0.93	0.026-0.048	3.46-5.32	-30.91to-29.46	7.12-9.85
	Hypophthalmichthys nobilis	Mean±SE	0.53±0.05	60.30±8.13	0.35±0.12	1.43±0.20	42.55±7.36	0.67±0.10	0.035±0.014	4.70±1.34	-29.39±0.48	9.60±0.47
		Range	0.44-0.65	39.47-73.93	0.13-0.66	0.94-1.85	26.92-61.48	0.48-0.95	0.013-0.074	2.36-7.52	-30.74to-28.46	8.46-10.55
	Cyprinus carpio	Mean±SE	0.20±0.05	57.96±5.24	0.26±0.03	1.86±0.23	46.28±2.88	0.92±0.29	0.076±0.027	5.29±1.15	-28.17±0.69	11.19±0.45
		Range	0.11-0.32	49.88-73.31	0.18-0.32	1.20-2.15	41.37-53.92	0.25-1.44	0.012-0.137	2.98-7.36	-30.20to-27.15	10.31-12.46
	Carassius auratus	Mean±SE	0.15±0.05	69.49±8.79	0.21±0.07	2.00±0.36	50.18±7.42	1.13±0.19	0.060±0.018	6.76±1.57	-27.46±0.69	11.88±0.36
		Range	0.05-0.28	52.38-86.47	0.09-0.35	1.10-2.75	33.47-68.36	0.63-1.55	0.015-0.092	2.50-9.46	-29.01to-26.18	11.36-12.95
	Culter alburnus	Mean±SE	0.53±0.10	74.39±4.38	0.45±0.10	1.99±0.41	66.50±5.96	0.93±0.09	0.170±0.104	7.15±1.06	-25.89±0.88	14.61±0.52
		Range	0.29-0.70	67.37-85.47	0.19-0.64	1.15-2.85	49.42-75.46	0.75-1.14	0.026-0.478	4.88-9.94	-27.90to-23.70	13.47-15.69
Taihu Lake Basin	*Hypophthalmichthys molitrix*	Mean±SE	0.39±0.07	56.41±7.63	0.59±0.15	1.54±0.16	45.68±3.18	0.29±0.03	0.101±0.020	9.96±1.40	-27.06±0.64	12.45±0.54
		Range	0.08-0.93	23.44-117.67	0.16-2.14	0.71-2.49	29.56-65.37	0.15-0.48	0.013-0.244	1.47-47.84	-31.00to-22.39	7.47-15.28
	Hypophthalmichthys nobilis	Mean±SE	0.54±0.16	65.64±7.42	0.59±0.18	2.14±0.28	53.61±2.95	0.38±0.05	0.136±0.051	8.47±1.23	-26.06±0.82	13.66±0.58
		Range	0.15-2.25	28.93-122.25	0.16-2.59	0.89-4.57	39.73-77.36	0.19-0.67	0.014-0.680	1.32-28.74	-30.50to-20.07	8.24-16.48
	Cyprinus carpio	Mean±SE	0.47±0.18	98.97±8.79	0.67±0.30	2.76±0.26	71.26±5.65	0.63±0.16	0.300±0.086	14.17±1.89	-26.12±0.63	14.95±0.53
		Range	0.10-2.60	47.25-158.75	0.12-4.18	1.27-4.74	44.01-118.27	0.18-7.27	0.063-0.926	2.17-84.86	-30.03to-22.82	9.72-17.15
	Carassius auratus	Mean±SE	0.37±0.04	104.79±6.68	0.35±0.03	3.59±0.45	81.42±6.19	1.02±0.17	0.161±0.039	16.86±1.74	-26.34±0.66	15.26±0.55
		Range	0.10-0.66	63.28-136.15	0.19-0.53	1.63-7.25	59.37-130.37	0.34-5.85	0.038-0.475	2.38-79.43	-30.92to-22.76	9.96-17.83
	Culter alburnus	Mean±SE	0.45±0.07	134.94±11.45	0.41±0.04	3.54±0.50	108.10±8.98	0.51±0.06	0.116±0.019	13.83±2.75	-26.96±0.70	17.05±0.56
		Range	0.13-1.06	64.31-206.21	0.19-0.63	1.20-6.75	64.27-175.37	0.18-6.85	0.016-0.268	1.10-97.46	-30.29to-22.79	11.6-19.31

SE is the standard error, range indicates minimum and maximum.