

Technology-critical elements in fishes from two of the Laurentian Great Lakes

José E. Celis  · Winfred Espejo · Karen Kidd · Daryl McGoldrick · Mandi Clark · Daiki Kitamura · Shosaku Kashiwada

Received: 25 August 2022 / Accepted: 10 October 2022 / Published online: 31 October 2022
© The Author(s) 2022

Abstract U.S. and Canada have long-term monitoring programs for metals which provide important information about the status of contaminants in the Great Lakes. However, some technology-critical elements (Ce, Gd, Hf, Ir, Os, Re, Ru, Ta, W, Y) that are increasingly extracted and used in electronics have not been included in such programs to understand their presence in aquatic ecosystems. We studied the concentrations of these elements in muscle of six fish species collected from Lakes Erie and Ontario, as well as their relationships to body size and condition to understand whether biological factors affect their bioaccumulation. The highest concentrations detected were for Ce in the muscle of trout-perch (*Percopsis omiscomaycus*) from Lake Erie, and in the muscle of round goby (*Neogobius melanostomus*) from Lake Ontario. There were negative relationships for W and Y with length in *S. namaycush* and deepwater sculpin (*Myoxocephalus thompsonii*), respectively. Also, there was a negative relationship for Gd with weight in *M. thompsonii*. The regressions showed that Ta showed positive relationship with both length and weight of yellow perch (*Perca flavescens*) from Lake Erie, whereas this element showed a negative correlation ($P < 0.05$) with the Fulton factor in *S. namaycush* from Lake Ontario. These first results suggest that technology-critical elements vary within and among species from two of the Great Lakes, with some decreasing with increasing fish size, and that these data could serve as baseline information to assess trends in fish populations in these systems.

Keywords Rare earth elements · Trace metals · Technological elements · Muscle · Fish · Aquatic environment

Introduction

The study of trace elements in aquatic environments is very important, because they accumulate in the organism, are difficult to eliminate, and can cause deleterious effects in biota (Shukla et al. 2007; Heydarnejad et al. 2013; Donadt et al. 2021; Taslima et al. 2022). Certain rare earth elements such as Ce, Gd and Y, along with some other less-known trace elements (Hf, Ir, Os, Re, Ru, Ta, W), which are part of the composition of the continental crust (Rudnick and Gao 2003), have been in high demand for the production of emerging

José E. Celis
Department of Animal Science, Facultad de Ciencias Veterinarias, Universidad de Concepción, Av. Vicente Méndez 595, Chillán, Chile

Winfred Espejo (✉)
Department of Soils & Natural Resources, Facultad de Agronomía, Universidad de Concepción, Av. Vicente Méndez 595, Chillán, Chile
e-mail: winfredespejo@udec.cl

Karen Kidd
Department of Biology & School of Geography and Earth Sciences, McMaster University, 1280 Main Street W., Hamilton, ON L8S 4K1, Canada

Daryl McGoldrick · Mandi Clark
Water Quality Monitoring & Surveillance Division, Environment and Climate Change, Canada

Daiki Kitamura · Shosaku Kashiwada
Research Center for Life and Environmental Sciences, Toyo University, Japan

technologies such as cell phones, portable computers, hybrid cars, biomedicines, and photovoltaic cells (O'Hara and Demkov 2014; Pagano et al. 2015; Aliff et al. 2020). As their extraction from the earth's crust and use in products increases, there is greater risk of contamination of aquatic environments from mining runoff and disposal of end-of-life goods. Freshwater fish are important indicators of the health status of lakes, and several studies have been conducted around the world to see how trace elements bioaccumulate in these species, being very useful for environmental monitoring (Chen et al. 2000; Kucykbay and Orun 2003; Zhang et al. 2007; Klavins et al. 2009; Rajeshkumar and Li 2018). A study found that freshwater fish exhibit greater rare earth element levels than marine fish (Yang et al. 2016). Though some elements are essential to aquatic biota at trace levels, above certain thresholds they become deleterious (Newman 2005), thus their releases to and concentrations in surface waters are regulated by protocols and directives (Jaishankar et al. 2014; Romero-Freire et al. 2019).

Many elements (most of so called “heavy metals”) are genotoxic and carcinogenic, capable of inducing oxidative stress which causes DNA damage and cell death (Lushchak 2011); however, much less is known about the toxicity of technology-critical elements. Some in vitro studies indicate that Ce might induce toxicity in cells of fish and humans (Lin et al. 2006; Park et al. 2008; Gaiser et al. 2009). Animal cell lines exposed to Gd display necrosis, apoptosis, and cytotoxicity (Rogosnitzky and Branch 2016). Similarly, rat fibroblasts exposed to Ir had cytotoxicity and genotoxicity (Iavicoli and Leso 2015). Rhenium (Re) delays the hatching time and increased birth defects of zebrafish (*Danio rerio*) (Haase et al. 2019). In vitro and in vivo assays using high Ru concentrations delayed hatching, amniotic fluid alteration, red blood cell accumulation and yolk sac alteration in zebrafish (Mello-Andrade et al. 2018). There are no studies on Ta toxicity in aquatic species, but some evidence exists that Ta inhalation can cause bronchitis and interstitial pneumonitis in mammals (Chen et al. 1999). Though the toxicity of W alone has not been examined, in vitro studies using W alloys showed DNA damage in rats (Harris et al. 2015). Collectively these studies suggest that the bioaccumulation of technology-critical and other elements may be adversely affecting wild fish population (Espejo et al. 2018a; Celis et al. 2020).

Lake Erie and Lake Ontario are located between Canada and the United States, surrounded by areas with a large amount of anthropogenic activities. Studies of metals in the Great Lakes have evidenced a history of contamination from agricultural, mining, forest fires, urban and industrial development, dating back to 1850 with the settlement of European immigrants (Aliff et al. 2020). Lakes Ontario and Erie are among the most chemically contaminated of the Great Lakes, and monitoring data have shown that differences in sources, physical characteristics of the lakes and food web characteristics can affect concentrations of chemicals in fish (Carlson and Swackhamer 2006). However, to our knowledge, these studies have not considered less-studied trace elements, such as those that are the focus of the current study. We hypothesize here that these lesser-known elements are widely distributed in fish in the Great Lakes. Considering the growing demand for these elements and the paucity of data on them in aquatic species in the Great Lakes, the objective of this work was to assess their levels among several fishes and contribute new knowledge on their fate in aquatic ecosystems.

Materials and methods

Fishes from Lake Ontario and Lake Erie were collected during the field campaign of 2014 (Fig. 1). Lake Erie is the smallest in volume (488 km³) and the shallowest (with an average depth of only 13 m). It is located at 173 m above sea level, and has a surface area of 25,700 km². Lake Ontario (74 m above sea level) has the smallest surface area (18,960 km²), although it exceeds Lake Erie in volume (1,639 km³) and an average depth of 84 m (USEPA 2011).

Six species of fish were collected from Lake Erie: yellow perch (*Perca flavescens*); emerald shiner (*Notropis atherinoides*); trout-perch (*Percopsis omiscomaycus*); round goby (*Neogobius melanostomus*); rainbow smelt (*Osmerus mordax*); walleye (*Sander vitreus*). Four species were sampled at Lake Ontario: lake trout (*Salvelinus namaycush*); rainbow smelt (*Osmerus mordax*); round goby (*Neogobius melanostomus*); deepwater sculpin (*Myoxocephalus thompsonii*).

All fish were collected as part of Environment and Climate Change Canada's contaminant monitoring activities in the Great Lakes utilizing standard operating procedures approved under The Ontario and Quebec Region Aquatic Animal Care Committee of ECCC (Clark et al. 2022a; Clark et al. 2022b). The





Fig. 1 Map of The Great Lakes of North America with red points showing sampling sites in Lake Erie and Lake Ontario (field campaign in 2014).

Table 1 Biological samples collected by group of species, total length (T_L), total weight (T_w), and Fulton's condition factor (CF) from the Lake Erie and Lake Ontario (Canada).

Lake	Species	N	T_L (cm)	T_w (g)	CF
Erie	<i>P. flavescens</i>	10	16.74 ± 6.51	73.60 ± 65.40	1.08 ± 0.36
	<i>N. atherinoides</i>	4	5.35 ± 0.24	1.78 ± 0.36	1.19 ± 0.43
	<i>P. omiscomaycus</i>	2	8.80 ± 0.99	8.80 ± 1.56	1.30 ± 0.21
	<i>N. melanostomus</i>	3	7.08 ± 2.67	5.93 ± 3.50	1.80 ± 0.74
	<i>O. mordax</i>	5	6.06 ± 0.56	1.42 ± 0.28	0.64 ± 0.09
	<i>S. vitreus</i>	10	52.43 ± 2.47	$1,280.31 \pm 460.29$	0.89 ± 0.31
Ontario	<i>S. namaycush</i>	5	66.90 ± 8.97	$3,855.12 \pm 1,309.94$	1.24 ± 0.11
	<i>O. mordax</i>	3	21.75 ± 25.26	$1,036.79 \pm 1,673.57$	0.48 ± 0.07
	<i>N. melanostomus</i>	3	9.90 ± 1.73	11.13 ± 4.65	1.14 ± 0.31
	<i>M. thompsonii</i>	4	13.35 ± 2.19	28.73 ± 11.91	1.15 ± 0.07

samples provided for this specific investigation were whole body homogenates removed from the National Aquatic Biological Specimen Bank and processed according to the procedures described in McGoldrick et al. (2010). Fulton's condition factor (CF) was calculated as $CF = 100 \times (TW)/(TL)^3$ to assess the health status of the fish (Balzani et al. 2021). Thus, when the calculated value is higher it implies that the fish exhibits a better condition (Schloesser and Fabrizio 2017). Table 1 shows the values of the length, weight, and Fulton's condition factor for each species collected from the Lake Erie and Lake Ontario (Canada).

Once in the laboratory, all samples were freeze-dried until dry masses were constant. After that, they were homogenized into a fine powder (by using a glass mortar), cleaned (2% Conrad Merck® solution x 24 h), washed (deionized water + HCl 1 M), and rinsed with distilled water (Wassenaar and Hendry 2000). Then, a mass of about 0.2 g of each sample was placed into a Teflon beaker (50 mL capacity) containing 5 mL of ultrapure nitric acid, and heated at 110°C for 3 h (until almost dry). Following, 1 mL of hydrogen peroxide and 5 mL of ultrapure nitric acid were added, and the mixture was heated again to near dryness for another 3 h. The residue left was dissolved with 5 mL of 1% ultrapure nitric acid, then filtered (glass fiber filter < 0.45 µm), and finally relocated to a centrifuge tube. This process of digestion and filtration was repeated four times in order to obtain a final volume of 25 mL. The concentrations of the trace elements were determined through mass spectrometry coupled with a plasma inductor (ICP-MS Perkin



Table 2 Concentrations of different elements (mean \pm standard deviation) in fishes from Lake Erie (ng/g, dry weight)

Elements	Fish species					
	<i>P. flavescens</i>	<i>N. atherinoides</i>	<i>P. omiscomaycus</i>	<i>N. melanostomus</i>	<i>O. mordax</i>	<i>S. vitreus</i>
Ce	255.07 \pm 110.79	49.54 \pm 9.86	349.08 \pm 60.63	276.35 \pm 129.07	140.05 \pm 57.47	18.20 \pm 5.47
Gd	25.87 \pm 9.67	6.09 \pm 0.85	32.74 \pm 6.07	27.35 \pm 12.06	15.13 \pm 4.78	3.49 \pm 0.78
Hf	89.92 \pm 31.34	94.70 \pm 20.07	89.93 \pm 10.84	80.29 \pm 6.30	132.80 \pm 79.58	73.58 \pm 8.33
Ir	6.01 \pm 9.77	3.17 \pm 3.10	0.91 \pm 0.11	0.69 \pm 0.07	7.17 \pm 11.08	0.75 \pm 0.25
Os	1.62 \pm 1.87	2.56 \pm 1.48	0.73 \pm 0.16	0.45 \pm 0.13	3.94 \pm 4.71	0.66 \pm 0.20
Ta	0.60 \pm 0.36	1.54 \pm 0.58	1.26 \pm 0.03	0.93 \pm 0.03	2.90 \pm 1.96	0.56 \pm 0.15
W	23.27 \pm 1.91	27.19 \pm 7.57	88.22 \pm 8.88	98.11 \pm 31.32	21.96 \pm 10.01	13.81 \pm 6.92
Y	103.33 \pm 36.46	36.37 \pm 4.14	136.61 \pm 14.24	114.33 \pm 43.29	70.01 \pm 20.32	26.99 \pm 3.30

Ce: Cerium; Gd: Gadolinium; Hf: Hafnium; Ir: Iridium; Os: Osmium; Ta: Tantalum; W: Tungsten; Y: Yttrium

Elmer NexION-350D) at the Environmental Health Science Laboratory of the Toyo University, Japan. For ensuring the quality of the chemical element measurements, a seven-point calibration curve was made for each element studied here that allowed obtaining a median response factor, which was used to compute the element concentration in the sample. Because certified reference materials for Ce, Gd, Hf, Ir, Os, Re, Ru, Ta, W, or Y in biological materials are not available, a Multi-element Calibration Standard 5 by Perkin Elmer (n=7) was used. We used the element In (a stable isotope of indium with atomic weight 115) as an internal standard. All chemical element concentrations were expressed on a dry weight basis.

Before any statistical analyses were done, metal concentrations were \log_{10} -transformed. A linear model was used to identify relationships between element concentrations, size (length, weight) and body condition. All statistical analyses were performed using the software R (4.0 version, R Core Team 2020), and the level of significance at $P \leq 0.05$ was considered.

Results

For Lake Erie (Table 2), the highest Ce (349.1 ng/g), Gd (32.7 ng/g) and Y (136.6 ng/g) contents in the muscle of fish were found in trout-perch (*Percopsis omiscomaycus*), the highest levels of Hf (132.8 ng/g), Ir (7.2 ng/g), Os (3.9 ng/g) and Ta (2.9 ng/g) were found in rainbow smelt (*Osmerus mordax*), while round goby (*Neogobius melanostomus*) exhibited the highest W concentrations (98.1 ng/g, Table 2). On the other hand, the lowest levels of Ce, Gd, Hf, Ta, W and Y were measured in the muscle of walleye (*Sander vitreus*), while the lowest contents of Ir and Os in the muscle of round goby (*Neogobius melanostomus*) (Table 2).

For Lake Ontario (Table 3), the highest Ce, Gd and Y levels were found in the muscle of round goby (*N. melanostomus*) with 1,266.1, 163.4 and 671.7 ng/g, respectively. The highest concentrations of Hf (82.8 ng/g) were measured in the muscle of lake trout (*Salvelinus namaycush*), while the highest Ir (1.3 ng/g), Os (1.8 ng/g) and Ta (1.5 ng/g) levels in the muscle of deepwater sculpin (*Myoxocephalus thompsonii*) exhibited the highest W contents (118.9 ng/g, Table 3). The element Re was only analytically detected in the muscle of *S. namaycush*. In contrast, the lowest contents of Ce, Gd, W and Y were found in muscle tissue of lake trout *S. namaycush*, whereas the lowest Ir and Os values were found in rainbow smelt *O. mordax*, whereas the round goby *N. melanostomus* exhibited the lowest Ta contents (Table 3). The concentrations of Ru were below the detection limit (<DL) in all fish studied.

In Lake Erie, taking into consideration the distribution of trace metal contents in the muscle of yellow perch (*P. flavescens*), the sequence was as follows: Ta < Os < Ir < W < Gd < Hf < Y < Ce. With the emerald shiner (*N. atherinoides*) it was Ta < Os < Ir < Gd < W < Y < Ce < Hf, while it was Os < Ir < Ta < Gd < Hf < W < Y < Ce for the round goby (*N. melanostomus*), Ta < Os < Ir < Gd < W < Y < Hf < Ce for the rainbow smelt (*O. mordax*), and Ta < Os < Ir < Gd < W < Ce < Y < Hf for the walleye (*Sander vitreus*).

In Lake Ontario, the levels of trace metals found in muscle of fish showed the following sequence: Os < Re < Ir < Ta < Gd < W < Ce < Y < Hf for the lake trout (*S. namaycush*), Os < Ir < Ta < W < Gd < Hf < Y < Ce for the rainbow smelt (*O. mordax*), Os < Ir < Ta < W < Hf < Gd < Y < Ce for the round goby (*N. melanostomus*), and Ir < Ta < Os < Gd < W < Y < Ce < Hf for the deepwater sculpin (*M. thompsonii*).

For Lake Erie, there were positive relationships between Ce with length in *P. flavescens*, and Hf and Ir with weight in *N. atherinoides* ($P < 0.05$, Table 4); only Ta showed positive relationship with both length



Table 3 Concentrations of different elements (mean \pm standard deviation) in fishes from Lake Ontario (ng/g, dry weight)

Elements	Fish species			
	<i>S. namaycush</i>	<i>O. mordax</i>	<i>N. melanostomus</i>	<i>M. thompsonii</i>
Ce	14.51 \pm 2.30	140.55 \pm 22.09	1,266.05 \pm 792.91	43.03 \pm 15.38
Gd	3.02 \pm 0.26	22.92 \pm 7.93	163.41 \pm 114.63	7.26 \pm 1.87
Hf	82.81 \pm 7.86	79.29 \pm 10.13	74.76 \pm 10.74	72.22 \pm 4.52
Ir	0.81 \pm 0.10	0.53 \pm 0.04	0.54 \pm 0.07	1.26 \pm 0.32
Os	0.44 \pm 0.20	0.02 \pm 0.10	0.20 \pm 0.22	1.83 \pm 0.57
Re	0.56 \pm 0.07	<DL	<DL	<DL
Ta	1.00 \pm 0.20	0.65 \pm 0.29	0.62 \pm 0.07	1.52 \pm 0.35
W	3.24 \pm 1.67	12.60 \pm 9.01	44.94 \pm 14.50	36.16 \pm 7.30
Y	24.83 \pm 1.97	117.84 \pm 15.78	671.67 \pm 465.68	41.30 \pm 5.08

DL: detection limit. Ce: Cerium; Gd: Gadolinium; Hf: Hafnium; Ir: Iridium; Os: Osmium; Re: Rhenium; Ta: Tantalum; W: Tungsten; Y: Yttrium.

Table 4 Regressions of log₁₀-transformed element concentrations (ng/g dw) in fishes versus total length (T_L), total weight (T_W) or Fulton factor (CF)

Lake	Species	Elements	Covariate	Slope	Intercept	R ²	t value	p value	F
Lake Erie	<i>P. flavescens</i>	Ce	T _L	-0.03 \pm 0.01	2.85 \pm 0.16	0.58	-3.31	0.0107*	F _{1,10} =10.94
			T _W	-0.003 \pm 0.001	2.60 \pm 0.07	0.72	-4.56	0.0018*	F _{1,10} =20.8
		Gd	T _L	-0.02 \pm 0.01	1.78 \pm 0.13	0.56	-3.22	0.0122*	F _{1,10} =10.39
		Os	T _L	0.05 \pm 0.02	-0.80 \pm 0.32	0.45	2.58	0.0325*	F _{1,10} =6.67
		Ta	T _L	0.04 \pm 0.01	-0.94 \pm 0.20	0.60	3.46	0.0085*	F _{1,10} =12
			T _W	0.003 \pm 0.001	-0.55 \pm 0.12	0.45	2.55	0.034*	F _{1,10} =6.52
	<i>N. atherinoides</i>	Y	T _L	-0.02 \pm 0.01	2.36 \pm 0.11	0.60	-3.50	0.0081*	F _{1,10} =12.25
			T _W	-0.0025 \pm 0.001	2.17 \pm 0.05	0.76	-5.01	0.001*	F _{1,10} =25.06
		Hf	T _W	0.24 \pm 0.06	1.55 \pm 0.10	0.90	4.28	0.050*	F _{1,4} =18.31
		Ir	T _W	1.01 \pm 0.23	-1.43 \pm 0.41	0.91	4.39	0.0482*	F _{1,4} =19.26
Lake Ontario	<i>S. namaycush</i>	Ta	CF	-0.74 \pm 0.18	0.91 \pm 0.22	0.86	-4.21	0.0245*	F _{1,5} =17.72
			T _L	0.01 \pm 0.002	-0.66 \pm 0.12	0.94	6.96	0.0061*	F _{1,5} =48.39
		W	T _W	0.0001 \pm 0.0002	-0.12 \pm 0.09	0.83	3.76	0.0328*	F _{1,5} =14.17
			T _L	-0.02 \pm 0.004	1.75 \pm 0.24	0.90	-5.32	0.013*	F _{1,5} =28.32
	<i>M. thompsonii</i>	Gd	T _W	-0.01 \pm 0.002	1.11 \pm 0.05	0.93	-5.08	0.0367*	F _{1,4} =25.79
			T _L	-0.02 \pm 0.001	1.93 \pm 0.02	0.99	-18.86	0.0028*	F _{1,4} =355.58
		Y	T _L	-0.02 \pm 0.001	1.93 \pm 0.02	0.99	-18.86	0.0028*	F _{1,4} =355.58
			T _W	0.004 \pm 0.0005	1.74 \pm 0.01	0.98	-9.01	0.0121*	F _{1,4} =81.21

Ce: Cerium; Gd: Gadolinium; Hf: Hafnium; Ir: Iridium; Os: Osmium; Ta: Tantalum; Re: Rhenium; W: Tungsten; Y: Yttrium.

and weight of fish (*P. flavescens*).

For Lake Ontario, the regressions showed that only Ta in a single species (*S. namaycush*) was found to significantly affect the species' health as indicated by the Fulton factor (Table 4, $P < 0.05$). There were positive relationships for Re with length and weight in *S. namaycush*, and Y with weight in *M. thompsonii*. There were negative relationship for W and Y with length in *S. namaycush* and *M. thompsonii*, respectively. Also, there was a negative relationship for Gd with weight in *M. thompsonii*.

Discussion

Fishes accumulate metals through their gills and skin, as well as through the consumption of contaminated food sources (Squadrone et al. 2013). Trace element contents can be affected by the level of environmental contamination and the duration of exposure (Kouba et al. 2010). Hence, larger fishes might have accumulated higher metal concentrations than smaller individuals (Balzani et al. 2021).

The technology-critical elements examined herein varied within and among the different fish species, likely because of differences in age, body size and feeding habits (Sandor et al. 2001). Measurements of these elements in freshwater fish muscle are rare, which makes it difficult to compare our results to other species and locations. The levels of Ce (72–742 ng/g) reported by Squadrone et al. (2016) in *Dicentrarchus labrax* from the Mediterranean Sea are within the range (1,266.1–18.2 ng/g) found in the present study. Our maximum Gd concentrations in muscle fish (163.4 ng/g) are 20.4 times higher than the mean background



concentration of Gd in fish (whole body basis) collected from a reservoir in Washington state (Mayfield and Fairbrother 2015). Our Ir values in muscle fish (7.17–0.53 ng/g) are higher than those reported in internal tissues of fish (0.0015 ng/g) from the Gulf of Mexico (Wells et al. 1988). The only concentrations of Re found in muscle of *S. namaycush* (Table 3, 0.56 ng/g) are 1.4 times higher the same element in marine fish (Eisler 2010). The concentrations of Ta in fishes examined herein ranged from 0.53 ng/g to 2.9 ng/g (Table 2), and are lower than Ta contents (0.61 to 14 ng/g) for marine fishes from Chilean coastal zones and Antarctica (Espejo et al. 2018b). Our highest W concentrations (118.87 ng/g, *S. cognatus*, Table 3) are 4 times higher than those levels found in marine fish tissues from Norway (Eisler 2010). Our highest Y contents in muscle fish (671.67 ng/g, Table 3) are 28 times higher than the mean background concentration of Y in fish (whole body collected) from a reservoir (Mayfield and Fairbrother 2015). To our knowledge, there are no previous studies on Hf, Os or Ru in fish tissues. In general, results to date suggest that some of these elements are present at higher levels in Great Lakes fishes than species from other freshwater systems, but the reason(s) for these differences are unknown.

Some lab studies that exposed fish to metals found reduced condition, but because the element versus condition relationships are only correlative and not causative, other factors such as physiological condition or metabolic activity, may affect fish bioaccumulation of many metals, which should be taken in consideration to obtain more reliable information on water pollution (Dragun et al. 2007; Yi and Zhan 2012; Dragun et al. 2016; Jiang et al. 2022). With the exception of Ta in *S. namaycush* (Table 4), which showed negative relationships, we found that the Fulton factor was unaffected by metal concentration, as previously reported by Jovičić et al. (2015) and Balzini et al. (2021) for other metals. While some researchers have stated this relationship can be quite variable (Alhashemi et al. 2012; Dragun et al. 2016; Rakocevic et al. 2018), fish might possess some physiological defenses that reduce the influence of metals on body condition (Tenji et al. 2020).

There is evidence that some metals bioaccumulate within fish through time, leading to positive size and age dependent relationships, thus larger fish tend to bioaccumulate more metals (Rakocevic et al. 2018; Barzini et al. 2021). We found only a few significant relationships ($P < 0.05$) between metal concentrations and total length, as similarly found with more studied elements (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn) in *Silurus glanis* from the Danube River (Jovičić et al. 2015). The regressions showed positive significant relationships with both fish length and weight for Ta and Re in *P. flavescens* and *S. namaycush*, respectively. We found only positive relationships with only length for Os in *P. flavescens*, while Hf, Ir and Y were positive for only weight in *N. atherinoides* and *M. thompsonii* (Table 4). On the other hand, Ce and Y are negative correlated with both length and weight in *P. flavescens* (Table 4). We found a negative relationship with only fish length for Ce, Gd and Y in *P. flavescens*, W in *S. namaycush*, and Y in *M. thompsonii*. Biodilution, a higher growth rate of tissues than metal uptake, could explain negative relationships we found in fish here (Merciai et al. 2014; Dragun et al. 2016). For some elements, the concentrations did not depend on body weight of the fish, however some size ranges were limited.

In conclusion, some of the element concentrations in the muscles of freshwater fish determined in this study showed a great variability, and were higher than other regions. Despite some findings, there are no clearly defined relationships between the concentration of metals such as those studied here and the size of fish in both lakes. So far, there is no scientific evidence about the biological effects of these elements in fish. It is unclear whether they poses a risk to upper-trophic-level consumers, therefore more studies are required to assess their toxicity in the environment. It is necessary to realize in advance the potential impacts of these emerging chemical elements on aquatic ecosystems to better design any environmental risk assessment for wildlife conservation. Baseline data for these technology-critical elements are now required upon any possible changes in their concentrations in the future.

Conflict of interest The authors declare no conflicts of interest.

Acknowledgments The current study was supported by the Agencia Nacional de Investigación y Desarrollo (ANID) through project postdoc FONDECYT 3200302 (W. Espejo). The authors give thanks to the projects FONDECYT 1161504, FONDECYT Initiation 11180914 and Project 2022000466-INI (W. Espejo) of the Dirección de Investigación de la Universidad de Concepción.

References

Alhashemi AH, Karbassi A, Kiabi BH, Monavari SM, Sekhavatjou MS (2012) Bioaccumulation of trace elements in different tissues of



- three commonly available fish species regarding their gender, gonadosomatic index, and condition factor in a wetland ecosystem. *Environ Monit Assess* 184:1865–1878
- Aliff MN, Reavie ED, Post SP, Zanko LM (2020) Metallic elements and oxides and their relevance to laurentian great lakes geochemistry. *Peer J* 8:e9053. <https://doi.org/10.7717/peerj.9053>
- Balzani P, Haubrock PJ, Russo F, Kouba A, Haase P, Veselý L, Masoni A, Tricarico E (2021) Combining metal and stable isotope analyses to disentangle contaminant transfer in a freshwater community dominated by alien species. *Environ Pollut* 268:115781. <https://doi.org/10.1016/j.envpol.2020.115781>
- Carlson DL, Swackhamer DL (2006) Results from the U.S. great lakes fish monitoring program and effects of lake processes on bioaccumulative contaminant concentrations. *J Great Lakes Res* 32:370–385
- Celis J, Espejo W, González D (2020) Chemical elements of emerging technologies are being increasingly demanded worldwide: a possible menace for wildlife conservation? *Anim Conserv* 23(1):3–6
- Chen CY, Stemberger RS, Klaue B (2000) Accumulation of heavy metals in food web components across a gradient of lakes. *Limnol Oceanogr* 45:1525–1536
- Chen Y, Yin X, Ning G, Nie X, Li Q, Dong J (1999) Effects of tantalum and its oxide on exposed workers. *Chin J Prev Med* 33:234–235
- Clark MG, McDaniel T, Mummery A (2022a) Guideline for the collection of prey fish by trawl net. SOP-FCMSP-016, Canada
- Clark MG, McDaniel T, Mummery A (2022b) Guideline for collection of fish by bottom set gill netting. SOP-FCMSP-007, Canada
- Donadt C, Cooke C, Graydon J, Poesch MS (2021) Biological factors moderate trace element accumulation in fish along an environmental concentration gradient. *Environ Toxicol Chem* 40:422–434
- Dragun Z, Raspor B, Podrug M (2007) The influence of the season and biotic factors on the cytosolic metal concentrations in the gills of the european chub (*Leuciscus cephalus* L.). *Chemosphere* 69:911–919
- Dragun Z, Tepić N, Krasnić N, Teskeredžić E (2016) Accumulation of metals relevant for agricultural contamination in gills of european chub (*Squalius cephalus*). *Environ Sci Pollut Res* 23:16802–16815
- Eisler R (2010) Compendium of trace metals and marine biota: vertebrates. Elsevier, Oxford OX5, 1GB, UK
- Espejo W, Galbán-Malagón C, Merimoyu GC (2018a) Risks from technology-critical metals after extraction. *Nature* 557:492–493
- Espejo W, D Kitamura, K Kidd, J Celis, S Kashiwada, C Galbán-Malagón, R Barra, G Chiang (2018b) Biomagnification of tantalum through diverse aquatic food webs. *Environ Sci Technol Lett* 5:196–201
- Gaiser B, Fernandes T, Jepson M, Lead J, Tyler C, Stone V (2009) Assessing exposure, uptake and toxicity of silver and cerium dioxide nanoparticles from contaminated environments. *Environ Health* 8:S2. <https://doi.org/10.1186/1476-069X-8-S1-S2>
- Haase A, Bauer E, Kühn F, Crans D (2019) Speciation and toxicity of rhenium salts, organometallics and coordination complexes. *Coord Chem Rev* 394:135–161
- Harris RM, Williams TD, Waring RH, Hodges NJ (2015) Molecular basis of carcinogenicity of tungsten alloy particles. *Toxicol Appl Pharmacol* 283:223–233
- Heydarnejad M, Khosravian-Hemamai M, Nematollahi A (2013) Effects of cadmium at sub-lethal concentration on growth and biochemical parameters in rainbow trout (*Oncorhynchus mykiss*). *Ir Vet J* 66:1–7
- Iavicoli I, Leso V (2015) Iridium. In: Nordberg G, Fowler B, Nordberg M (eds) Handbook on the toxicology of metals, fourth edn. Academic press, New York
- Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN (2014) Toxicity, mechanism and health effects of some heavy metals. *Interdiscip Toxicol* 7:60–72
- Jiang X, Wang J, Pan B, Li D, Wang Y, Liu X (2022) Assessment of heavy metal accumulation in freshwater fish of dongting lake, China: effects of feeding habits, habitat preferences and body size. *J Environ Sci* 112:355–365
- Jovićić K, Nikolić DM, Višnjić-Jeftić Ž, Đikanović V, Skorić S, Stefanović SM, Lenhardt M, Hegediš A, Krpo-Četković J, Jarić I (2015) Mapping differential elemental accumulation in fish tissues: assessment of metal and trace element concentrations in wels catfish (*Silurus glanis*) from the Danube river by ICP-MS. *Environ Sci Pollut Res* 22:3820–3827
- Klavins M, Potapovics O, Rodinov V (2009) Heavy metals in fish from lakes in Latvia: concentrations and trends of changes. *Bull Environ Contam Toxicol* 82:96–100
- Kouba A, Buřič M, Kozák P (2010) Bioaccumulation and effects of heavy metals in crayfish: a review. *Water Air Soil Pollut* 211:5–16
- Kucykbay FZ, Orun I (2003) Copper and zinc accumulation in tissues of the freshwater fish *Cyprinus carpio* L 1758 collected from the Karakaya dam lake, Malatya (Turkey). *Fresenius Environ Bull* 12:62–66
- Lin W, Huang YW, Zhou XD, Ma Y (2006) Toxicity of cerium oxide nanoparticles in human lung cancer cells. *Int J Toxicol* 25:451–457
- Lushchak V (2011) Environmentally induced oxidative stress in aquatic animals. *Aquat Toxicol* 101:13–30
- McGoldrick DJ, Clark MG, Keir MJ, Backus SM, Malecki MM (2010) Canada's national aquatic biological specimen bank and database. *J Great Lakes Res* 36:393–398
- Mayfield DB, Fairbrother A (2015) Examination of rare earth element concentration patterns in freshwater fish tissues. *Chemosphere* 120:68–74
- Mello-Andrade F, Cardoso C, Ribeiro e Silva C, Chen-Chen L, de Melo-Reis P, Pereira A, Oliveira R, Bryan I, Ferraze M, Grisoliae K, Pinheiro A, Azevedo A, Silveira-Lacerda E (2018) Acute toxic effects of ruthenium (II)/amino acid/diphosphine complexes on Swiss mice and zebrafish embryos. *Biomed Pharmacother* 107:1082–1092
- Merciai R, Guasch H, Kumar A, Sabater S, García-Berthou E (2014) Trace metal concentration and fish size: variation among fish species in a Mediterranean river. *Ecotoxicol Environ Saf* 107:154–161
- Newman MC (2015) Fundamentals of ecotoxicology: the science of pollution. CRC Press, Boca Raton
- O'Hara A, Demkov A (2014) Oxygen and nitrogen diffusion in alpha-hafnium from first principles. *Appl Phys Lett* 104:211909
- Pagano G, Aliberti F, Guida M, Oral R, Siciliano A, Trifuoggi M, Tommasi F (2015) Rare earth elements in human and animal health: state of art and research priorities. *Environ Res* 142:215–220
- Park EJ, Choi J, Park YK, Park K (2008) Oxidative stress induced by cerium oxide nanoparticles in cultured BEAS-2B cells. *Toxicol* 245:90–100
- Rajeshkumar S, Li X (2018) Bioaccumulation of heavy metals in fish species from the Meiliang Bay, Taihu Lake, China. *Toxicol Rep* 5:288–295



- Rakocevic J, Sukovic D, Maric D (2018) Distribution and relationships of eleven trace elements in muscle of six fish species from Skadar Lake (Montenegro). *Turkish J Fish Aquat Sci* 18:647–657
- R Core Team (2020) R: a language and environment for statistical computing. R foundation for statistical computing. Vienna, Austria
- Rogosnitzky M, Branch S (2016) Gadolinium-based contrast agent toxicity: a review of known and proposed mechanisms. *Biometals* 29:365–376
- Romero-Freire R, Santos-Echeandía J, Neira P, Cobelo-García A (2019) Less-studied technology-critical elements (Nb, Ta, Ga, In, Ge, Te) in the marine environment: review on their concentrations in water and organisms. *Front Mar Sci* 6:532. doi: 10.3389/fmars.2019.00532
- Rudnick R, Gao S (2003) Composition of the continental crust. *Treat Geochem* 1:1–64. doi: 10.1016/b0-08-043751-6/03016-4
- Sandor Z, Csengeri I, Oncsik M, Alexis M, Elena Z (2001) Trace metal levels in freshwater fish, sediment and water. *Environ Sci Pollut Res Int* 8:265–268
- Schloesser RW, Fabrizio MC (2017) Condition indices as surrogates of energy density and lipid content in juveniles of three fish species. *Trans Am Fish Soc* 146:1058–1069
- Shukla V, Dhankhar M, Prakash J, Sastry KV (2007) Bioaccumulation of Zn, Cu and Cd in *Channa punctatus*. *J Environ Biol* 28:395–397
- Squadrone S, Prearo M, Brizio P, Gavinelli S, Pellegrino M, Scanzio T, Guarise S, Benedetto A, Abete MC (2013) Heavy metals distribution in muscle, liver, kidney and gill of european catfish (*Silurus glanis*) from italian rivers. *Chemosphere* 90:358–365
- Squadrone S, Brizio P, Stella C, Prearo M, Pastorino P, Serracca L, Ercolini C, Abete M (2016) Presence of trace metals in aquaculture marine ecosystems of the northwestern Mediterranean sea (Italy). *Environ Pollut* 215:77–83
- Taslina K, Al-Emran, Md, Rahman, M, Hasan J, Ferdous Z, Rohani Md, Shahjahan Md (2022) Impacts of heavy metals on early development, growth and reproduction of fish – A review. *Toxicol Rep* 9:858–868
- Tenji D, Micic B, Sipos S, Miljanovic B, Teodorovic I, Kaisarevic S (2020) Fish biomarkers from a different perspective: evidence of adaptive strategy of *Abramis brama* (L.) to chemical stress. *Environ Sci Eur* 32:1–15
- USEPA (2011) Great Lakes. US environmental protection agency. Washington DC
- Wassenaar L, Hendry M (2000) Mechanisms controlling the distribution and transport of ^{14}C in a clay-rich till Aquitard. *Groundwater* 38:343–349
- Wells M, Boothe P, Presley B (1988) Iridium in marine organisms. *Geochi Cosmochim Acta* 15:1731–1739
- Yang L, Wang X, Nie H, Shao L, Wang G, Liu Y (2016) Residual levels of rare earth elements in freshwater and marine fish and their health risk assessment from Shandong, China. *Mar Pollut Bull* 107:393–397
- Yi YJ, Zhan SH (2012) The relationships between fish heavy metal concentrations and fish size in the upper and middle reach of Yangtze River. *Procedia Environ Sci* 13:1699–1707
- Zhang Z, He L, Li J, Wu Z (2007) Analysis of heavy metals of muscle and intestine tissue in fish in banan section of chongqing from three gorges reservoir, China. *Pol J Environ Stud* 16:949–958

Publisher's Note

IAU remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

