Neuroendocrinology Letters Volume 36 Suppl. 1 2015
ISSN: 0172-780X; ISSN-L: 0172-780X; Electronic/Online ISSN: 2354-4716
Web of Knowledge / Web of Science: Neuroendocrinol Lett
Pub Med / Medline: Neuro Endocrinol Lett

Concentration of heavy and toxic metals in fish and sediments from the Morava river basin, Czech Republic

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Submitted: 2015-07-18 *Accepted: 2015-09-09* *Published online: 2015-10-15*

Key words: **fish; sediment; heavy metals; ecological risk; the Morava river basin**

Neuroendocrinol Lett 2014; **35**(Suppl. 1):126–132 **PMID:** 26757111 NEL360915A06 © 2015 Neuroendocrinology Letters • **www.nel.edu**

Abstract

OBJECTIVES: The monitoring survey to assess the environmental pollution status of the river Morava – was carried out in 2014.
DESIGN: This study presents the concentrations of heavy metals (Hg, Cr, Zn, Pb and Cd) in the water, sediment and muscle tissue of fish from the middle and lower reaches of the Morava river basin (Bečva, Dřevnice, Haná, Kyjovka and Morava rivers), in the Czech Republic. Atomic absorption spectrometry (AAS) was used for the analysis of toxic metals. European chub (*Squalius cephalus*) was chosen as a reference fish species for the comparison of monitored localities.
RESULTS: Results showed a positive significant correlation between concentration of Hg, Pb, Cd, Cr and Zn in muscles and age of fishes ($p<0.05$). The contents of the analyzed metals in European chub muscles were low Hg 0.049–0.402, Pb 0.005–0.035, Cd 0.006–0.026, Cr 0.016–0.042 and Zn 5.59–64.31 mg.kg^{-1} wet weight basis and did not exceed the values of limits admissible in the Czech Republic.
CONCLUSIONS: The contents of the analyzed metals in European chub muscles were low at monitoring sites and did not exceed the values of limits admissible in the Czech Republic.

Abbreviations

B	- Bečva River
D	- Dřevnice River
H	- Haná River
K	- Kyjovka River
M	- Morava River
MeHg	- methyl mercury
SD	- standard deviation
SL	- standard length
TW	- total weight

INTRODUCTION

Heavy metals such as Hg, Cr, Zn, Pb and Cd play important biochemical roles in the life processes of many organisms, and their presence in trace amounts are essential. However, at high concentrations toxic effects are observed. Some, such as mercury or lead, are highly toxic and have no known beneficial effect. The impact of increasing concentrations of such metals in the environment is further enhanced by their poor degradability, which results in bioaccumulation and transport along successive links of the food chain (Ciesielski *et al.* 2010).

Mercury is neurotoxic in both its organic and inorganic forms (Atchison & Hare 1994). The commonly encountered form of mercury, methyl mercury (MeHg), is the most toxic form affecting aquatic biota (Larosa & Allen-Gil 1995; Maceda-Veiga *et al.* 2012). MeHg is primarily responsible for bioaccumulation in the muscle tissue of fish with a methyl mercury/total mercury ratio of 83–90% (Kannan *et al.* 1998; Marsalek *et al.* 2005; Kruzikova *et al.* 2008). Lead is known to be carcinogenic to both aquatic biota and humans (Malik *et al.* 2010), induce renal tumors, reduce cognitive development, and increase blood pressure. Other symptoms of lead toxicity include gastrointestinal disorders and some liver impairment (Gupta *et al.* 2009). Cadmium has neurotoxic effects as some other heavy metals including mercury (Svobodova *et al.* 2002). Cadmium may induce kidney dysfunctions, osteomalacia and reproductive deficiencies in long-term exposure to even trace concentrations (Strömgren 1998; Toman *et al.* 2005). Zinc reduces immune function and the levels of high density lipoproteins. Zinc may produce adverse nutrient interactions with copper (Spears 2000).

Excess amounts of toxic substances entering into the aquatic ecosystem may pollute the environment and also affect the food chain and ultimately pose serious human health risks to those who depend directly or indirectly on the water body for the supply of fish and water (Weldegebriel *et al.* 2012; Hostovsky *et al.* 2014). Fish are at the top of the aquatic food chain, and can accumulate both essential and toxic metals which they absorb from contaminated sediments and water through their gills and skin as well as from organisms which are consumed by the fish (Saha & Zaman 2012; Akerblom *et al.* 2014). The response of fish to environmental change makes it suitable for use as an indicator for environmental pollution. Fish is again a good bioindicator because it is easy to obtain in large quantities and has the potential to accumulate metal (Chalmers *et al.* 2011; Dvorak *et al.* 2014).

The river basin of the Morava River is in the long-term focus of ichthyological and toxicological research. Spurný & Mares (2005; Přerov region) and Hauserova *et al.* (2006; Moravia rivers) assessed the influence of negative anthropogenic factors on fish community in the rivers of the river basin of the Morava River. The content of heavy metals in water ecosystem, in locations selected by us, was not monitored in the last 5 years.

Analysis of fish muscle helps to determine the direct transfer of heavy metals and other contaminants to humans via fish consumption. This study presents a data on concentrations of some heavy metals in muscle of European chub (*Squalius cephalus)*, the most abundant and widely distributed fish species in the Morava river basin.

MATERIAL AND METHODS

Samples of water, sediment (Table 1) and fish muscle were obtained during the season of 2014 from 5 sites of the Morava river basin – Morava (M) 48.689N, 16.993E,

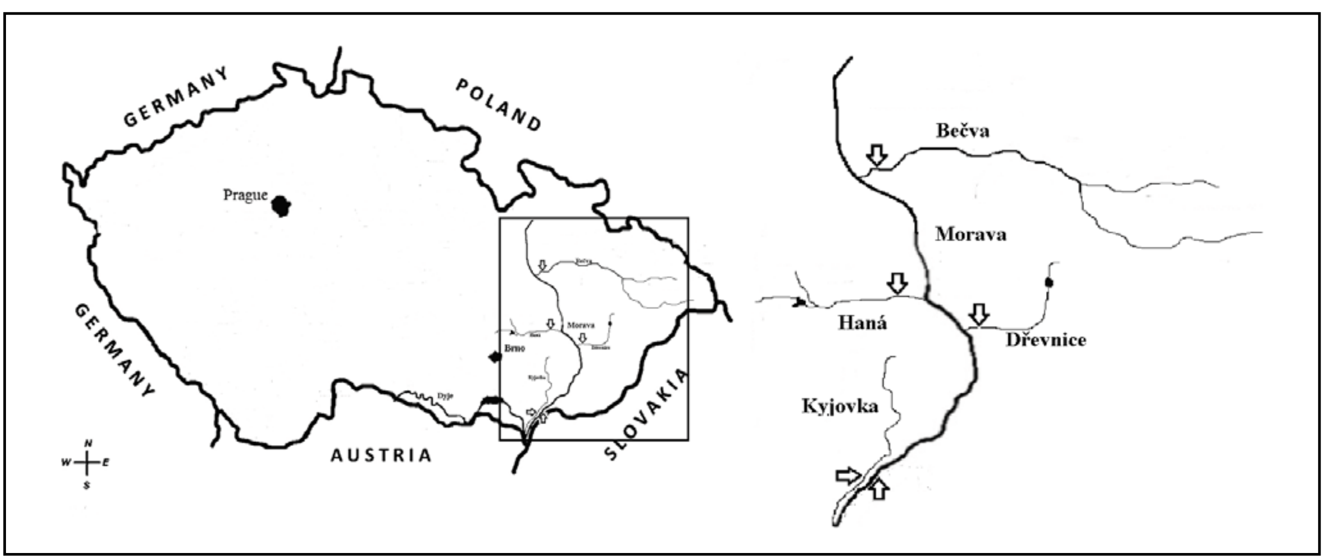

Fig. 1. Map of the rivers studies with the location of sampling sites indicated.

Tab. 1. Mean concentrations of analyzed metals in water and sediment.

Site	water (µg.L-1)					sediment (mg.kg-1 dry mass)				
	Hg	Pb	Cd	Cr	Zn	Hg	Pb	Cd	Cr	Zn
(B)	0.05	0.5	0.05	1.74	5	0.06	21.9	0.28	42.3	113
(D)	0.05	0.5	0.05	1.59	12.1	0.062	9.14	0.31	26.5	83
(H)	<0.05	1.96	<0.05	1.79	5.15	0.043	19.6	0.59	27.8	107
(K)	<0.05	1.21	<0.05	1.25	11.6	0.09	17.4	0.56	31.0	137
(M)	<0.05	4.11	0.083	2.14	33.5	0.02	9.15	0.10	15.4	64.7

B – Bečva River; D – Dřevnice River; H – Haná River; K – Kyjovka River; M – Morava River

Tab. 2. Characteristics of analyzed specimens of chub (*Squalius cephalus*).

Site	N	Age (years)	SL (mm) Mean ± SD	TW (g) Mean ± SD
(B)	10	1–4	179±50.50	89±63.66
(D)	10	1–5	180±44.33	80±58.91
(H)	10	2–4	183±38.48	87±48.95
(K)	10	1–5	182±63.38	99±104.40
(M)	10	1–4	214±63.12	135±93.65

B – Bečva River; D – Dřevnice River; H – Haná River; K – Kyjovka River; M – Morava River; N – number of individuals; SD – standard deviation; SL – standard length; TW – total weight

Kyjovka (K) 48.696N, 16.960E, Haná (H) 49.337N, 17.296E, Dřevnice (D) 49.208N, 17.561E and Bečva (B) 49.437N, 17.341E rivers (Figure 1).

The fish were obtained by electrofishing (220–250 V, 1.5–2.5 A, 63 Hz). As the reference species was chosen chub (*S. cephalus*) due to its occurrence in all of the evaluated fishing grounds. Specimens of fish were collected at each site and killed at the bankside, as required under Czech law (Act No. 246/1992 Coll., on the Protection of Animals Against Cruelty, as amended 2008). The fish (n=50) were evaluated by standard methods used in ichthyology (standard length – SL, total weight – TW measurements and age determination by scales). Upon recording the biometric data (Table 2), samples of fish muscles were obtained from the dorsal part of their body, without skin and bones. The collected tissue, sediment and water samples were kept at −18 °C.

The total mercury content was determined directly in the sample units by the selective mercury analyzer (Advanced mercury analyzer, AMA-254) based on atomic absorption spectroscopy (wavelength 253.65 nm; limit of quantity 0.002 mg.kg^{-1}).

Other toxic metals (Pb, Cd, Cr and Zn) were measured by the means of electrothermal (flameless) atomic absorption spectrometry with Zeeman background correction (graphite furnace atomic absorption spectrometry GF-AAS, SpectrAA 220Z, Varian) after microwave mineralization of the samples (EN13 804, 13805 and 14084). The concentrations of all target analytes in the samples were determined and expressed in wet weight (w.w.) and compared with the Czech hygienic limits presented in Commission Regulation (EC) No. 1881/2006, as amended by Commission Regulation (EC) No. 629/2008.

For statistical analysis, the Anova one-way test, Multiple Range test (LSD method), Kruskal-Wallis test, and Linear Model of Simple Regression (least squares fit) were used together with the computer program Statgraphics Centurion XV.

RESULTS

Content of analyzed metals in fish

Contents of analyzed metals in muscle of chub from analyzed sites of Morava River basin are given in Table 3.

Mercury in muscle of analyzed chub specimens was in relatively close range (Table 3). Its mean concentration achieved the values from 0.19–0.22 mg.kg^{-1} w.w., with highest value at site (K) and lowest value at site (H). Statistically significant differences among sites were not observed. These values are in accordance with the studies of Dvorak *et al.* (2014; Dyje river basin) and Valova *et al.* (2013; River Morava). Lower mercury contamination was found in carp muscle (*Cyprinus carpio*) or roach muscle (*Rutilus rutilus*) at a majority of the localities, because it is typically stocked in open waters in a catchable size and thus comes from generally uncontaminated pond breeding facilities (Andreji *et al.* 2012; Akoto *et al.* 2013). Mean concentrations of lead in muscle samples of chub were almost identical and varied between 0.01–0.02 mg.kg^{-1} w.w. Lower values at site (D), in comparison to other sites have been observed. Despite a very close range of recorded values, statistically significant differences ($p<0.05$) among site were noted (Table 3). Valova *et al.* (2013) reported higher concentrations of lead in the muscle of chub from the Bečva River. The same situation reported Cerveny *et al.* (2014) from the Dyje River (Vranov reservoir) in the range from 0.03 to 0.08 mg.kg^{-1}.

Similar situation to lead was detected for cadmium. Very close range of estimated mean concentrations

Tab. 3. Contents of analyzed metals in muscle of chub (in $mg.kg^{-1}$ w.w.).

Site	Hg	Pb	Cd	Cr	Zn
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
(B)	0.20±0.11^{a}	0.02±0.01^{ab}	0.01±0.00^{a}	0.21±0.15^{a}	30.83±18.88^{a}
(D)	0.21±0.12^{a}	0.01±0.00^{a}	0.02±0.01^{a}	0.11±0.08^{a}	23.06±15.21^{a}
(H)	0.19±0.07^{a}	0.02±0.01^{ab}	0.02±0.01^{a}	0.17±0.08^{a}	27.00±17.99^{a}
(K)	0.22±0.13^{a}	0.02±0.01^{ab}	0.02±0.01^{a}	0.14±0.11^{a}	31.62±20.58^{a}
(M)	0.20±0.07^{a}	0.02±0.01^{b}	0.01±0.00^{a}	0.16±0.12^{a}	19.66±6.96^{a}

B – Bečva River; D – Dřevnice River; H – Haná River; K – Kyjovka River; M – Morava River; The values with identical superscript in the column are not significant at the $p<0.05$ level.

Tab. 4. Correlations among analyzed metals in chub.

	Hg	Pb	Cd	Cr	Zn
Hg	–				
Pb	0.6791***	–			
Cd	0.6594***	0.4331**	–		
Cr	0.6898***	0.6771***	0.5314***	–	
Zn	0.8338***	0.6552***	0.6708***	0.7260***	–

Significant differences $^{**}p<0.01$; $^{***}p<0.001$.

(0.01–0.02 $mg.kg^{-1}$ w.w.) were also noted, but without significant differences among sites. Lower concentrations at sites (B) and (M) and higher at sites (D), (H) and (K), have been recorded (Table 3). Lower cadmium contamination in muscle of chub was confirmed in a study by Noel *et al.* (2013) in concentration 0.005 $mg.kg^{-1}$. Teodorof *et al.* (2009) reported the similar concentration in muscle of cyprinid species.

Chromium is an essential trace element in human and some animals but in excess, it could have undesirable lethal effect on fish and wildlife (Alkan *et al.* 2009). Detected mean chromium concentrations achieved the values from 0.11 to 0.21 $mg.kg^{-1}$ w.w. (Table 3), with lowest value at site (D) and highest value at site (B). Also here no significant differences among sites were observed.

Highest concentrations from all analyzed metals were recoded for zinc (Table 3). Estimated mean concentrations fluctuated between 19.66–31.62 $mg.kg^{-1}$ w.w. Highest content was noted at site (K) in comparison to lowest observed concentration at site (M). Statistically significant differences among sites were not recorded. Zinc concentrations in the fish species were form as describe Akoto *et al.* (2013) in the lake Fosu, 18.25–23.15 $mg.kg^{-1}$ w.w. These amounts of Zn in the tissues cannot cause harm to the fish themselves as well as humans who consume them.

Correlations

Statistically high significant ($p<0.001$) positive correlations between all analyzed metals and SL, TW as well as age, were confirmed (Figures 2 and 3). In the case of cadmium and mercury, similar results for fish weight were reported by Burger *et al.* (2002) in fishes from the Savannah River. Also Yi & Zhang (2012) observed positive correlations between metal levels and fish size in fishes from northeast China. Opposite relationships between metal concentrations and fish size have been noted by Canli & Atli (2003), as well as by Farkas *et al.* (2003). According these studies, there are no definite or established relationships between heavy metal concentrations and fish size and age. As main factors that play important role in metal accumulation in fish are the metabolic activity (Roesijadi & Robinson 1994) and exposure time (Di Giulio & Hinton 2008).

Relationships among individual analyzed metals (Table 4) show in all combinations positive correlations, also with high statistical significance. Positive correlations among these same metals have been presented by Mendil *et al.* (2005) in fish *Capoeta tinca* from Yesilirmark River, Turkey. Positive significant correlation between Pb and Zn has been recorded by Sonmez *et al.* (2012) in two fish species in Karasu River. These relationships between elements may denote the participation in the detoxification as part of the enzymes of the antioxidant systems, such as superoxide dismutase, and in metallothioneins (Sanchez-Chardi *et al.* 2007; Yılmaz *et al.* 2007).

Hygienic limits

The limits of heavy metals in surface water for mercury, lead, cadmium, chromium, zinc are defined as 0.05, 7.2, 0.3, 18 and 92 $\mu g.L^{-1}$ (Government Regulation No. 61/2003 in the Czech Republic), respectively. The values of contaminants in monitored locations did not exceed the limits set by the regulation.

The limits of heavy metals in sediment for mercury, lead and cadmium are defined as 0.470, 53 and 2.3 $mg.kg^{-1}$ (Government Regulation No. 61/2003 in the Czech Republic), respectively. The limit for chromium and zinc is not defined in the regulation. The values of contaminants in monitored locations did not exceed the limits set by the regulation.

The hygienic limits for mercury, lead, cadmium, chromium are defined as 0.5, 0.3, 0.05 and 0.5 $mg.kg^{-1}$ w.w. in Codex Alimentarius valid in the Czech Republic, respectively. The limit for zinc in Codex Alimen-

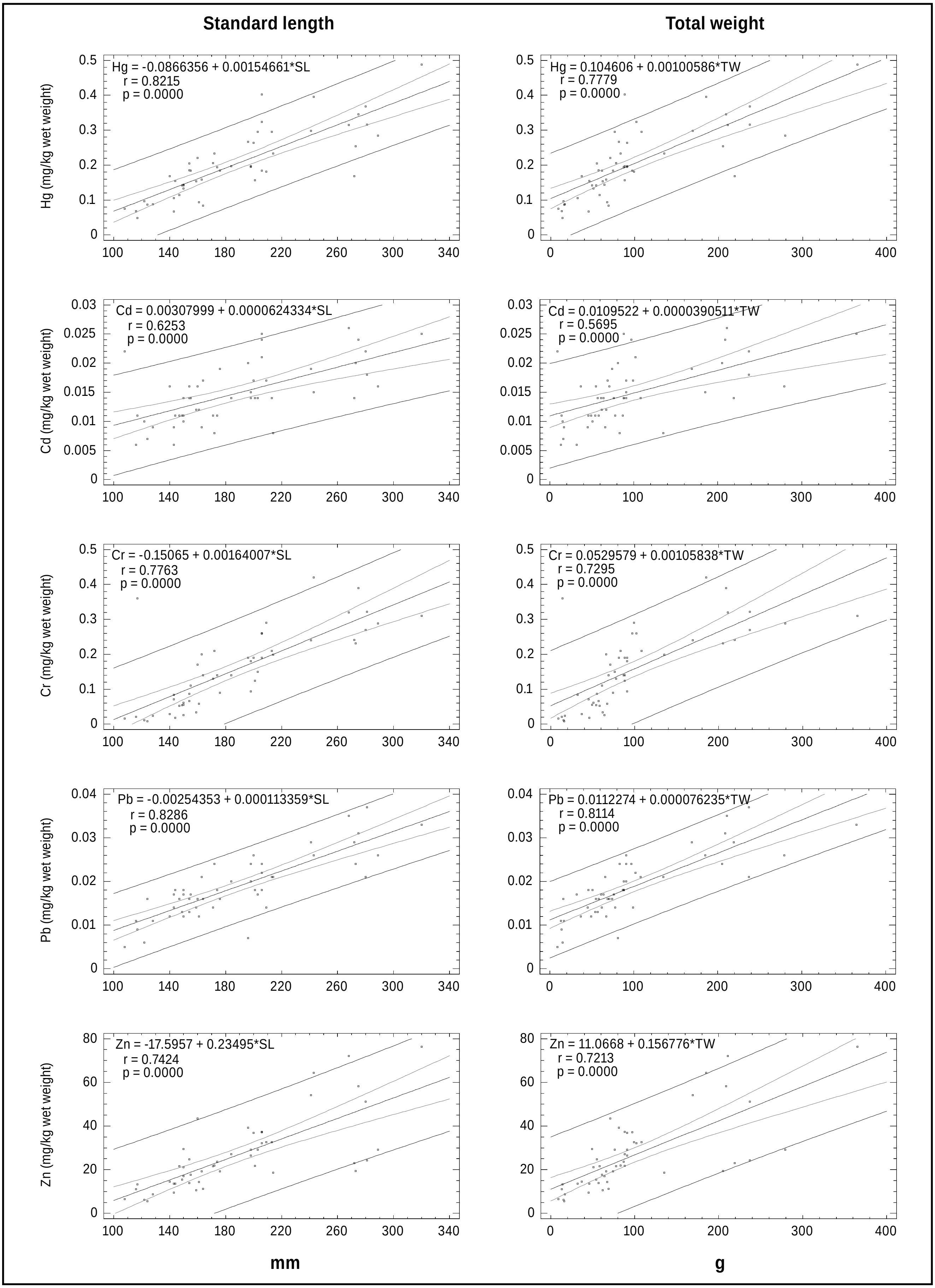

Fig. 2. Content of analyzed heavy metals in relation to standard length and total weight of chub.

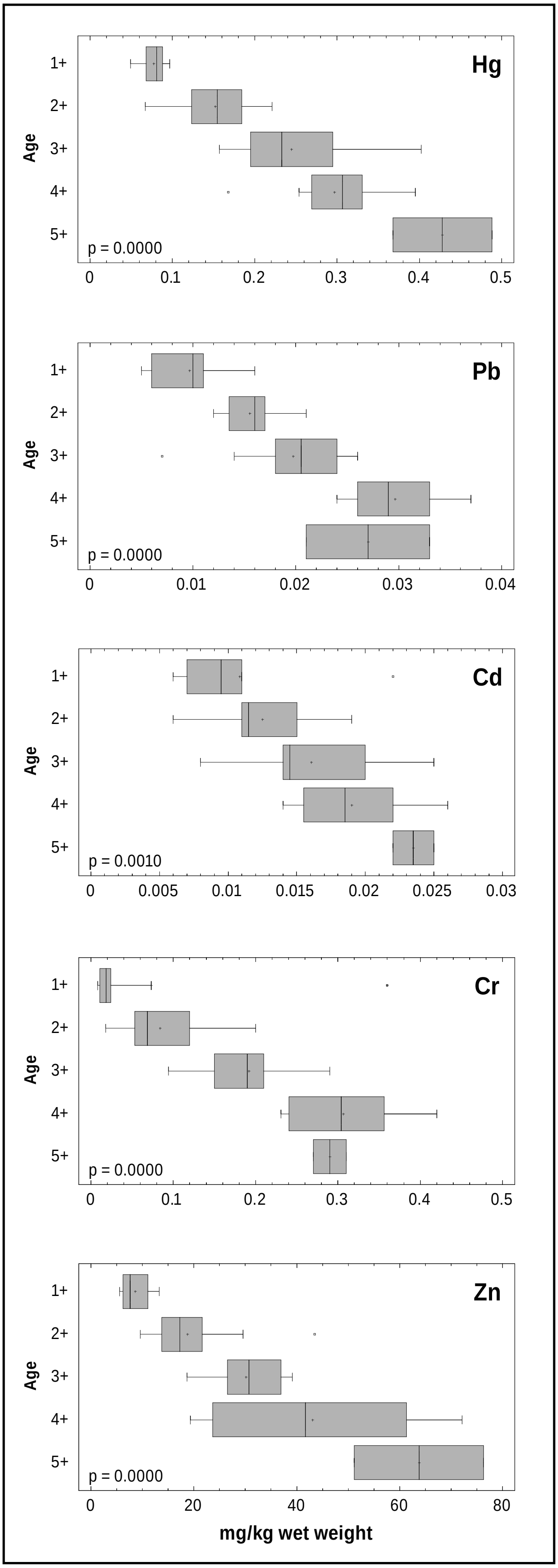

Fig. 3. Content of analyzed heavy metals in relation to age of chub.

tarius is not defined. The contaminants (mercury, lead, cadmium and chromium) did not exceed hygienic limits. Codex Alimentarius was not exceeded at any single fish, only in one chub caught in the Kyjovka river it was near the maximum allowed limit level in mercury 0.488 $mg.kg^{-1}$ (limit 0.5)

CONCLUSION

Our research has presented data on the levels of heavy and toxic metals in water, sediment, and fish muscles obtained from European chub (*Squalius cephalus*), from 5 sites of the Morava river basin.

Although the results obtained does not show any form of danger posed to consumers of fish meat and water from this river but the possibility of deleterious effects after long period cannot be ruled out.

There is therefore the need for continual assessment of the level of pollution of these 5 researched sites of the Morava river basin with metals from the mentioned sources with a view to reducing the level of pollution via education and public enlightenment.

Monitoring performed did not show any increased burden of the river system by observed pollutants from industrial agglomerations of Central and South Moravia. Despite the fact that the content of observed pollutants does not exceed the hygienic limits, the quality of water environment needs to be regularly checked, especially in the industrial area of Central Moravia.

ACKNOWLEDGMENTS

We would like to express our gratitude to Natalie Czaban, M.A. for the critical reading and correction of the manuscript. This study was financially supported by the projects “CENAKVA” (No. CZ.1.05/2.1.00/01.0024) and “CENAKVA II” (No. LO1205 under the NPU I program).

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