

Accumulation of selected metals pollution in aquatic ecosystems in the Smeda river (Czech republic)

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Abstract

OBJECTIVES: Biomonitoring of some selected heavy metals in the Smeda river (Czech Republic) was carried out during 2015–2016 to assess the extent of environmental pollution. Attempts were also made to map the intensity of bioaccumulation in brown trout which was used as an indicator species. Monitoring of the environmental pollution of the Smeda river was carried in 2016.

DESIGN: Concentrations of some heavy metals i.e. Mercury (Hg), Lead (Pb), Cadmium (Cd) and Cobalt (Co) were quantified in the fish muscles. Correlations (Pearsons, 2-tailed) among selected metals with some morphometric parameters (standard length and total weight) in brown trout (*Salmo trutta fario*) were also examined.

RESULTS: Results showed a significant positive correlation between concentrations of Hg, Pb (group-I) and Pb, Cd (group-II) with the muscles and age of fishes ($p < 0.05$). The groups of heavy metals i.e. group-I (Hg and Pb) and group-II (Pb and Cd) were purposively synthesized for better inference of the data since Pb formed significant ($p < 0.05$) but distinct positive correlations with Hg and Cd. The contents of the analyzed metals in brown trout muscles were low Hg 0.06–0.5; Pb 0.01–0.3; Cd 0.01–0.04 and Co 0.01–0.03 mg.kg⁻¹ wet weight basis and did not exceed the values of limits admissible in the Codex Alimentarius for safe human consumption except in the case of Hg which is little vulnerable to reach critical limit.

CONCLUSIONS: The contents of the analyzed metals in Brown trout muscles were lower at monitoring sites and did not exceed the values of limits admissible in the Czech Republic. Potential ecological risk analysis of toxic metals concentrations in sediments suggested only two sites (2 and 3) with elevated values that posed a

middle environmental risks. Strict periodical monitoring of Hg levels in the selected stretches of the River Smeda is recommended.

INTRODUCTION

Many natural rivers have been exposed to metal contamination from anthropogenic sources. Industrial and agricultural progress has resulted in increasing pollution by heavy metals representing a significant environmental hazard (Maceda-Veiga *et al.* 2012). Toxic metals may be released into a water column in response to hydrological changes during floods (Agarwal *et al.* 2005) and become potential threat to invertebrates, fish and humans (Arantes *et al.* 2016; Smylie *et al.* 2016; Hope 2006). The pollution monitoring using bioaccumulators is one of the methods for the evaluation of xenobiotic levels (Dvorak *et al.* 2014; Remon *et al.* 2013). Although, effects of toxic metals may as well be detected on land as a result of their bioaccumulation and bioconcentration in the food chain (Dvorak *et al.* 2015; Haluzová *et al.* 2010). Fish consumption has positive health benefits but also brings higher risks of intake of heavy metals for humans. Garzon *et al.* (2016) evaluating from an economic perspective how important are these health and biodiversity components for those in the fish value chain, from fishermen to final consumers.

Smeda river was chosen because it is polluted by the textile and glass industries that are a major source of trace elements and other pollutants that affect the development of ecosystems (Koslor *et al.* 2015; Maiti 2007). The Smeda river was known by presence of dams, as a source of technological water for small glass and textil factories. This way they got trace elements and other pollutants influencing ecosystem development into the river (Maiti 2007). The Smeda River (Luzicka Nisa) belongs to the most contaminated rivers in the Poland,

polluted with Bogatynia lignite industry sewage (Koslor *et al.* 2015).

The aim of this study was to investigate the level of contaminants (Hg, Pb, Cd and Co) in brown trout (*Salmo trutta morpha fario*) from the upper course of the Smeda river (Czech Republic) and their comparison with permitted limits for safe consumption, defined in the Commission Regulations No. 1881/2006 and 629/2008. Furthermore, correlations among the metal concentrations, standard length, total weight and age of fish were analysed. These results were juxtaposed with similar analyses of water samples collected from the same sites, which allowed us to determine the elemental composition.

MATERIALS AND METHODS

Samples of water, sediments were collected in 2016 year from 10 sites of the Smeda river (Czech Republic) (Figure 1). Brown trout by was colleted by electrofishing (220–250 V, 1.5–2.5 A, 63 Hz) from same sites and time period.

Fish (n=100) were evaluated by standard methods used in ichthyology (standard length – SL and total weight – TW measurements, age determination by scales). Upon recording the biometric data (Table 2), samples of fish muscles were obtained from the dorsal part of their body. The collected tissue and sediment samples were kept at –18°C.

The total mercury content was determined directly in the sample units by the selective mercury analyser (Advanced mercury analyser, AMA-254) based on atomic absorption spectroscopy (AAS wavelength 253.65 nm; limit of quantity 0.002 mg.kg⁻¹). Other toxic metals (Pb, Cd and Co) were measured by the means of electrothermal (flameless) atomic absorption spectrometry with Zeeman background correction (graphite furnace atomic absorption spektrometry (GF-AAS, SpectrAA 220Z, Varian) after microwave mineralisation of the samples (EN13 804, 13805 and 14084). The concentrations of all target analytes in samples were determined and expressed in wet weight (w.w.) and compared with the Czech nationwide regulation no. 305/2004 (Czech Republic, 2004) setting the maximum residue levels in foodstuff.

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 18 Professional.

RESULTS AND DISCUSSIONS

Content of analysed metals in fish

Hg – detected values varied from 0.06 to 0.49 mg.kg⁻¹ w. w. (Table 1), with higher mean concentrations at lower river sites (sites 1–3) and lowest mean concentrations at higher situated sites (sites 8–10). Statistical significant

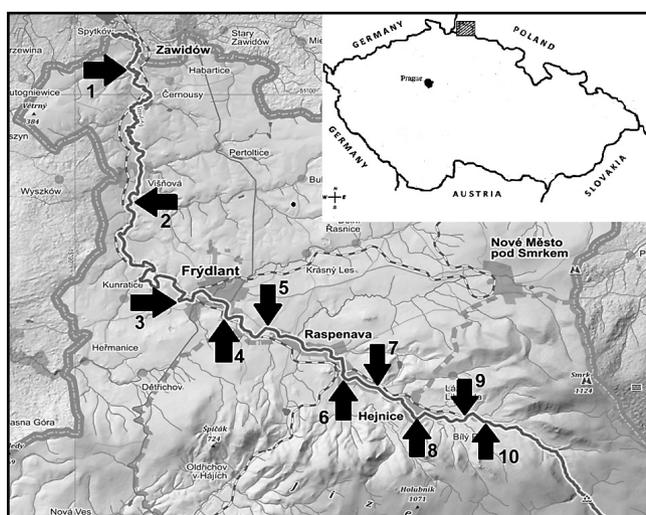


Fig. 1. The site of sample collection from the Smeda river

Tab. 1. Mean concentration of analyzed metals, water and sediment.

Site	water (mg/l)				sediment (mg/kg dry mass)			
	Hg	Pb	Cd	Co	Hg	Pb	Cd	Co
1	0.05	0.06	<0.05	<0.05	0.32	0.29	<0.05	<0.05
2	0.05	0.21	<0.05	<0.05	0.42	0.29	<0.05	<0.05
3	0.05	0.16	<0.05	<0.05	0.41	0.33	<0.05	<0.05
4	0.05	0.08	<0.05	<0.05	0.27	0.19	<0.05	<0.05
5	<0.05	0.06	<0.05	<0.05	0.24	0.21	b. d.	<0.05
6	<0.05	0.07	<0.05	<0.05	0.13	0.14	b. d.	<0.05
7	<0.05	0.05	b. d.	<0.05	0.09	0.1	<0.05	<0.05
8	<0.05	0.06	b. d.	b. d.	0.06	0.13	<0.05	<0.05
9	<0.05	<0.05	<0.05	b. d.	0.08	0.08	b. d.	b. d.
10	<0.05	<0.05	<0.05	b. d.	0.06	0.13	b. d.	b. d.

b.d. – below detectable limit

Tab. 2. Characteristics of analysed fish

Site	N	Age	SL (mm)	BW (g)
1	10	3.4±0.5 (3–4)	221.7±18.6 (200–254)	200.1±46.0 (159–284)
2	10	3.1±0.3 (3–4)	205.4±14.4 (184–240)	163.9±30.1 (139–246)
3	10	3.1±0.3 (3–4)	207.9±11.8 (195–233)	167.8±20.4 (147–213)
4	10	3.2±0.4 (3–4)	210.4±17.1 (189–241)	178.7±34.1 (140–254)
5	10	3.3±0.7 (3–5)	224.1±25.2 (194–284)	207.2±57.4 (159–349)
6	10	3.1±0.3 (3–4)	210.4±13.7 (195–241)	178.6±31.8 (145–254)
7	10	3.0±0.0 (3)	203.0±12.0 (186–221)	163.7±17.7 (145–198)
8	10	2.8±0.4 (2–3)	190.0±10.9 (168–206)	151.6±10.5 (136–167)
9	10	2.9±0.3 (2–3)	196.3±14.6 (169–214)	158.8±12.8 (138–180)
10	10	3.0±0.0 (3)	198.5±12.3 (178–218)	161.3±10.3 (144–179)

(mean ± SD and minimum – maximum in parenthesis)

Tab. 3. Content of selected metals.

Site	Hg	Pb	Cd	Co
1	0.35 ^e ±0.06 (0.26–0.44)	0.03 ^a ±0.01 (0.01–0.04)	0.01 ^a ±0.00 (0.01–0.02)	0.01 ^{bc} ±0.01 (0.01–0.02)
2	0.34 ^e ±0.09 (0.20–0.50)	0.20 ^e ±0.06 (0.11–0.30)	0.02 ^{ab} ±0.01 (0.01–0.04)	0.01 ^{bc} ±0.01 (0.00–0.03)
3	0.34 ^e ±0.05 (0.28–0.42)	0.24 ^f ±0.04 (0.18–0.29)	0.03 ^b ±0.01 (0.02–0.04)	0.01 ^c ±0.00 (0.01–0.02)
4	0.21 ^{cd} ±0.06 (0.10–0.31)	0.14 ^d ±0.05 (0.08–0.21)	0.01 ^{ab} ±0.00 (0.01–0.02)	0.01 ^{ab} ±0.00 (0.00–0.01)
5	0.22 ^d ±0.11 (0.08–0.41)	0.09 ^{bc} ±0.03 (0.04–0.13)	0.03 ^{ab} ±0.02 (0.01–0.09)	0.01 ^{ab} ±0.00 (0.00–0.01)
6	0.19 ^{bcd} ±0.08 (0.09–0.36)	0.13 ^{cd} ±0.05 (0.06–0.21)	0.01 ^{ab} ±0.00 (0.01–0.02)	0.01 ^{ab} ±0.00 (0.00–0.01)
7	0.16 ^{abc} ±0.04 (0.09–0.22)	0.15 ^d ±0.04 (0.08–0.21)	0.02 ^{ab} ±0.01 (0.01–0.03)	0.02 ^c ±0.03 (0.01–0.09)
8	0.11 ^a ±0.04 (0.07–0.19)	0.13 ^d ±0.04 (0.06–0.20)	0.03 ^{ab} ±0.05 (0.01–0.15)	0.01 ^{ab} ±0.00 (0.00–0.07)
9	0.13 ^{ab} ±0.05 (0.06–0.21)	0.09 ^b ±0.03 (0.05–0.16)	0.02 ^{ab} ±0.01 (0.01–0.03)	0.00 ^a ±0.00 (0.00–0.01)
10	0.11 ^a ±0.04 (0.06–0.17)	0.12 ^{bcd} ±0.04 (0.08–0.21)	0.02 ^{ab} ±0.00 (0.02–0.02)	0.00 ^a ±0.00 (0.00–0.01)

(mean ± SD and minimum – maximum in parenthesis) in muscle of analysed fishes (mg.kg⁻¹ w.w.); The values with identical superscript in the column are not significant at the $p < 0.05$ level.

differences in Hg accumulation among sites have been recorded ($p < 0.05$).

Comparable results are presented by Stewart *et al.* (2011) for brown trout muscle from the South Canterbury rivers, New Zealand. Higher Hg concentrations in fish muscle have been presented for brown trout from

the Olsina and Spicak brooks, Czech Republic (Dvorak *et al.* 2016). Opposite, lower mean concentrations are known from upper Morava River, Czech Republic (Valova *et al.* 2010) and upper Nitra River, Slovakia (Andreji *et al.* 2018).

Hg in relation to other metals as well as to age, standard length and total weight shows a positive correlations with statistically high significant differences ($p < 0.05$), except Cd (Table 4).

Pb – levels in analysed muscle samples of brown trout reached the values $0.01–0.29 \text{ mg.kg}^{-1} \text{ w.w.}$ (Table 3). The highest mean concentration at site 3 and lowest mean concentration at site 1, were noted. In this case statistically significant differences in Pb accumulation among sites have been recorded ($p < 0.05$). Lower Pb concentrations ($< 0.06 \text{ mg.kg}^{-1}$) are given from the upper Jihlava River (Valova *et al.* 2010) and South Canterbury rivers, New Zealand (Stewart *et al.* 2011). Higher values of Pb ($0.36–0.54 \text{ mg.kg}^{-1}$) in analysed muscle of brown trout are known from the upper Nitra River (Stranai 1998). Comparable results to our findings have been presented by Dvorak *et al.* (2016) in brown trout muscle from the brooks of the military training area of Boletice, Czech Republic.

A positive correlation relationships between Pb and other metals, age, standard length and total weight were detected (Table 4).

Cd values fluctuated in relatively close range ($0.01–0.04 \text{ mg.kg}^{-1} \text{ w.w.}$). The highest mean concentration was recorded at site 3 and lowest mean concentration was detected at site 1 (Table 3). Statistically significant differences for Cd accumulation in brown trout muscle were noted among analysed sites. Mean muscle concentrations at levels $0.04–0.10 \text{ mg.kg}^{-1}$ have been presented from upper Nitra River, Slovakia (Stranai 1996; Andreji *et al.* 2018). Lower Cd concentrations have been published for brown trout from the upper Jihlava River, Czech republic (Valova *et al.* 2010) and South Canterbury rivers, New Zealand (Stewart *et al.* 2011), as well as for relative *Salmo trutta macrostygma* from Munzur Stream, Tunceli, Turkey (Can *et al.* 2012). On the other hand, comparable results to our have been published by Dvorak *et al.* (2016) from brooks of military training area of Boletice (Czech Republic).

In the case of Cd a positive correlation relationships between all analysed indicators were found (Table 4), but without statistically significant differences ($p > 0.05$).

Co muscle concentrations reached a very close range ($0.00–0.03 \text{ mg.kg}^{-1} \text{ w.w.}$), similar to Cd (Table 3). Higher mean concentrations at lower situated sites (mainly site 3) and lower concentrations at higher sites

(sites 9–10) were detected, similar to Hg. Significant differences have been confirmed in Co accumulation in trout muscle among monitored sites ($p < 0.05$). Higher Co concentrations for brown trout muscle from the Otra River, southern Norway were presented by Brothridge *et al.* (1998). Authors Ylmaz *et al.* (2007) found higher Co accumulation in tissues of chub (*Leuciscus cephalus*) from the Saricay river. On the other hand, Erdogru *et al.* (2007), Karadede *et al.* (2004) and Karadede *et al.* (2000) did not find Co in fish samples. Co is accumulated in some enzymes as vitamin B12 and 500 mg/day is toxic to man (Bowen, 1979).

In the case of Co accumulation in muscle a positive correlation relationships were confirmed between analysed metals, age, standard length and total weight (Table 4), but without statistical significances ($p > 0.05$).

Hygienic limits

The hygienic limits (Codex Alimentarius, Czech Republic) for mercury, lead, cadmium and cobalt are defined as $0.5, 0.3, 0.05$ and $0.05 \text{ mg.kg}^{-1} \text{ w.w.}$, respectively. In our study the contaminants (Hg, Pb, Cd and Co) did not exceed hygienic limits. Codex Alimentarius was not exceeded at any single fish, however in lower sites of the river stream were caught some fish with higher level in mercury – max 0.496 mg.kg^{-1} (sites 1–3), lead max 0.297 mg.kg^{-1} (sites 2–3).

CONCLUSIONS

Our research has presented data on the levels of toxic metals in water, sediment, and fish muscles obtained from brown trout – *Salmo trutta morpha fario*, from 10 localities of the Smeda River. Toxic metals as pollutants play important role in human health, because they contaminate environment and food chain. The potential ecological risk of toxic metal concentrations in the sediments indicated that five sites in the middle and lower reaches posed small to moderate ecological risk. Two sites (2, 3) represent a potential higher ecological risk.

From our correlations, there is evidence of elevated mercury values in larger trout (predation) and lower values in young minor pollutants (benthophagus). We also observed an increase in Hg and Co from site 10 to site 2. In site 1, the level of the listed elements was low, the site was under the natural reserve of Meandry Smeda, and there is no regular sediment extraction and excretion. The river between the sites 1 and 2 has the character of a low floodplain, and the water is flooded during the floods and thus does not transport the sediment as in the upper sites. That's why metals do not get so much into circulation. Pb and Cd is concentration-sensitive in lead shows slightly increased concentration at sites No. 10, 8, 7, 4, 3, 2. Near this sites are located textiles, glassworks and other metals processing manufacturing with a long tradition. Our results confirmed that the mean values of analysed fish did not exceed the limits valid in the Czech Republic.

Tab. 4. Correlations among analysed metals, age, standard length and total weight.

	Hg	Pb	Cd	Co	Age	SL (mm)	TW (g)
Hg	-	0.2534*	0.0072-	0.2960**	0.4941***	0.5785***	0.5092***
Pb		-	0.2115*	0.1121-	0.0974-	0.0898-	0.0020-
Cd			-	0.0654-	0.0767-	0.1408-	0.1116-
Co				-	0.1887-	0.1728-	0.1400-

$p > 0.05$, * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

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