

Monitoring of risk metals in chub (*Leuciscus cephalus* L.) from the Svitava and Svatka rivers in the urban area of Brno, Czech Republic

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Received December 11, 2011

Accepted February 14, 2012

Abstract

The aim of this study was to assess the impact of the Brno agglomeration on the distribution of risk elements (Pb, Cd, Cu, Zn, As) in tissues of a total of 50 chub (*Leuciscus cephalus* L.). Contamination by metals was monitored in fish from different sites on the Svitava and Svatka rivers in the urban agglomeration of Brno in 2008. Metal concentration was determined in the muscle, liver and kidney by high-resolution atomic absorption spectrometry. Electrothermic technique was used to assess lead, cadmium and copper concentrations; zinc content was determined by flame technique and arsenic by hydride generation. The highest concentrations of cadmium, lead, arsenic and zinc in individual tissues, ranked in a descending order as follows: kidney > liver > muscle; for copper it was liver > kidney > muscle. The highest concentrations of cadmium, arsenic and zinc were determined in chub kidney from the locality of Kníničky (1.35 ± 0.97 , 0.186 ± 0.076 , and 299.7 ± 123.4 mg·kg⁻¹ respectively); the highest concentration of lead was on the Svatka before junction (0.28 ± 0.19 mg·kg⁻¹). The highest contamination with risk metals was found in chub from the Svatka. The assessed concentrations have shown minimum participation of the Brno agglomeration in the accumulation of metals. The concentrations of all risk elements in chub from all of the monitored localities do not pose any environmental or health threat. This study updates published data on chub from the Rivers Svitava and Svatka on concentration of risk elements.

Indicator fish, cadmium, lead, arsenic, zinc, copper

Heavy metals such as mercury, cadmium, lead and arsenic constitute a significant potential threat to human health (Castro-González and Méndez-Armenta 2008). Because of low levels of their degradation, the metals accumulate in soil and water sediments and subsequently enter the food chain (Cornelis et al. 2005).

The impact of urban agglomerations on concentrations of risk metals in fish is the subject of many studies, e.g. in the Seine River in France (Chevreuil et al. 1995), in the Savannah in the USA (Burger et al. 2002), and in the Neretva in Croatia (Has-Schön et al. 2006).

The aim of this study was to assess the impact of the Brno urban agglomeration on the concentration and distribution of risk metals in tissues of chub (*Leuciscus cephalus* L.) as an indicator species caught in the Svatka and Svitava rivers. The work completes existing findings from the mentioned locality regarding the concentration and distribution of other toxic substances in chub (Kružíková et al. 2008, 2009, 2011; Kovářová et al. 2009a; Blahová et al. 2009, 2010).

Materials and Methods

Study of concentrations of risk elements and their distributions in chub tissues was conducted on the Svatka and Svitava rivers in the urban agglomeration of Brno.

Before reaching the agglomeration, the Svatka flows through an industrial zone (Veverská Bitýška and Tišnov), and its water forms a vast water surface of the Kníničky reservoir in the northwest part of Brno. Then the river flows through the western part of town without any other industrial burden. The Svitava

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Table 1. Localities around Brno

River	Sampling site	River km	Latitude	Longitude
Svitava	Bilovice nad Svitavou	18.0	49°15'6.076"N	16°40'13.641"E
	before junction	0.6	49°8'52.372"N	16°37'51.818"E
Svratka	Kniničky	56.2	49°13'14.847"N	16°32'9.821"E
	before junction	40.9	49°8'40.073"N	16°37'42.134"E
	Rajhradice	35.0	49°5'36.502"N	16°37'10.68"E
	Židlochovice	30.0	49°2'33.312"N	16°36'48.766"E

Table 2. Characteristics of chub (*Leuciscus cephalus* L.)

River	Sampling site	Fish (n)	Weight (g) mean (median)	Total length (mm) mean (median)
Svitava	Bilovice nad Svitavou	9	293 (280)	258 (255)
	before junction	9	328 (211)	252 (250)
Svratka	Kniničky	10	162 (141)	210 (200)
	before junction	11	176 (156)	216 (210)
	Rajhradice	11	141 (114)	200 (190)

springs in the woody and hilly country around the town of Svitava and flows through a narrow heavily settled valley with advanced mechanical engineering (Blansko and Adamov). Then the river flows through the east part of Brno (a former industrial zone) and after leaving the town joins the Svratka. Table 1 shows the sites on the Svitava and Svratka rivers where chub were captured by electrofishing. Table 2 shows the number of fish caught in each locality, their mean weight, mean total length, and the median of analysed chub samples.

Samples of individual fish tissues were collected immediately after the fish were killed and kept at -18 °C until they were analysed. Concentrations of individual metals (lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) and arsenic (As)) were determined in muscle, liver and kidney samples. Prior to the determination of metal content, the samples were mineralized with nitric acid and hydrogen peroxide in laboratory autoclaves equipped with microwave heating (ETHOS SEL, Milestone Italy). Then, for the determination of arsenic, the samples were burnt to ashes with added Mg(NO₃)₂ in muffle furnace. The ashes were dissolved in HCl and As⁵⁺ was reduced to As³⁺ with the aid of KI (Čelechovská et al. 2005, 2011).

The concentrations of metals were determined by high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS), using a spectrometer ContraAA 700 (Analytik Jena, Germany). The detection limits (3σ) of As, Cd, Pb, Cu and Zn were 2.49, 3.04, 36.6, 80.3 μg·kg⁻¹ and 1.35 mg·kg⁻¹, respectively. Standard deviations of parallel determinations were less than 5%. Samples of certified standard material DORM-2 (dogfish muscle-NRC), BCR 186 (pig kidney) and 1577a (bovine liver-NIST) were used to check the validity and accuracy of the method.

The acquired data were processed by statistical software Unistat 5.1. To assess the agreement ($P < 0.05$) or differences between individual tissue groups, nonparametric median multiple comparisons by Tukey-HSD tests were used.

Results

Mean concentrations of metals, including standard deviations in individual fish tissues from each individual locality are shown in Table 3. Lower concentrations of metals were found in tissues of chub from the Svitava, which is in agreement with lower concentrations of metals in sediments (Kovářová et al. 2009b). The highest concentrations of cadmium, lead, arsenic and zinc were in kidney. The highest concentrations of copper were analyzed in the liver. The results have shown that metals differ in their affinity to different fish tissues and were in agreement with the study of Has-Schön et al. (2006), Čelechovská et al. (2007) and Yilmaz et al. (2007).

Discussion

Cadmium

Cadmium content in individual tissues ranked in a descending order as follows: kidney > liver > muscle. When compared with muscle samples, the concentrations in kidney and

Table 3. Assessed concentrations (mean and standard deviations) of metals in tissues of chub (*Leuciscus cephalus* L.)

Metal	Locality	Tissue concentration of metals (mg/kg)		
		Muscle	Liver	Kidney
Cd	Bilovice nad Svitavou	0.009 ± 0.004 ^b	0.068 ± 0.038 ^c	1.350 ± 0.977 ^c
	Svitava - before junction	0.009 ± 0.001 ^b	0.031 ± 0.017 ^a	0.440 ± 0.209 ^a
	Svratka - Kníničky	0.010 ± 0.002 ^c	0.069 ± 0.064 ^{bc}	0.711 ± 0.626 ^{ab}
	Svratka - before junction	0.006 ± 0.002 ^a	0.041 ± 0.016 ^{bc}	0.419 ± 0.209 ^c
	Svratka - Rajhradice	0.008 ± 0.002 ^b	0.037 ± 0.018 ^{ab}	0.473 ± 0.240 ^{ab}
Pb	Bilovice nad Svitavou	0.077 ± 0.056 ^{ab}	0.093 ± 0.042 ^a	0.116 ± 0.068 ^a
	Svitava - before junction	0.073 ± 0.056 ^a	0.076 ± 0.052 ^a	0.277 ± 0.187 ^b
	Svratka - Kníničky	0.115 ± 0.048 ^c	0.190 ± 0.223 ^a	0.199 ± 0.181 ^a
	Svratka - before junction	0.089 ± 0.068 ^{ab}	0.118 ± 0.100 ^a	0.253 ± 0.184 ^{ab}
	Svratka - Rajhradice	0.106 ± 0.057 ^{bc}	0.143 ± 0.090 ^a	0.189 ± 0.106 ^{ab}
As	Bilovice nad Svitavou	0.030 ± 0.006 ^a	0.06 ± 0.017 ^b	0.058 ± 0.017 ^a
	Svitava - before junction	0.040 ± 0.010 ^b	0.04 ± 0.013 ^a	0.058 ± 0.015 ^a
	Svratka - Kníničky	0.058 ± 0.012 ^d	0.164 ± 0.012 ^c	0.186 ± 0.076 ^c
	Svratka - before junction	0.055 ± 0.038 ^c	0.04 ± 0.016 ^a	0.094 ± 0.04 ^b
Zn	Svratka - Rajhradice	0.051 ± 0.014 ^{cd}	0.069 ± 0.018 ^b	0.092 ± 0.044 ^{ab}
	Bilovice nad Svitavou	4.340 ± 1.271 ^{bc}	21.41 ± 5.12 ^a	125.5 ± 32.4 ^a
	Svitava - before junction	4.034 ± 1.430 ^{ab}	27.31 ± 7.81 ^b	216.9 ± 59.2 ^{bc}
	Svratka - Kníničky	4.916 ± 1.447 ^c	29.78 ± 6.93 ^b	299.7 ± 123.4 ^c
	Svratka - before junction	3.918 ± 1.153 ^{ab}	29.01 ± 8.20 ^b	263.2 ± 54.7 ^c
Cu	Svratka - Rajhradice	4.912 ± 1.264 ^c	27.11 ± 6.96 ^b	225.4 ± 61.5 ^c
	Bilovice nad Svitavou	0.097 ± 0.089 ^a	11.06 ± 10.89 ^a	1.35 ± 0.13 ^a
	Svitava - before junction	0.207 ± 0.098 ^c	16.00 ± 9.67 ^{abc}	1.57 ± 0.21 ^b
	Svratka - Kníničky	0.253 ± 0.093 ^c	21.98 ± 8.79 ^c	1.27 ± 0.30 ^a
	Svratka - before junction	0.141 ± 0.086 ^b	20.31 ± 10.17 ^{bc}	1.36 ± 0.20 ^a
	Svratka - Rajhradice	0.203 ± 0.083 ^c	9.99 ± 5.74 ^a	1.43 ± 0.21 ^{ab}

Significance of differences between localities at the level of $P < 0.05$ is indexed by different superscripts

liver samples were $100 \times$ and $10 \times$ higher, respectively. Kidneys are considered the primary part of body for cadmium accumulation (Has-Schön et al. 2006).

Significantly the highest cadmium content ($P < 0.05$) in chub from the Svitava was assessed upstream of Brno in the locality of Bilovice nad Svitavou. In the Svratka the highest concentrations were found in all tissues of chub from the Kníničky locality, upstream of Brno. Concentrations of cadmium in chub muscle from the Svitava did not vary and concentrations in the liver and in kidneys were decreasing simultaneously with the river flowing through the town. That might be the proof that fish did not ingest any more cadmium. Very similar findings have been published by Kovářová et al. (2009b).

Lead

Lead distribution between individual tissues, ranked in a descending order as follows: kidney > liver > muscle, which is in accordance with Linde et al. (1999), Has-Schön et al. (2006) and Čelechovská et al. (2007). The highest lead content in muscle ($P < 0.05$) was assessed in the Kníničky locality. Concentrations of lead in kidneys were significantly higher ($P < 0.05$) in fish caught upstream of Brno. Concentrations of lead in the liver did not show any significant differences.

Arsenic

Arsenic distribution between individual tissues ranked in a descending order kidney > liver > muscle, which is similar to the study of Burger et al. (2002) and Čelechovská

et al. (2005). At a prolonged exposure of rainbow trout to small doses of arsenic in feeds, its accumulation in muscle was higher than in the liver and kidneys (Čelechovská et al. 2011). We found a negative correlation between the arsenic content in muscle and the chub weight, and between the arsenic content in muscle and the chub total length ($r = -0.83$; $r = -0.87$, respectively). On the other hand, Burger et al. (2002) found a positive correlation between the body weight and the arsenic content in various fish from the Savannah river.

The highest concentrations ($P < 0.05$) in all the tissues of chub were found in fish from the Kníničky locality. As for chub muscle, concentrations from the Svitava were lower ($P < 0.01$) in fish caught upstream of Brno. On the Svatka the highest concentrations were found in chub muscle before the river entered Brno and significantly lower ($P < 0.01$) after leaving Brno. This trend on the Svatka was found also for liver and kidney samples, where the difference was highly significant ($P < 0.01$).

Arsenic often accompanies phosphorus due to their similar chemistry, and so higher arsenic concentrations may be caused by the release of phosphates into environment. Formerly, phosphates were a common component of detergents and fertilisers.

Copper and zinc

Copper and zinc are essential elements carefully regulated by physiological mechanisms in the organism (Bowen 1979). At higher concentrations, copper ions are toxic to fish and some microorganisms. Copper compounds are widely used in industry and are component parts of various preparations used in agriculture and households.

Concentrations of copper in individual tissues ranked in a descending order liver > kidney > muscle; concentrations of zinc ranked in the order kidney > liver > muscle. Many authors have reported uneven organ distribution of zinc in chub (Andres et al. 2000). Concentrations of zinc assessed in chub were higher than reported in fish by other authors (Yilmaz et al. 2007; Čelechovská et al. 2007) and correlated with concentrations of arsenic assessed in chub kidneys ($r = 0.76$). Higher zinc content in kidneys is connected with its wide metabolic activity and affinity to SH-groups of proteins, including metallothioneins present in kidneys (Yilmaz et al. 2007).

In the Svitava, higher values of zinc concentration were found after its flowing through the town ($P < 0.05$). In the Svatka, the highest concentrations of zinc were assessed in the Kníničky locality (muscle, liver), where the concentrations of zinc in all tissues were significantly the highest ($P < 0.05$) of all of the sites on the Svatka and also when compared to the Svitava.

Generally, concentrations of metals found in chub from the Svitava and Svatka rivers were lower than reported in other studies of fish from other countries (Chevreuil et al. 1995; Linde et al. 1999; Burger et al. 2002; Andreji et al. 2005, 2006; Has-Schön et al. 2006). They did not exceed hygienic limits for muscle meat of fish (Cd: 0.050 mg/kg; Pb: 0.30 mg/kg) set by the Commission Regulation (EC) No 629/2008 of 2 July 2008 amending Regulation (EC) No 1881/2006. The highest load by risk metals was found in tissues of fish from the Kníničky locality on the Svatka at the inflow to Brno. The locality is situated right below the dammed reservoir which is an important holiday resort area. High intensity of emissions from the traffic and accumulation of metals in the water sediment, and their subsequent washing out by erosion may be major sources of high accumulation of metals in this locality. For most part of the year the water from reservoir flows out through the bottom discharge outlets, so particles of sediment from the reservoir bed may be carried into discharged water. The whirled sediment easily gets into an organism through the digestive system and gills. Lower metal contents in tissues of chub from the localities farther away from Brno (Rajhradice) may be influenced by the sewage treatment plant on the Svatka, downstream of Brno (Modřice, river km 38.7, 49°7'34.913"N, 16°37'42.171"E), by the lower residential density there and also by the reduced industrial production. The assessed

concentrations of metals have shown minimum contribution of the urban agglomeration of Brno to the accumulation of metals there. After the Svitava and Svatka rivers flow through the town, the concentrations do not vary or they show a slightly declining tendency. The concentrations of all risk elements in chub from all of the monitored localities do not pose any environmental or health threat.

Acknowledgements

This research was supported by the University of Veterinary and Pharmaceutical Sciences IG202111 and by project of Ministry of Education, Youth and Sports of the Czech Republic MSM 6215712402 and 2B06093.

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