Mercury and Methylmercury in Muscle Tissue of Chub from the Elbe River Main Tributaries

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Abstract

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The aim of the present study was to investigate the concentrations of total mercury and methylmercury in muscle of 55 chub (*Leuciscus cephalus*) from seven main tributaries (Orlice, Chrudimka, Cidlina, Jizera, Vltava, Ohře, Bílina) of the Elbe River and to evaluate the health risks of eating fish from the tributaries monitored. Mercury was determined by means of cold vapour atomic absorption spectrometry using AMA-254, methylmercury in the form of CH_3HgCl by gas chromatography. The highest mean concentrations of total mercury and methylmercury were found in the Jizera (0.27 ± 0.19 mg/kg and 0.23 ± 0.15 mg/kg, respectively) and the lowest mean concentrations of total mercury and methylmercury were found in the chub from the Cidlina (0.07 ± 0.05 mg/kg and 0.06 ± 0.04 mg/kg, respectively). The average methylmercury-to-total mercury ratio was 83 ± 15%. The fish intake hazard indexes calculated for the individual tributaries monitored were between 0.01 and 0.03. The results of this study show that the Elbe River is not significantly affected by mercury contamination from its main tributaries

Keywords: *Leuciscus cephalus*; mercury/methylmercury ratio; risk assessment

In the environment, mercury occurs in a number of forms that differ substantially from one another by their physical and chemical properties, such as solubility in the aquatic environment, reactivity, ability to accumulate, toxicity, and the behaviour in the ecosystem. Inorganic forms of mercury practically do not participate in mercury bioaccumulation in ecosystems, and the determination of its organic forms is therefore essential for the research into mercury bioaccumulation. Inorganic mercury is methylated in freshwater ecosystems to form methylmercury (MeHg) (WHO 1990). Methylation involves both biotic and abiotic pathways. The mercury methylation mechanism was first described by Wood (1971) and in the same year also by Landner (1971). Biological production of

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methylmercury depends largely on anaerobic sediment bacteria, e.g., of the genus *Methanobacterium* (Hamasaki 1995). As it advances in the food chain, MeHg accumulates in fish, and fish thus become the main source of human contamination with methylmercury (WHO 1990). Methylmercury makes up over 95% of total mercury (THg) in fish tissues (Mason *et al.* 1995; Houserová *et al.* 2006b).

With its 1103 km in length and the drainage area extending over 148 268 km^2, the Elbe is one of the largest freshwater ecosystems in Central Europe. In the Czech Republic, the Elbe and its tributaries traverse not only a number of big cities with major industrial enterprises, but also important rural areas with intensive agriculture.

The aim of the present study was:

– to determine THg and MeHg concentrations in muscle tissues of the chub as the indicator species caught in 7 main tributaries of the Elbe in the Czech Republic
– to assess the contribution of the individual tributaries to the contamination of the Elbe with mercury
– to evaluate health risks of eating fish from the Elbe tributaries monitored.

MATERIAL AND METHODS

In June 2006, a total of 55 male chub (*Leuciscus cephalus*) were captured in the main tributaries of the Elbe (Figure 1). The tributaries and locations of their confluence with the Elbe are as follows: Orlice (river km 992), Chrudimka (river km 967), Cidlina (river km 907), Jizera (river km 868), Vltava (river km 837), Ohře (river km 792) and Bílina (river km 765). Fish were captured in the lower reaches of each of the tributaries, upstream of the first migration barrier.

The fish were caught by electrofishing. The fish caught were immediately weighed and muscles tissue samples were taken for the analysis of total mercury and methylmercury. The age of fish was determined from their scales. The samples of muscle tissue were put into polyethylene bags, labelled and stored in a freezer at –18°C.

The determination of total mercury content in fish muscle was performed by means of cold vapour atomic absorption spectrometry using AMA-254 (Altec Ltd., Czech Republic) single-purpose mercury analyser (detection limit 1 µg/kg, recovery 82 ± 6%).

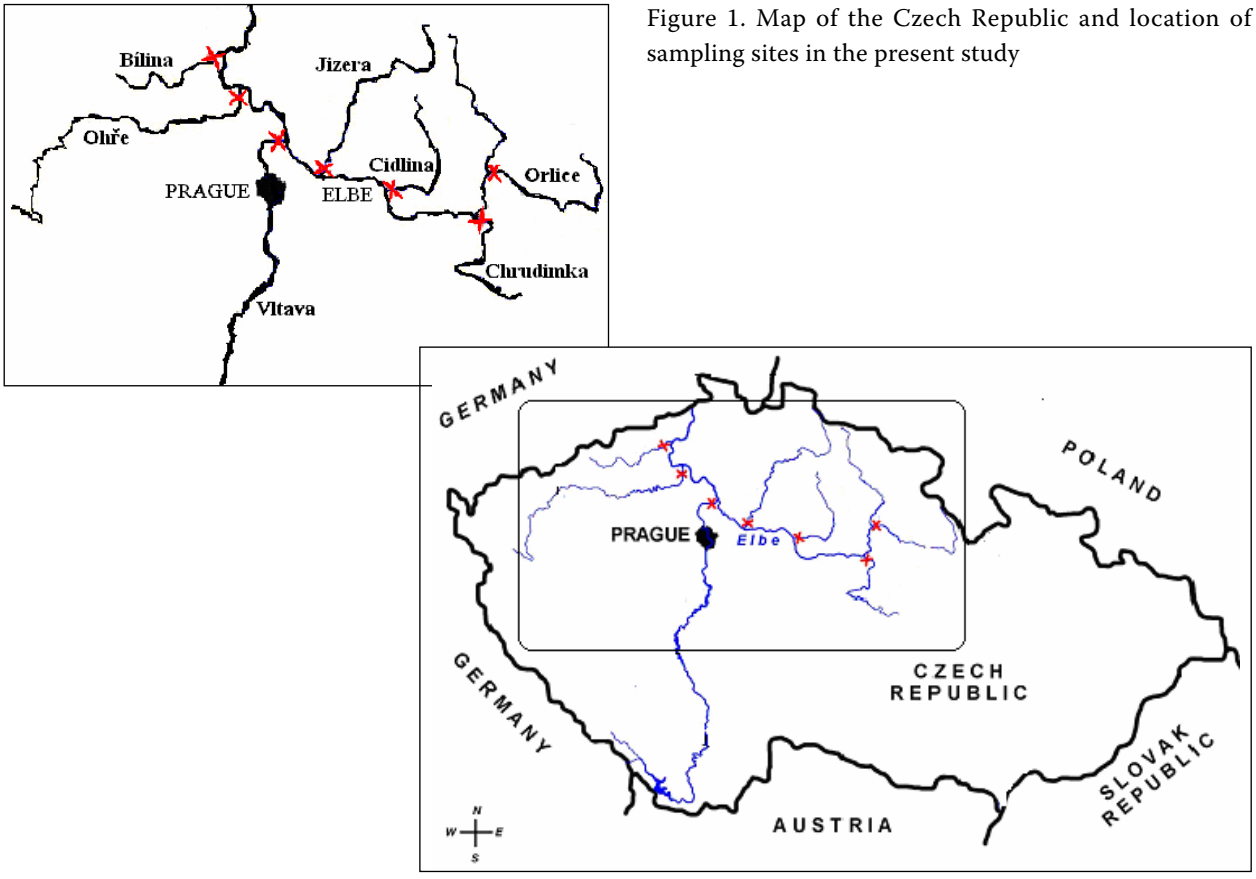

Figure 1. Map of the Czech Republic and location of sampling sites in the present study

Methylmercury was determined in the form of CH_3HgCl by gas chromatography (Caricchia *et al.* 1997; Maršálek & Svobodová 2006). The sample preparation was based on acidic digestion and extraction with toluene (Maršálek & Svobodová 2006). The GC 2010A gas chromatograph (Shimadzu GmbH, Czech Republic) was used for the analysis. The capillary column DB 608 (30 m × 0.53 mm × 0.83 μm; J&W Scientific, Chromservis, Czech Republic) and the electron capture detector (ECD) (Shimadzu GmbH, Czech Republic) were used. The evaluation was made using GC Solution software (Shimadzu GmbH, Czech Republic) and MS Excel software. The limit of detection was 21 μg/kg and the limit of quantification was 62 μg/kg (recovery 89 ± 2.5%).

The accuracy of the results of THg and MeHg determination was validated using standard reference material BCR-CRM 463 and 464 (IRMM, Belgium), respectively.

The results were tested using Statistica Version 7.0 (StatSoft, Czech Republic), and the non-parametric Kruskal-Wallis test was used.

Total mercury and methylmercury contents are given in mg/kg fresh weight (FW).

The hazard index was calculated according to Kannan *et al.* (1998) using the reference dose (RfD) for THg (0.3 μg/kg body weight per day) set forth by US EPA.

To determine the maximum consumption possible of fish meat, the provisional tolerable weekly intake limit (PTWI) of 1.6 μg MeHg per kg body weight per week was used (JECFA FAO/WHO).

RESULTS AND DISCUSSION

Mercury and methylmercury concentrations

Total mercury and methylmercury wer found in all 55 samples examined samples. In four samples from the Cidlina, methylmercury concentrations were below the detection limit. The characteristics of the fish captured are given in Table 1. The mean total mercury and methylmercury concentrations from the individual sites are given in Figure 2. The lowest mean concentrations of mercury and methylmercury were 0.07 ± 0.05 mg/kg and 0.06 ± 0.04 mg per kg, respectively. These concentrations were found in the chub from the Cidlina. The highest mean concentrations of total mercury and methylmercury, on the other hand, were found in the Jizera (0.27 ± 0.19 mg/kg and 0.23 ± 0.15 mg/kg, respectively).

THg concentrations in the Ohře were significantly higher than those ascertained in the Cidlina

Table 1. Basic characteristics of chub captured in individual tributaries of the Elbe and muscle tissue MeHg/THg ratios

Tributary	*n*	Body weight (g) mean ± SD min–max	Age (years) mean ± SD min–max	MeHg/THg % mean ± SD min–max
Orlice	6	232 ± 94.9	3.8 ± 0.4	92.0 ± 7.7
		155–405	3–4	85.2–106.2
Chrudimka	10	180 ± 35	3.2 ± 0.4	82.3 ± 11.4
		140–240	3–4	60.7–95.7
Cidlina	9	238 ± 160.3	3.7 ± 0.9	76.8 ± 17.1
		65–595	2–5	37.2–89.3
Jizera	3	377 ± 326.8	4 ± 1	85.4 ± 10.3
		95–735	3–5	78.9–97.4
Vltava	7	290 ± 78	3.3 ± 0.5	86.4 ± 11.5
		180–400	3–4	64.4–96.9
Ohře	10	541 ± 201.8	4.8 ± 1.3	83.32 ± 8.0
		235–920	3 –7	65.2–91
Bílina	10	121 ± 57.4	2.3 ± 0.5	77.6 ± 19.6
		85–275	2–3	40.2 –104.4

n – number of fish captured in individual rivers

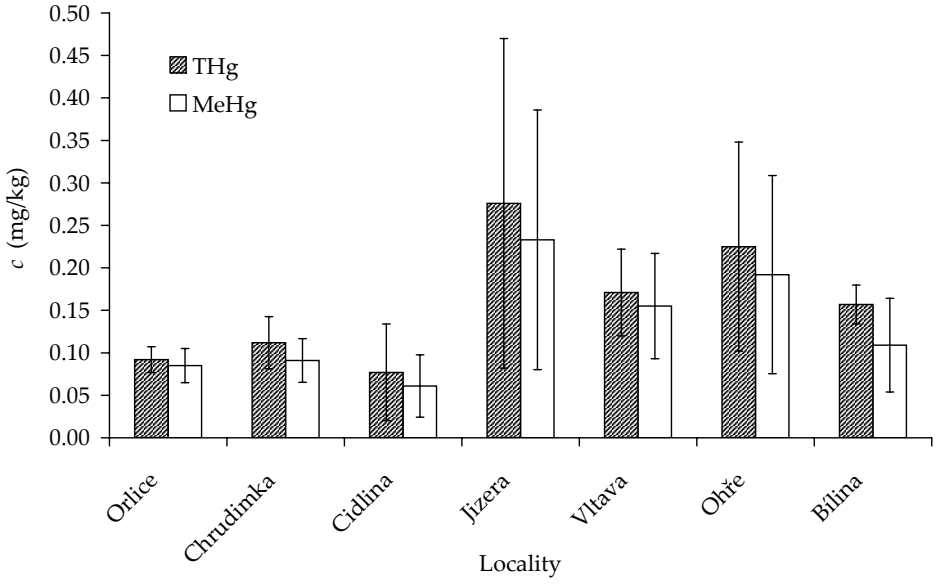

Figure 2. Mean of THg and MeHg concentrations in muscle tissue of chub from individual tributaries of the Elbe River (Error bars indicate the standard deviation SD)

($P < 0.01$), the Chrudimka ($P < 0.05$) and the Orlice ($P < 0.05$). THg concentrations in the chub from the Jizera were also significantly higher ($P < 0.05$) than those found in the Cidlina and the Orlice. MeHg concentrations were statistically significantly higher ($P < 0.01$) in the Ohře than in the Cidlina and the Chrudimka ($P < 0.05$). MeHg concentrations in the Jizera were significantly higher ($P < 0.05$) than those in the Cidlina (Table 2).

From the analyses it follows that the Ohře and the Jizera are the Elbe tributaries the most contaminated with mercury. High concentrations of mercury in fish of various species in the Ohře were also reported by Svobodová and Hejtmánek (1976). The Skalka Reservoir in the upper reaches of the Ohře is an important source of contamination of that river. Analysing various species of fish captured in the Skalka Reservoir in 2003, Maršálek *et al.* (2005) found the highest mercury concentrations (3.4 mg/kg) in muscle tissue of the asp (*Aspius aspius*), while in other species the concentrations were around 1.1 mg/kg. The upper reaches of the Skalka Reservoir have been polluted for several decades with mercury-contaminating waste water from a factory that manufactured mercury-based technical chemicals and preparations in the town of Marktredwitz (Germany).

In the Jizera River, significantly higher ($P < 0.05$) mercury and methylmercury concentrations were found than in the Cidlina and the Orlice, respectively. The results are similar to those reported by Svobodová *et al.* (1993) who found the mean THg concentration of 0.19 mg/kg in the chub. In the case of the Jizera, the likely source of the aquatic

Table 2. Differences in THg and MeHg concentrations between tributaries at $^{*}P < 0.05$, $^{**}P < 0.01$

River	Orlice		Chrudimka		Cidlina		Jizera		Ohře	
	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg
Orlice							*		*	
Chrudimka									*	*
Cidlina							*	*	**	**
Jizera	*				*	*				
Ohře	*		*	*	**	**				

The significant different was not found in the Vltava and the Bílina

Table 3. Hazard indexes for a standard consumer and a member of a fisherman's family, and maximum tolerable weekly intakes of chub meat from the monitored tributaries of the Elbe River

Tributary	Hazard index*		Maximum weekly tolerable intake** (kg)
	standard consumer	fisherman's family	
Orlice	0.01	0.12	1.3
Chrudimka	0.02	0.15	1.2
Cidlina	0.01	0.10	1.8
Jizera	0.04	0.35	0.4
Vltava	0.02	0.22	0.7
Ohře	0.03	0.29	0.5
Bílina	0.02	0.21	0.9

* calculation of THg according to Kannan *et al.* (1998); ** calculation of MeHg according to WHO

environment contamination is the automobile industry in the Mladá Boleslav region.

Low THg and MeHg concentrations (mean 0.09 mg/kg and 0.058 mg/kg, respectively) were found in the lower reaches of the Orlice River. On the other hand Svobodová *et al.* (2004) found higher THg concentrations in the common trout (*Salmo trutta* morpha *fario*) from the Lichkov site in the upper reaches of the river (0.4 mg/kg in 2000 and 0.3 mg/kg in 2001). The distance is 88 river km.

The results obtained in our study were compared with the study by Dušek *et al.* (2005) who monitored mercury contamination in the Elbe between 1991 and 1996. An increased mercury concentration (0.3 mg/kg) in the Elbe was found both upstream and downstream of the Jizera discharge into the Elbe which seems to suggest that the Jizera does not play a significant role in the increased mercury contamination of the Elbe. Žlábek *et al.* (2005) also mention higher THg concentrations in the chub captured in the Elbe at Lysá nad Labem in 2003 (upstream of the Jizera discharge into the Elbe; 0.9 mg/kg).

The mean MeHg/THg ratio was 83 ± 15%. None statistically significant differences were found between mean MeHg/THg ratios from the individual study sites. Houserová *et al.* (2006a) and Maršálek *et al.* (2005) reported in their studies a similar high representation of MeHg in THg in the chub ranging from 74% do 100%. In our study, the mean of methylmercury-to-mercury ratios found in individual localities were between 76.8% and 92%, which is indicative of different conditions for mercury methylation in the sediments of the rivers monitored, which is indicative of different conditions for mercury methylation in the sediments of the rivers monitored.

Health hazard assessment

Potential health hazard caused by mercury in fish was calculated according to the method of Kannan *et al.* (1998), who described the calculation of the hazard index associated with fish consumption. The hazard indexes calculated for Hg are given in Table 3. The hazard indexes below 1 indicate no hazard for consumers. In the hazard index calculations the average consumptions of freshwater fish in the Czech Republic was used, i.e. 1 kg per capita (and 10 kg per member of fisherman's household). The figures given are low, in fact several times lower than the hazard index of 1. The methylmercury issue has been monitored for some time by the World Health Organisation (WHO), and for that reason it has set the maximum recommended dose of MeHg. Its Provisional Tolerable Weekly Intake (PTWI) is 1.6 μg MeHg/kg body weight/week. This value can be used to calculate the amount that can be eaten by a consumer at a specific site. Thus, in view of MeHg contamination, the best rivers of those monitored in the present study were the Cidlina and the Orlice, because the amount of up to 1.8 kg and 1.3 kg, respectively, of fish captured there may be consumed per week. On the other hand, the maximum tolerable weekly intakes of fish from the Jizera and the Ohře are 0.48 kg and 0.59 kg, respectively.

CONCLUSION

Based on the comparison of the results of this study and the data published by Žlábek *et al.* (2005), Maršálek *et al.* (2006), Svobodová and Hejtmánek (1976) Svobodová *et al.* (2004), and Dušek *et al.* (2005), who studied various sites along the Elbe River, we may conclude that the Elbe main tributaries do not significantly affect its contamination with mercury.

The hazard indexes estimated signal no significant health risk of the consumption of fish from the localities followed in this study. From the tributaries of the Elbe River analysed, up to 0.49 kg per week (Jizera) or up to 1.8 kg per week (Cidlina), can be consumed.

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