

## Concentration of some metals in the muscles of fish from selected lakes of Warmia and Mazury region (Poland)

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### Abstract

In view of very scarce and limited information concerning the content of heavy metals in tissues of fish from the lakes in north-eastern Poland, the aim of the study was to determine the content of some heavy metals in the muscle tissue of two fish species: bream (*Abramis brama*) (n = 60) and pikeperch (*Sander lucioperca*) (n = 60) caught in selected lakes of Warmia and Mazury region (Poland) in 2010 as well as to assess human health safety. The concentration of lead (Pb), mercury (Hg), copper (Cu), iron (Fe) and zinc (Zn) in the muscle tissue of bream and pikeperch was determined by atomic absorption spectrometry. The mean concentration of toxic metals (Pb and Hg) in muscles of bream was 0.07 mg/kg and 0.03 mg/kg, respectively, and 0.10 mg/kg and 0.13 mg/kg in muscles of pikeperch, respectively. The mean concentration of Cu, Fe and Zn found in the muscles of bream was 0.33 mg/kg, 7.27 mg/kg and 6.12 mg/kg in muscles of pikeperch it was 0.21 mg/kg, 5.56 mg/kg and 6.02 mg/kg, respectively. It was found that the content of the analysed metals in fish muscles was low and did not exceed the values of limits admissible in the European Union. At the assumed mean and maximum concentration of Pb and Hg, the values of PTWI (provisional tolerable weekly intake) were not exceeded (i.e. 0.56% PTWI for Pb and 3.01% PTWI for Hg), therefore the consumption of fish originating from selected lakes of Warmia and Mazury does not constitute a threat to consumer health.

*Toxic metals, essential metals, concentration, bream, pikeperch*

Among the compounds that can lead to pollution of water ecosystems, special focus should be placed on elements, particularly heavy metals. They originate primarily from anthropogenic sources (the production of iron and steel, mining wastewaters, municipal and industrial sewage, the production and application of artificial fertilizers and pesticides and water and overland transportation) (Pyle et al. 2005). The process of biomagnifications, which involves the increase of concentration of metals in organisms on the upper level of the trophic chain, is most visible in the aquatic environment. Fish as one of the final links of the food chain are considered to be good bioindicators of water environment contamination by these elements.

Lakes selected for the study (Nidzkie, Niegocin, Gołdap and Jeziorak) are used mainly as places of recreation and water tourism. They are located in the Warmia and Mazury region (north-eastern Poland), which plays a significant role in the fishery industry in the country. It is also an area of high ecological value. The Nidzkie and Niegocin lakes belong to Great Masurian Lakes, the largest complex of lakes and canals in Poland and one of the most attractive regions in terms of landscape. Lake Gołdap is located in the northern part of the Warmia and Mazury, on the border between Poland and Russia. Jeziorak is the longest lake in Poland and the sixth lake in size, situated in the western part of the region. A part of this water body belongs to the Natura 2000 area (Plate VI, Fig. 1).

Heavy metals are food pollutants posing a particular threat for human and animals (Järup 2003). It is of crucial importance to determine the concentrations of pollution in the environment in order to assess the degree of human health safety, since food of animal origin is one of the best indicators of an ecosystem's exposure to toxic factors.

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As information concerning the content of heavy metals in tissues of fish from the lakes in north-eastern Poland is scarce and limited, an examination of this subject for the Warmia and Mazury region was undertaken.

The aim of the study was to determine the concentration of lead (Pb), mercury (Hg), copper (Cu), iron (Fe) and zinc (Zn) in the muscle tissue (edible parts) of bream and pikeperch caught in selected lakes of Warmia and Mazury region and to assess human health safety.

### Materials and Methods

Concentrations of Pb, Hg, Cu, Fe and Zn were determined in the muscle tissues of two commonly occurring fish species, one typically benthophagous: bream (*Abramis brama*), and the other predatory: pikeperch (*Sander lucioperca*), which represent the first and the last links in the food chain. Both species constitute an important component of commercial fish catches in Warmia and Mazury region.

Fifteen ready-marked fish of each species (body weight range: 1.4–2.0 kg for bream and 1.6–2.3 kg for pikeperch) from each selected lake (Nidzkie, Niegocin, Gołdap and Jeziorak) were used in the study. Fish were caught from November to December 2010.

Each sample of the dorsal muscle was taken from one fish and stored in polyethylene bags at -25 °C prior to analysis. For Pb, Cu, Fe and Zn analysis, approximately 10 g of each muscle tissue sample was dried at 105 °C and dry-digested at 450 °C. The white ash was dissolved in 1M suprapur HNO<sub>3</sub> (Merck, Germany) and each sample was quantitatively transferred to a 25 ml volumetric flask. The metal analysis of samples (Pb, Cu, Fe and Zn) were measured with flame atomic absorption spectrometry (UNICAM Solar 939) and corrected with a deuterium lamp. The detection limits were: 0.05 mg/kg for Pb, 0.05 mg/kg for Cu, 0.5 mg/kg for Fe and 0.1 mg/kg for Zn.

Total Hg concentrations were determined by the AMA 254 single-purpose analyser, which is based on combustion-amalgamation atomic absorption. No chemical pre-treatment of the samples was needed. Detection limit of Hg was 0.002 mg/kg.

Standard reference materials CRM 422 cod muscle (lyophilized sample) was used to prove the accuracy of the method. All samples were processed in triplicate.

The concentrations of metals in fish muscles, expressed in mg/kg of wet weight, are given as mean, standard error of the mean (SEM) and min-max range. Statistical analysis was conducted using Statistica 9.0 for Windows software. One-way analysis of variance (ANOVA) followed by a Duncan test was applied to detect significant differences between selected lakes. Significance was established at a level of  $P \leq 0.05$ .

### Results

The average concentrations of heavy metals in muscle tissues of fish (bream, pikeperch) are presented in Table 1.

None of the examined samples of bream and pikeperch muscle tissue exceeded the limits for toxic metals (Pb, Hg) acceptable in the European Union (0.30 mg/kg for Pb and 0.50 mg/kg for Hg), although the concentration of these metals varied among fish species as well as lakes. Concentration of Pb in bream ranged from 0.054 mg/kg (Lake Nidzkie) to 0.084 mg/kg (Lake Niegocin) and concentration of Hg between 0.009 mg/kg (Lake Jeziorak) and 0.060 mg/kg (Lake Niegocin). Concentrations of Pb and Hg in muscles of pikeperch were higher. The highest content of Pb was found in fish caught in Niegocin and Jeziorak lakes (0.126 mg/kg and 0.119 mg/kg, respectively) and Hg in fish from Gołdap and Niegocin lakes (0.193 mg/kg and 0.176 mg/kg, respectively). The average concentration of Cu in bream ranged from 0.27 mg/kg (Lake Niegocin) to 0.41 mg/kg (Lake Nidzkie), Fe from 5.04 mg/kg (Lake Niegocin) to 9.16 mg/kg (Lake Jeziorak) and Zn from 5.47 mg/kg (Lake Niegocin) to 6.68 mg/kg (Gołdap Gołdap). The lowest content of those metals was noted in bream from Lake Niegocin, and in pikeperch from lakes Gołdap and Niegocin (Table 1).

### Discussion

In comparison to our results, Łuczyńska and Brucka-Jastrzębska (2006) found higher values of Pb and Hg content in muscles of fish from four lakes of the Olsztyn Lake

Table 1. Mean concentrations of selected metals in muscle tissue of fish (expressed by mean value  $\pm$  SEM and min-max range)

Lakes	Species	Metals (mg/kg b.w.)				
		Pb	Hg	Cu	Fe	Zn
Nidzkie	Bream n = 15	0.054 <sup>abd</sup> $\pm$ 0.004	0.010 <sup>a</sup> $\pm$ 0.001	0.41 <sup>a</sup> $\pm$ 0.038	7.58 $\pm$ 1.586	5.94 <sup>c</sup> $\pm$ 0.248
	Pikeperch n = 15	0.050–0.068	0.006–0.10	0.24–0.63	2.47–16.69	4.78–7.17
Niegocin	Pikeperch n = 15	0.075 <sup>abd</sup> $\pm$ 0.01	0.082 $\pm$ 0.01	0.22 $\pm$ 0.03	8.92 <sup>d</sup> $\pm$ 2.18	6.25 $\pm$ 0.43
	Bream n = 15	0.062–0.091	0.071–0.101	0.09–0.46	2.48–23.11	3.38–8.20
	Bream n = 15	0.084 <sup>a</sup> $\pm$ 0.01	0.060 $\pm$ 0.01	0.27 $\pm$ 0.019	5.04 $\pm$ 0.312	5.47 $\pm$ 0.164
Goldap	Pikeperch n = 15	0.068–0.129	0.029–0.114	0.23–0.40	3.26–6.20	4.88–6.39
	Bream n = 15	0.126 <sup>a</sup> $\pm$ 0.01	0.176 $\pm$ 0.02	0.18 <sup>b</sup> $\pm$ 0.02	4.25 $\pm$ 0.26	5.44 <sup>c</sup> $\pm$ 0.24
Jeziorak	Bream n = 15	0.088–0.188	0.128–0.222	0.12–0.30	3.26–5.97	4.14–6.63
	Bream n = 15	0.080 <sup>a</sup> $\pm$ 0.008	0.040 <sup>ab</sup> $\pm$ 0.01	0.35 $\pm$ 0.043	7.28 $\pm$ 0.585	6.68 <sup>b</sup> $\pm$ 0.199
	Pikeperch n = 15	0.066–0.112	0.026–0.074	0.18–0.67	5.69–11.58	5.86–7.29
Jeziorak	Bream n = 15	0.095 $\pm$ 0.02	0.193 $\pm$ 0.01	0.17 $\pm$ 0.01	4.06 $\pm$ 0.23	6.46 <sup>b</sup> $\pm$ 0.24
	Bream n = 15	0.068–0.142	0.179–0.203	0.12–0.23	3.32–5.79	5.09–7.84
Jeziorak	Bream n = 15	0.079 <sup>a</sup> $\pm$ 0.005	0.009 <sup>a</sup> $\pm$ 0.001	0.30 <sup>a</sup> $\pm$ 0.007	9.16 $\pm$ 2.973	6.37 $\pm$ 0.162
	Pikeperch n = 15	0.067–0.099	0.004–0.014	0.27–0.34	3.37–33.14	5.72–7.42
Jeziorak	Bream n = 15	0.119 <sup>a</sup> $\pm$ 0.01	0.058 $\pm$ 0.002	0.26 <sup>b</sup> $\pm$ 0.03	5.02 <sup>a</sup> $\pm$ 0.42	5.93 $\pm$ 0.21
	Pikeperch n = 15	0.084–0.154	0.051–0.067	0.16–0.39	3.75–8.09	5.12–7.20

$P < 0.05$  – significant difference compared to: a - Nidzkie Lake; b - Niegocin Lake; c - Goldap Lake; d - Jeziorak Lake; n - number of fish samples; SEM - standard error of the mean

of Pb was found in zooplankton and organisms living in the bottom sediments, and the lowest in predatory fish. In the case of Hg, our results were consistent with the studies of other authors (Dušek et al. 2005; Łuczyńska and Brucka-Jastrzębska 2006). Particular exception was the higher concentration of Hg found in muscles of white bream and roach than in pike and perch from Świdwie Lake, Poland (Perkowska and Protasowicki 1999). Elevated concentration of Hg in non-predatory species was explained by a higher concentration of this metal in the surface layer of sediments. Admittedly mercury in water sediments is stable, but in surface layer of sediments (where fish feed), humic acids which take part in the binding of Hg are still relatively poorly formed and as a result of various processes (biotic and abiotic) this

District (Warmia and Mazury region, Poland). Compared to our studies, lower concentration of Pb, but higher concentration of Hg was recorded by Kenšová et al. (2010) in muscle tissue of bream and pikeperch caught in the Věstonice Reservoir, Czech Republic. Definitely higher concentrations of toxic metals were reported by Staniskiene et al. (2006) in various species of fish originating from 20 lakes of Lithuania. The differences in the contents of analysed metals in fish from various water bodies can be explained both by their location and by their type and use.

It was demonstrated that fish accumulate heavy metals depending on their mode of nutrition and position in the food chain (Altındağ and Yiğit 2005). The results of our study reveal a several-fold higher accumulation of both Pb and Hg in muscles of pikeperch (the last link in the food chain) compared to bream. According to Svobodová et al. (1996), the content of Pb in fish as the final link of the food chain tends to decrease. In their studies, the highest concentration

metal may be released and available to water organisms (Boszke et al. 2002; Belzile et al. 2004).

Concentration of heavy metals in fish tissue also depends on the degree of pollution in the water environment. Our research demonstrated that the highest amounts of Pb were present in muscles of fish from Niegocin, Gołdap and Jeziorak lakes, and the highest amounts of Hg were present in muscles of fish from Niegocin and Gołdap lakes. Although no large human settlements or industrial plants are located around the lakes selected for the study, those water bodies are attractive tourist localities with holiday resorts, numerous marinas and the Masurian Navigation port. Another reason for increased Hg concentration in fish originating from the studied lakes could be their eutrophication. The shortage of oxygen increases Hg methylation capability, and consequently, easier absorption of this form by organisms (Boszke et al. 2002).

The currently applicable Commission Regulation (EC) No 1881/2006 (as amended) sets maximum acceptable concentrations for certain contaminants in foodstuffs and specifies limits related to the content of elements that are dangerous to human health, such as lead and mercury in fish. However, other metals analysed in our study, i.e. Cu, Fe and Zn are not limited by the EC regulation. Their contents are regulated by the organism itself, on the other hand, their excess can pose a threat to the health of animals and people.

Higher Cu and Zn concentrations compared to our studies were noted by Łuczyńska et al. (2009) in muscles of fish originating from the Great Masurian Lakes, whereas the Fe content was similar. Definitely lower concentrations of those elements were observed by Lidwin-Kaźmierkiewicz et al. (2009) for bream, pike and perch from West Pomerania lakes (Poland). When examining the content of selected heavy metals in various species of fish from Lithuanian water bodies, Staniskiene et al. (2006) found comparable concentration of Cu (0.29 mg/kg), lower concentration of Fe (2.06 mg/kg), and higher concentration of Zn (14.84 mg/kg). Kenšová et al. (2010) found the Zn content in the muscle tissue of bream and pikeperch comparable (about 6 mg/kg) to our results but the Cu content was clearly lower (0.01 mg/kg).

Literature data indicate that the content of essential metals in various species of fish depends foremost on their mode of nutrition. It was found that plankton eaters and those feeding on invertebrates contain more Cu, Fe and Zn than omnivorous and predators. This could result from the large concentration of those metals in bottom sediments and in plankton (Papagiannis et al. 2004). Therefore, it may seem that the concentration of Cu, Zn and Fe is inversely proportional to the place occupied by the fish in the food chain. This is also confirmed by the results of our own research. Regardless of the lake from which the fish originated, concentrations of these metals in the muscle tissue of bream were higher than in pikeperch.

In order to improve human health safety, world organizations have established the maximum intake limits of toxic elements, PTWI (provisional tolerable weekly intake) which should not be exceeded. The PTWI for humans established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) amounts to 25 µg/kg body weight (b.w.) for Pb, 4 µg/kg b.w. for total Hg and 1.6 µg/kg b.w. for MeHg (WHO Technical Report Series 2011). Since concentration of methylmercury in muscles of fish makes up 80–100% of total mercury, 100% MeHg of total Hg was used in calculation of PTWI for this compound. Taking into consideration the mean concentration of Pb and Hg in the muscles of both species of fish and the data of the Polish Central Statistical Office 2011 concerning fish consumption in Poland, the intake of those metals by an adult weighing 70 kg amounts to 0.56% PTWI for Pb, 3.01% PTWI for Hg and 7.89% PTWI for MeHg. It should be also emphasized that in the case of pikeperch which as a predator accumulates more toxic metals, the intake of those elements expressed as % PTWI is low and amounts to 0.67% for Pb, 4.88% for Hg and 12.79% for MeHg.

To summarize the results, it can be concluded that the mean concentration of toxic metals, i.e. Pb and Hg, in the muscle tissue of bream and pikeperch does not exceed the limits acceptable in the European Union and the content of Cu, Fe and Zn was within the ranges considered as low by other authors. The data obtained can also demonstrate that consumption of fish originating from Warmia and Mazury lakes does not pose any risk to consumer health since the values of PTWI at the assumed mean and maximum concentrations of Pb and Hg were not exceeded.

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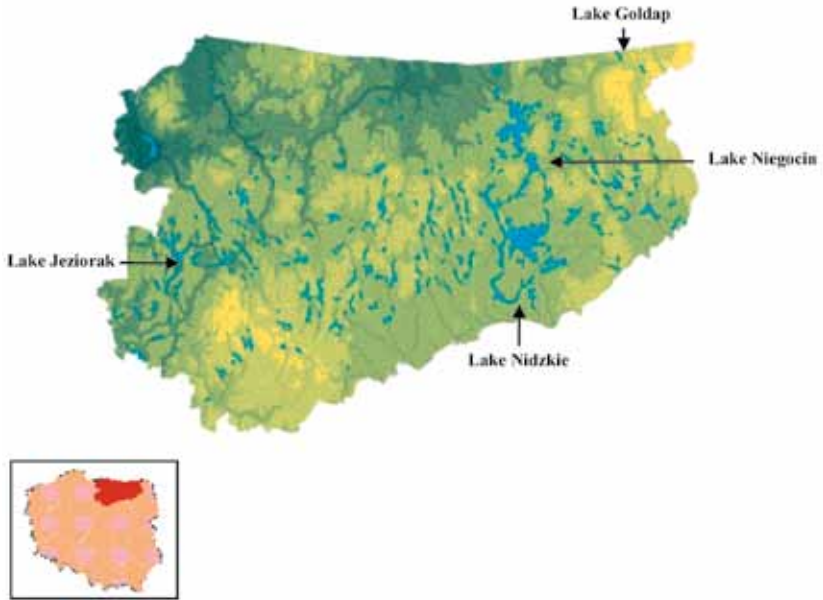


Fig. 1. Location of the Warmia and Mazury region in Poland with the sampling area of four lakes.