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Heavy metal and trace element bioaccumulation in target tissues of four edible fish species from the Danube River (Serbia)

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ABSTRACT

Pikeperch (*Sander lucioperca*), European catfish (*Silurus glanis*), burbot (*Lota lota*), and common carp (*Cyprinus carpio*) were collected from the Danube River (Belgrade section, Serbia), and samples of liver, muscle, and gills were analyzed for Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Se, Sr, and Zn using inductively coupled plasma optical emission spectrometry (ICP-OES) to highlight the importance of species and tissue selection in monitoring research, contaminant studies, and human health research. The Kruskal–Wallis test revealed significant differences between fish species in regard to metal levels in liver, muscle, and gills. The principal component analysis (PCA) indicated that the studied fish species could be grouped on the basis of the level of analyzed elements in liver and gills. The Mann–Whitney test showed two subsets (one comprising two piscivorous species, pikeperch and catfish, and the other, two polyphagous species, burbot and carp) in regard to Cr and Hg levels in liver (higher levels in piscivorous species), as well as B, Fe, and Hg in gills (B and Fe with higher levels in polyphagous and Hg in piscivorous species), and As in muscle (higher levels in polyphagous species). Carp had distinctly higher levels of Cd, Cu, and Zn in liver in comparison to other three species. None of the elements exceeded the maximum acceptable concentrations (MAC). However, since Hg levels are close to the prescribed MAC levels, the consumption of these fishes can be potentially hazardous for humans.

1. Introduction

Heavy metal pollution in rivers has become a matter of great concern, not only because of the threat it poses to public water supplies, but also because of the hazard to human consumption of fishery resources (Terra et al., 2008). The Danube is the second largest river in Europe with the length of 2826 km. The Danube River Basin collects water from nineteen countries (Sommerwerk et al., 2009), and it is subjected to large amounts of wastewater input (Teodorović et al., 2000). A number of industrial centers (Milanović et al., 2010), such as Novi Sad, Belgrade, Pančevo, and Bor, continuously discharge various pollutants into the Danube in Serbia (Stanić et al., 2006).

Metals such as Fe, Cu, Zn, and Mn are essential metals for their important role in biological systems, whereas Hg and Cd are non-essential metals, toxic even in traces (Tüzen, 2003). However, essential metals may also have toxic effects at supraoptimal concentrations (Blanco-Penedo et al., 2006). Apart from the nature of the chemical, factors that determine the hazard to human health are fish consumption preferences, meal size, fish species, and species variation in bioaccumulation (Watanabe et al., 2003). Furthermore, the sampling location and season, as well as diet preferences and fish size may influence the level of bioaccumulation in the same fish species (Ural et al., 2012). Liver and gills, as metabolically active organs, are target organs for metal accumulation (Yilmaz et al., 2007), while the accumulation in muscle tissue is lower (Jarić et al., 2011; Poleksić et al., 2010; Višnjić-Jeftić et al., 2010).

Studies on bioaccumulation of pollutants in fish are important in determining the tolerance limits of fish species, effects of specific pollutants on fish, and biomagnification through food chains (Asuquo et al., 2004). Piscivorous predators show higher levels of Hg in muscle and in liver than species from lower trophic levels (Farkas et al., 2005; Kenšová et al., 2010; Zrnčić et al., 2012). Also, in piscivorous predators, the highest level of Fe is found in liver (Karadede-Akin and Ünlü, 2007; Nabavi et al., 2012). On the other side, species from lower trophic levels accumulate higher levels of Cu in liver (Danabas and Ural, 2012; Kenšová et al., 2010; Papagiannis et al., 2004; Sunjog et al., 2012; Ural et al., 2011) and

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of Zn in liver and gills (Danabas and Ural, 2012; Kenšová et al., 2010; Papagiannis et al., 2004; Sunjog et al., 2012; Ural et al., 2011) in comparison to piscivorous predators.

In this paper, we analyzed eighteen elements in liver, muscle, and gills of four commercially exploited species, pikeperch (*Sander lucioperca*), catfish (*Silurus glanis*), burbot (*Lota lota*), and carp (*Cyprinus carpio*), from different trophic levels. Sampling was carried out at a sector of the Danube that receives large amounts of untreated industrial and communal waters. The main objective of the study was to highlight the importance of species and tissue selection in monitoring research, contaminant studies, and studies of potential impact of contaminated fish consumption on human health.

2. Materials and methods

2.1. Sample collection and preparation

Fishes were caught at two sampling sites with similar levels of pollution at the Belgrade section of the Danube River (from 1168th to 1170th river kilometer). These sites were chosen because of their proximity to the confluence of the Sava River (which carries additional amounts of wastewater) with the Danube River, as well as their proximity to the urban area of Belgrade, on one side, and to agricultural areas on the other side of the river (Fig. 1). The coordinates of sampling site 1 are 44°49′22.13″N, 20°26′19.22″E and that of sampling site 2 are 44°49′57.55″N, 20°28′28.95″E.

Ten pikeperch specimens were caught at sampling site 1, in October 2010, with average length of 45.2 ± 6.7 cm (length range: 38–59 cm) and average weight of 846.7 ± 508.6 g (weight range: 437–2000 g). Eleven catfish specimens were caught at sampling site 1, in October 2010, with average length of 66.8 ± 13.1 cm (length range: 55–100 cm) and average weight of 2325.5 ± 1579.5 g (weight range: 1095–6620 g). Fourteen carp specimens were caught at sampling site 1, in October and November 2010, with average length of 55.1 ± 15.6 cm (length range: 29–82 cm) and average weight of 3030.4 ± 2385.1 g (weight range: 405–8200 g). Twenty burbot specimens were caught at sampling site 2, in December 2010, with average length of 36.6 ± 5.9 cm (length range: 23.5–45.8 cm) and average weight of 375.7 ± 166.8 g (weight range: 99.1–680.3 g).

Water sampling for the calculation of the bioconcentration factor (BCF) was done at the same two sampling sites and in the same time.

Fishes were sampled by portable lift nets and traps and dissected with a plastic laboratory set. Liver, muscle, and gill samples were quickly removed, rinsed with distilled water, and stored at −18 °C prior to analysis.

We confirm that all procedures were performed in compliance with the relevant laws and institutional guidelines, and that the appropriate institutional committees have approved them.

2.2. Element analysis

All samples were freeze-dried using a rotational vacuum concentrator (GAMMA 1-16 LSC, Germany) and sample portions between 0.2 and 0.5 g (dry weight) were subsequently processed in a microwave digester (speedwave™ MWS-3+; Berghof Products+Instruments GmbH, Eningem, Germany), using 6 ml of 65 percent HNO_3 (Suprapur®, Merck) and 4 ml of 30 percent H_2O_2 (Suprapur®, Merck) at a food temperature program (100–170 °C). The potential presence of the analyzed elements in chemicals used for digestion was resolved by a number of blank samples. After cooling to room temperature, the digested samples were diluted with distilled water to a total volume of 25 ml. The analysis was performed by ICP-OES (Spectro Genesis EOP II, Spectro Analytical Instruments DmbH, Kleve, Germany), comprising the assessment of concentrations of eighteen elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Se, Sr, and Zn). The following wavelength lines of the ICP-OES analysis were used: Al 394.401 nm, As 189.042 nm, B 249.773 nm, Ba 233.527 nm, Cd 228.802 nm, Co 228.616 nm, Cr 205.552 nm, Cu 324.754 nm, Fe 259.941 nm, Hg 184.950 nm, Li 460.289 nm, Mn 259.373 nm, Mo 202.095 nm, Ni 231.604 nm, Pb 220.353 nm, Se 196.090 nm, Sr 460.733 nm, and Zn 206.191 nm. The quality of the analytical process was controlled through analysis of BCR-185R reference materials of bovine liver as well as IAEA-336 lichen reference material. The concentrations that found were within 90–115 percent of the certified values

Fig. 1. The sampling area.