

## Bioaccumulation of potentially toxic elements in fish species from aquatic environments located in crowded areas of southern Romania

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**Abstract.** Taking into consideration that fish are valuable bioindicators for assessing pollution with potentially toxic elements (PTEs) such as heavy metals from aquatic environments, this study aimed to assess bioaccumulation factors in relation to water (BAF) and sediment (BASF) for the following potential toxic elements: Cd, Pb, Hg, Cu, Cr, Ni and Zn from 6 different fish species (*Alburnus alburnus*, *Carassius gibelio*, *Scardinius erythrophthalmus*, *Ameiurus nebulosus*, *Perca fluviatilis*, *Lepomis gibbosus*). Fish species have been captured from the waters of the Arges River (Hotarele village area) and the Colentina River (particularly from Mogosoaia, Herastrau and Pantelimon lakes), from crowded areas located in the southern part of Romania. The results of the analysis indicated BAF values > 1 for the most fish species captured from the Colentina River. BASF values > 1 were obtained for BASF<sub>Pb</sub> (*Carassius gibelio* - Arges River), BASF<sub>Ni</sub> (*Scardinius erythrophthalmus* - Herastrau L. and *Perca fluviatilis* - Pantelimon L.), BASF<sub>Cr</sub> (*Perca fluviatilis* - Pantelimon L.) and BASF<sub>Zn</sub> (*Alburnus alburnus* and *Scardinius erythrophthalmus* - Mogosoaia L. and *Carassius gibelio* - Pantelimon L.). The obtained results can be used to describe the transfer of these elements from water and sediments to the fish tissue.

### 1. Introduction

At global level, the occurrence of toxic substances in the environment has raised concerns due to their direct toxicity on human health and aquatic environment and through their accumulation in the aquatic food chain [1, 2]. Of these, heavy metals are a group of the most important pollutants in the environment as they are indestructible and most of them have toxic effects on organisms [3, 4, 5, 6, 7,8]. Due to the constant exposure of aquatic organisms to the chemical substances from contaminated water, different trophic levels and different size and age, fish is a good indicator for the contamination with potentially toxic elements (PTEs) [9, 10]. Some heavy metals play an essential role in carrying out all the biochemical and energetic changes with a role in the living tissues, while others are highly toxic even at very low concentrations, causing numerous health problems [11, 12].

Unlike other metals, cadmium (Cd) is widely distributed at low levels in the environment and is not an essential element for humans, animals and plants [13]. Lead (Pb) is also a non-essential, toxic element with no biological functions, that tends to accumulate in animal tissues [14]. Mercury (Hg) and its organic and inorganic compounds may be transferred in sediments by mutilation in the presence of

microorganisms, with the formation of a toxic final product, methylmercury, able to penetrate the food chain and to bioaccumulate in the aquatic organisms [15, 16]. Copper (Cu) is an essential micronutrient necessary for growth and metabolism of all living organisms including fish, however at high concentrations it becomes one of the most toxic elements. Among its toxicity effects are damage to gills and necrosis to liver, growth depression [17]. Chromium (Cr) is also an essential element for organisms, with the trivalent Cr having an essential role in glucidic metabolism. As regards the hexavalent Cr, it is a toxic industrial pollutant and has been classified as carcinogen possessing mutagenic and teratogenic properties [18]. Zinc (Zn) is indispensable for growth and development of microorganisms, plants and animals, however excess levels may become toxic [19].

Uncontrolled development of constructions in urban areas, the lack of proper infrastructure and discharge of untreated municipal wastewaters is placing an unprecedented pressure on water quality and demand [20, 21]. In this context, the study aimed to assess bioaccumulation factors in relation to water (BAF) and sediment (BASF) for the potential toxic elements (PTE<sub>s</sub>) such as Cd, Pb, Hg, Cu, Cr, Ni and Zn from different fish species captured from aquatic environments located in the crowded areas from the southern part of Romania.

## 2. Materials and Methods

### 2.1. Sample Source

To achieve the study objective, fish, water and sediment, two sampling campaigns was organized in July 2016 and June 2018 on the Arges River and Colentina River (Mogosoiaia, Herastrau and Pantelimon Lakes). Table 2 shows details about the sampling campaigns.

**Table 1.** Sampling site locations.

	Notation of sampling site locations		Campaign/Year
<b>P1</b>	Arges River	Hotarele (village area)	II - 2018
<b>P2</b>		Mogosoiaia Lake	
<b>P3</b>	Colentina River	Herastrau Lake	I - 2016
<b>P4</b>		Pantelimon Lake	

The water samples were collected in polyethylene recipients (3 L) from approximately 30 cm below water surface and were kept at 4 °C during their transport to the laboratory, according to the in force standards [22, 23, 24]. Sediment samples were collected according to sampling procedure of the current standards [25]. For achieving the aim of the study, fish specimens belonging to six species (*Alburnus alburnus*, *Carassius gibelio*, *Scardinius erythrophthalmus*, *Ameiurus nebulosus*, *Perca fluviatilis*, *Lepomis gibbosus*) were purchased from local fishermen. All samples were kept at 4 °C during their transport to the laboratory.

### 2.2. Procedure

The water samples was acidified to prevent hydrolysis of the metals, by adding nitric acid (65%) in it [26]. Fish samples were gutted using a ceramic knife, skinless fillets and bone from the dorsal musculature were taken for analysis. Fish muscle tissue was dried to about 60 °C in the laboratory oven, milled to homogeneity in a non-metallic mortar. Microwave digestion system equipped with a temperature and pressure control was used to digest the fish samples. Approximately 0.5 g of sample were weighed and digested using a mixture of 7 mL of 65 % nitric acid (Suprapur) and 3 mL of 30% hydrogen peroxide (Suprapur) using the microwave digestion system.

The sediments samples were air dried at room temperature. After drying, in order to obtain representative samples, they were milled, sieved and to bring the sediment samples to the solution, mineralization of about 0.5 g of the sample from the fraction <63 μm has been performed in the presence of aqua regia.

### 2.3. Equipments and Materials

Samples were analysed using a High-Resolution Continuum source atomic absorption spectrometer - HRCSAAS ContrAA 700 (Analytikjena) to determine the following PTEs: Cd, Pb, Hg, Cu, Cr, Ni and Zn. The quality of the results was compared with reference materials (BB422-fish muscle certified reference material for trace metals; HC 73962555-ICP multi-element standard solution IV; LGC 6187-river sediment standard reference material). Analytical results of the quality control samples indicated a satisfactory performance of heavy metal detection within the range of certified values (90%–110%). All reagents used in this study were of analytical grade and all glassware used was washed with nitric acid 1.5 mol/L and rinsed in double distilled water and deionized water before use.

### 3. Results and Discussion

Within this study, the bioaccumulation of the potentially toxic elements in fish was quantified by means of bioaccumulation factor (BF) defined as the ratio between the concentration of the element in organism and the corresponding concentration in water and, respectively the sediments [27, 28, 29, 30]. The bioavailability of metals is one of the key factors that determine their accumulation in the aquatic organisms and it depends mainly on the physicochemical factors of both water and sediments including the water pH, the redox potential, temperature, hardness and total organic content [31]. Sediments provide nutrients and habitat for fish and benthos and thus favour the bioaccumulation of heavy metals from water and sediments in the aquatic organisms [31]. BF was calculated to estimate PTEs accumulation behavior and this can be used to describe the transfer of these elements from water and sediments to the fish tissue. If the  $BF > 1$ , then the fish samples may be regarded as accumulators, a  $BF = 1$  indicates no influence and if the  $BF < 1$ , then fish samples may be regarded as being excluders [32].

$$BAF = \frac{C_b}{C_a} \quad (1)$$

$$BSAF = \frac{C_b}{C_s} \quad (2)$$

where:

BAF = the bioaccumulation factor biota – water [L/Kg];

BSAF = the bioaccumulation factor biota – sediments (adimensionally);

$C_b$  = the concentration of metal in the biota [mg/Kg];

$C_a$  = the concentration of metal in water [ $\mu\text{g/L}$ ];

$C_s$  = the concentration of metal in sediments [mg/Kg].

For the investigated fish species, the bioaccumulation factors in biota reported to water and sediments were computed (Table 2). In general, the bioaccumulation factor biota - water (BAF) showed values higher than 1 for most of the species captured from the three lakes located on the Colentina River, except for: *Alburnus alburnus* - P2 for  $BAF_{Cd}$ , *Alburnus alburnus* - P4 for  $BAF_{Cu}$ ,  $BAF_{Ni}$ ,  $BAF_{Cd}$ ,  $BAF_{Pb}$  and *Leopomis gibbous* - P2 for  $BAF_{Pb}$  which showed BAFs values less than 1. The BAFs for the fish species captured from the P1 were below 1.

As regards the bioaccumulation factor biota - sediments (BSAF), values higher than 1 were obtained for:  $BAF_{Ni}$  (*Scardinius erythrophthalmus* - P3 and *Perca fluviatilis* - P4)  $BAF_{Pb}$  (*Carassius gibelio* - P1) and  $BAF_{Zn}$  (*Alburnus alburnus* and *Scardinius erythrophthalmus* - P2 and *Carassius gibelio* - P4).

**Table 2.** The bioaccumulation factors (BAF/BSAF) of heavy metals from water and sediments to biota.

Sampling location	Fish species	BAF						BSAF						
		Cu	Ni	Cd	Pb	Cr	Zn	Cu	Ni	Cd	Pb	Cr	Zn	Hg
<b>P1</b>	<i>Alburnus alburnus</i>	nd	nd			nd	nd	nd	nd			nd	nd	
	<i>Carassius gibelio</i>	nd	nd			nd	nd	nd	nd			nd	nd	
<b>P2</b>	<i>Alburnus alburnus</i>													
	<i>Ameiurus nebulosus</i>													
	<i>Scardinius erythrophthalmus</i>													
	<i>Lepomis gibbosus</i>													
<b>P3</b>	<i>Scardinius erythrophthalmus</i>													
	<i>Alburnus alburnus</i>													
<b>P4</b>	<i>Perca fluviatillis</i>													
	<i>Carassius gibelio</i>													

nd = nedetermined

■ BAF/BASF >1

■ BAF/BASF <1

Based on the computed values of the bioaccumulation factor, the order in which the bioaccumulation of metals from water and sediments varies was obtained and it is shown in table 3.

**Table 3.** Comparative analysis of the bioaccumulation factors.

Sampling location	Fish species	BAF	BSAF
<b>P1</b>	<i>Alburnus alburnus</i>	Cd>Pb	Hg>Cd>Pb
	<i>Carassius gibelio</i>	Pb>Cd	Pb>Hg>Cd
<b>P2</b>	<i>Alburnus alburnus</i>	Zn>Cr>Pb>Ni>Cu=Cd	Zn>Hg>Cr>Pb>Cd>Cu=Ni
	<i>Ameiurus nebulosus</i>	Zn>Pb>Cr>Cu>Ni>Cd	Hg>Zn>Pb>Cd=Cr=Cu>Ni
	<i>Scardinius erythrophthalmus</i>	Zn>Cr>Pb=Cu=Ni>Cd	Zn>Hg>Cr=Pb>Cd=Cu=Ni
	<i>Lepomis gibbosus</i>	Zn>Cr>Pb>Ni>Cu>Cd	Hg>Zn>Pb>Cr>Cd=Ni>Cu
	<i>Scardinius erythrophthalmus</i>	Ni>Zn>Cr>Cd>Cu>Pb	Ni>Cd>Zn>Hg>Cr>Cu>Pb
<b>P4</b>	<i>Alburnus alburnus</i>	Zn>Cr>Cu>Ni=Cd>Pb	Ni>Cd>Zn>Hg>Cr>Cu>Pb
	<i>Perca fluviatillis</i>	Cr>Ni>Zn>Cd>Cu>Pb	Ni>Cr>Zn>Cd>Hg>Cu>Pb
	<i>Carassius gibelio</i>	Zn>Cr>Cd>Ni=Cu>Pb	Zn>Cd>Hg>Cu=Ni>Cr=Pb

As it may be observed from table 3, the fish from P2 and P3 showed the tendency to bioaccumulate in muscle tissue mainly Zn, Cr and Pb from water and Zn and Hg from sediments.

The European perch (*Scardinius erythrophthalmus*) captured from P3 had the tendency to accumulate Ni and Zn from water and Ni and Cd from sediments.

As regards the fish from the P4, the bleak (*Alburnus alburnus*) shows the tendency to bioaccumulate Ni and Zn from water and Ni and Cd from sediments; the rudd (*Perca fluviatillis*) showed similar tendency for Cr, Ni and Zn from water and sediments, and *Carassius gibelio* showed the tendency to bioaccumulate Zn, Cr and Cd from water and Zn, Cd and Hg from sediments.

#### 4. Conclusions

Contamination with potentially toxic elements such as heavy metals at the aquatic ecosystems is a major problem as they accumulate in the trophic chains. The analysis of BAF showed that values higher than 1 were highlighted for most of the fish species captured from the Colentina River. As regards the BASF, values higher than 1 were obtained for  $BASF_{Pb}$  (*Carassius gibelio* - Arges River),  $BASF_{Ni}$  (*Scardinius erythrophthalmus* - Herastaru L. and *Perca fluviatilis* - Pantelimon L.),  $BASF_{Cr}$  (*Perca fluviatilis* - Pantelimon L.) and  $BASF_{Zn}$  (*Alburnus alburnus* and *Scardinius erythrophthalmus* - Mogosoaia L. and *Carassius gibelio* - Pantelimon L.).

A high bioaccumulation potential does not necessarily imply a high toxicity potential, the situation being different depending on each element. Monitoring contamination with potentially toxic elements of the aquatic environment by assessing the bioaccumulation in the muscle tissue of fish is a useful tool in assessing the quality of aquatic ecosystems.

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