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Determination of heavy metals in macrozoobenthos from the rivers Tisza and Szamos by total reflection X-ray fluorescence spectrometry ☆

S. Woelfl [a,*], M. Mages [b], M. Óvári [c], W. Geller [b]

[a] *Universidad Austral de Chile, Instituto de Zoología, Casilla 567, Valdivia, Chile*
[b] *Helmhotz Centre for Environmental Research (UFZ), Department of River Ecology, Brückstrasse 3a, D-39114, Magdeburg, Germany*
[c] *Óvári, M. Eötvös University, Department of Organic Chemistry, H-1117, Budapest, Pázmány P. stny. 1/a, Hungary*

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Abstract

In 2000, accidents in the Romanian mining industry in key catchment areas led to heavy metal contamination of the Hungarian rivers Tisza and Szamos resulting in substantial heavy metal loads in several sediments of the upper river basins. This enhanced metal content might have been bioaccumulated in benthic organisms during the following years. Therefore, the aim of this study was to test, whether the zoobenthic fauna showed an enhanced metal content 3 years after the industrial accident. Macrozoobenthic insect larvae (chironomids) were sampled 100 m below and above the confluent site of the rivers Tisza and Szamos during summer 2003 and for comparison purpose also in the river Maros, a tributary of the Tisza river, during 2005. In order to determine their heavy metal content, single specimens were prepared and analysed by Total Reflection X-ray Fluorescence Spectrometry (TRXF) according to the modified *dry method*. Fe was much lower and Mn and Zn much higher concentrated in benthos from the more contaminated Szamos river compared to the Tisza and Maros rivers. In this sense, the benthic organisms reflected very well the enhanced metal concentrations in the contaminated rivers being suitable as bioindicators of metal contamination. However, the sediment bioaccumulation factor was low at all sampling sites indicating a low bioavailability of trace metals for benthic organisms.

Keywords: Trace element analysis; Heavy metals; Zoobenthos; Total Reflection X-ray Fluorescence; Bioaccumulation

1. Introduction

Elemental analysis of different freshwater biota is an important task in today's environmental sciences [1]. In this sense, macrozoobenthos (e.g. insect larvae) are increasingly used for the biomonitoring of metal load of aquatic systems and of surveying temporal trends of metal pollution [2,3]. The macrozoobenthic organisms are very suitable for the assessment of contaminated sediments in freshwater ecosystems, because (1) they are important within the food web, and they are always present in aquatic environments, (2) they accumulate many organic and inorganic contaminants, and (3) they are easy to collect [4].

In 2000, accidents in the Romanian mining industry in key catchment areas led to heavy metal contamination of the Hungarian rivers Tisza and Szamos [5]. Investigations of water and sediment at selected sampling points from a longitudinal profile in 2000 showed substantial heavy metal loads (e.g. Cd, Pb, Cu and Zn) in several sediments of the Szamos as well as the Tisza rivers [5,6]. This enhanced metal content might have been bioaccumulated in benthic organisms during the following years in a similar way as already was shown for natural fish and periphyton populations [7,8]. Therefore, the aim of this study was to test, whether the benthic fauna showed an enhanced metal content 3 years after the industrial accident.

2. Methods and materials

2.1. Sampling and preparation procedure

The insect larvae Chironomus sp. (Diptera: Chironomidae) were sampled 100 m below the confluence of the rivers Tisza

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* Corresponding author. Fax: +56 63 221315.
E-mail address: swoelfl@uach.cl (S. Woelfl).

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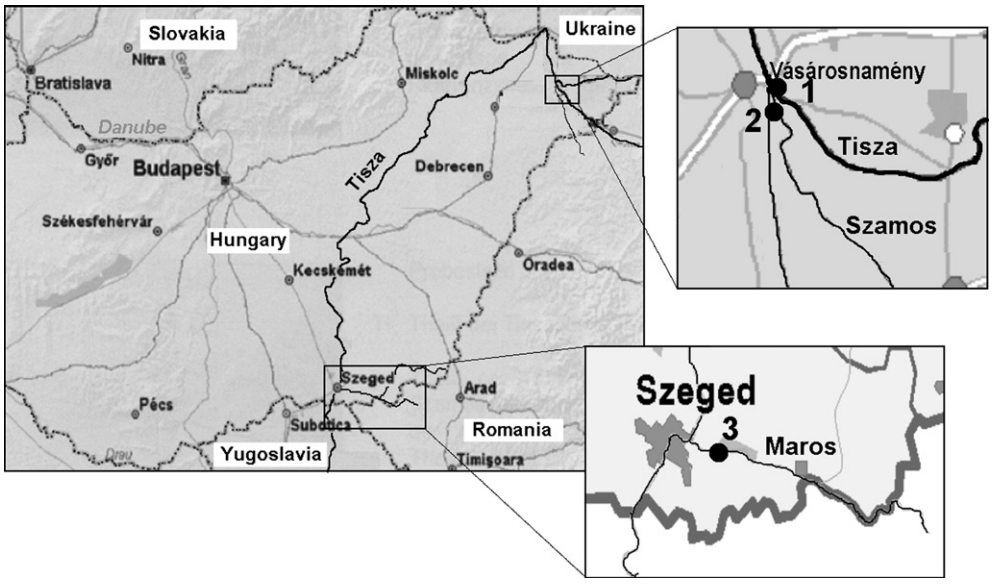

Fig. 1. Sampling sites: 1 = river Tisza, 2 = river Szamos, 3 = river Maros.

and Szamos and 100 m above the confluent site during summer 2003. For comparison purposes during July 2005 benthos was also sampled in the river Maros which is a tributary of the Tisza river near southern Hungarian border (Fig. 1). The animals were stored in polypropylene tubes, washed three times with 0.2 μm prefiltered river water and twice with pure water and finally frozen in liquid nitrogen [9,10].

After freeze drying, individual specimens were selected and the dry weight (DW) was determined using an ultra fine balance (Sartorius Ultramicro SE2, sensitivity 0.1 μg). After weighing, single specimens with a dry weight > 50 μg were put into PTFE vials (7 ml, Savillex, Canada), and 500 μl 65% HNO_3 (Suprapure grade, Merck, Germany) and 10 μl H_2O_2 (Suprapure grade, Merck, Germany) were added as digestion solution. Gallium as internal standard (100 ng) was also added directly into the PTFE vials. The vials were than tightly closed with screw caps. The digestion took 3 h at 120 °C on a hot plate. Finally, the element mass fractions were determined by TXRF on 10 μl subsamples.

In parallel, the dissolved and total element content of the surface river water and of the 0–3 cm sediment surface layer were determined according to standard procedures [6,8,10,11]. All water samples were taken directly with the sampling bottles (volume of 250 ml). To discriminate the dissolved and the particulate element concentration 50 ml of the samples were filtered through 0.45 μm syringe filters (Minisart, non-pyrogenic), stabilized with HNO_3 and stored in polypropylene capes. At the laboratory 1 ml of the filtered sample was mixed with an internal standard (100 μg L^{-1} Gallium), homogenized and analyzed by TXRF. The non-filtered samples were digested in a microwave digestion system (Mars 5, CEM, USA). For that a subsample was put into the vessels and hydrogen peroxide and nitric acid were added. The digestion took 20 min at 170 °C and 10 bar. The final preparation and measurement procedure was the same as for the dissolved samples.

The sediment samples were collected with an Ekman grab. The wet samples were placed in polyethylene bags, frozen in liquid nitrogen and afterwards freeze dried at −5 °C for 48 h (Alpha 1, Christ, Germany). The dried samples were subsequently homogenized in an agate mortar and sieved through a 0.63 mm plastic sieve (Frietsch, Idar-Oberstein, Germany). Finally, the samples were digested with aqua regia (microwave Mars 5, CEM, USA) and the metal content was determined by inductively coupled plasma mass spectrometry (Agilent 7500, Agilent Technologies, Waldbronn, Germany).

Quality assurance followed standard methods using BCR 414 plankton certified reference material and BCR 701 freshwater sediment reference material [8,12].

Table 1
TXRF analysis of reference material BCR 414 (European Community Bureau reference material 414, plankton with >98% of the cladoceran *Daphnia magna*; sample dry weight: 10–30 μg; $n=8$)

Element	Reference values of CRM 414		Relative S.D. (%)	TXRF: samples		Relative S.D. (%)	R_r
	Mean mass fraction (μg g^{-1} DW)	S.D. (μg g^{-1} DW)		Mean mass fraction (μg g^{-1} DW)	S.D. (μg g^{-1} DW)		(%)
Ca	65,000[c]	2000	3.1	64,000	1520	9.7	99
Cr	23.8[a]	1.2	5.0	20.8	3.3	18.7	97
Mn	299[a]	12	4.0	260	1.9	10.8	86
Fe	1850[b]	190	10.3	1680	19.5	16.8	91
Ni	18.8[a]	0.8	4.3	20.1	2.5	13.9	107
Cu	29.5[a]	1.3	4.4	27.4	0.3	13.8	93
Zn	112[a]	3	2.7	100	3.2	15.1	89
As	6.82	0.28	4.1	<5		13.7	
Rb	11.6	0.2	1.7	9.0	1.1	14.9	78
Sr	261[a]	25	9.6	205	2.6	10.6	79
Pb	3.97	0.19	4.8	<8		45.2	

R_r = recovery rate = ratio between measured and reference value, S.D. = standard deviation of the mean.
[a]certified, [b]indicative, [c]informative value.