Heavy metals and REE in bottom sediments and dreissenids of the Rybinsk reservoir

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The Rybinsk reservoir is the largest artificial water body in Europe and water supply of fresh water for Central Russia. This reservoir is affected by largest in Europe metallurgical plant situated in its northeast part in the town of Cherepovets. To assess the possible impact of this plant on the abiotic and biotic components of the reservoir ecosystem sediments and mollusk Dreissena polymorpha samples were collected in different compartments of the reservoir in 2005. A total of 33 elements including some heavy metals were determined in sediments, zebra mussel shells and soft tissues by means of NAA. High concentrations of some heavy metals were revealed in sediments, shells and soft tissues of zebra mussel in the close vicinity of metallurgical plant.

1 Introduction

Heavy metals from industrial and urban discharges are deposited in different components of the aquatic ecosystem, such as water, sediments, soils and biota. All heavy metals are potentially harmful to most organisms at some level of exposure and absorption. Under certain environmental conditions, heavy metals may accumulate to a toxic concentration, and cause ecological damage. During the last decades mining and industrial production of rare earth elements increased drastically, which led to enlarged input of these elements into the environment, primarily water bodies.

The Rybinsk Reservoir, the largest artificial water body in Europe, is the main source of drinking water for the towns located along its cost-line. The greatest potential risk of environmental contamination to this man-made lake is posed by the town of Cherepovets with its steel producing plant, largest in Europe.

Bottom sediments represent a sink for suspended matter including organic and inorganic pollutants in the freshwater ecosystem. They are frequently used for determining the contamination level of the water ecosystem as well as for assessing risk of potential remobilization of pollutants into the ecosystem.

For biomonitoring purposes in the Rybinsk reservoir two species of bivalve mollusk (*Dreissena polymorpha* and *D. Bugensis)* were used. These mollusks are characterized by their sedentary life style (which unsure representativeness towards a given water body or its part), good filtration capacity and resistance to acute toxicity of pollutants (Klerks et al., 1997; Pavlov, Frontasyeva, 2005). Although dreissenids are considered as reliable bioindicators by many authors (Bervoets et. al., 2001), some investigators debate this fact (Wiesner et al., 2001). The latter study revealed that the mean concentrations of some heavy metals in soft tissues of the mollusks were 9, and in some cases 170 times lower than those in seston and bottom sediments. The authors suggest that dreissenids have great ability to detoxicate heavy metals, which diminishes their bioindicating importance. Bottom sediments in this context can serve as more trustworthy and simple indicators.

The aim of the study is first of all to determine chemical elements, including heavy metals and rare earth elements in tissues of the dreissenids and sediments in different compartments of the reservoir. This can make it possible to assess the contamination level of the reservoir as well as to evaluate the possibility of using dreissenids for monitoring fresh water ecosystems.

2 Methods and materials

Sampling was carried out from research ships of the Institute of Inland Water Biology in 2005-2006 at different areas of the reservoir (Fig. 1). Sediment samples were collected using bottom sampler and dreissenids – using bottom drag.

Mollusk samples were frozen at -18^{o}C for further sample preparation. Mollusks were dissected into a soft part and a shell being preserved separately.

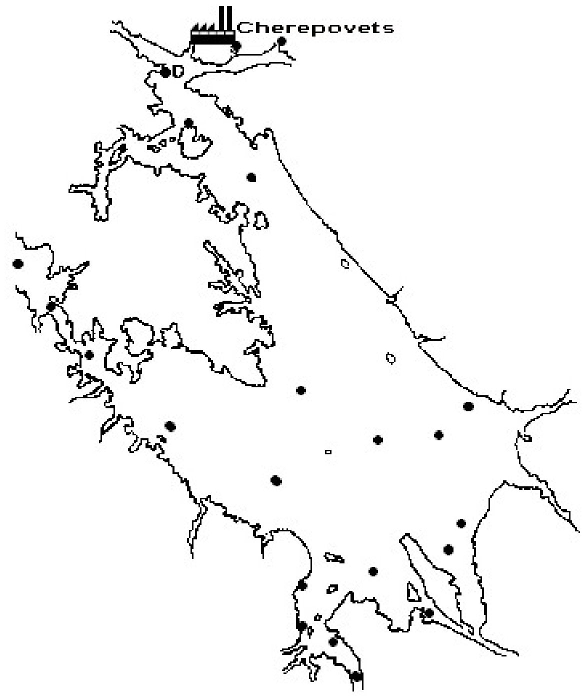

Fig. 1. Study area with sampling sites

Both sediment and mollusk specimens were dried at 40 C^{0} and then homogenized with the help of mortar and pastel. The specimens were packed into aluminum cups and polyethylene bags for long and short irradiation, respectively, and analyzed for elemental composition using instrumental epithermal neutron activation analysis (ENAA) at the IBR-2 reactor (JINR, Dubna).

The statistical analyses were performed using the software package Statistica 6.0 for Windows (Statsoft). P values <0.05 were considered statistically significant.

3 Results and discussions

ENAA enabled identification of 31 elements in bottom sediments and zebra mussels.

Concentrations of such elements like scandium, vanadium, manganese, barium, lanthanum, samarium, hafnium, tantalum in the soft tissues of dreissenids differ insignificantly from those in the shell. La, Sm, Hf, Ta content in the soft tissues is no more than twice as much as their shell content, while Mg and Ba concentrations are a little higher in the shell. At the same time cobalt, nickel, zinc, selenium and bromine concentrations in the soft tissues are 1-2 orders of magnitude higher than those in the shell, while strontium and calcium contents in the shell substantially exceed those in the soft tissues (Fig. 2 and 3). The last observed phenomenon is explained by the fact that calcium is a bulk material for a mineral matrix of the shell and strontium actively replaces calcium in this tissue.

Bottom sediments concentrations for most elements are one order of magnitude higher than those in the soft tissues of the mollusks. The reverse pattern is observed for Ca, Co, Ni and Zn, whose concentrations in the soft tissues differ from those in the sediments insignificantly, while Se and Br concentrations are ten times higher in the soft tissues than in the sediments (Fig. 2 and 3).

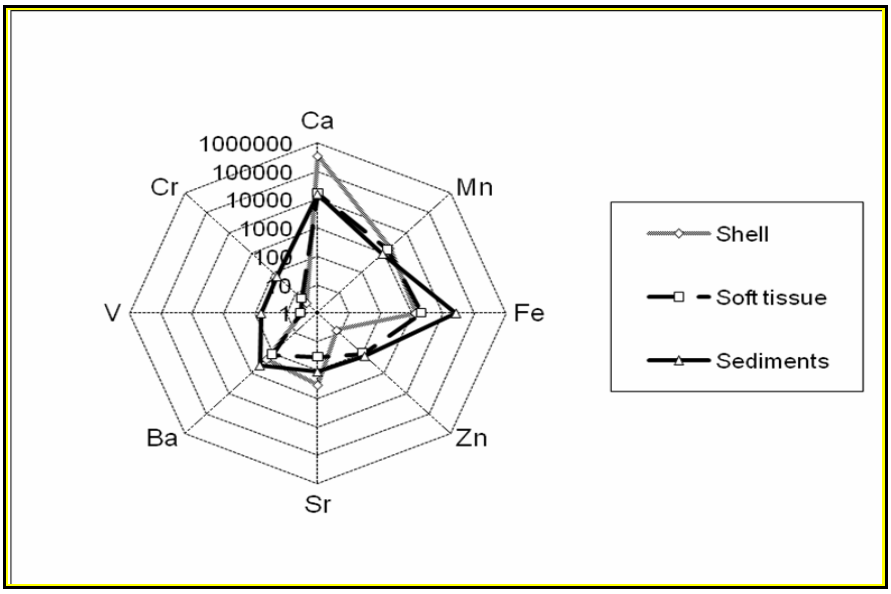

Fig. 2. Concentrations of some elements in the shell, soft tissue of the mollusks and bottom sediments (logarithmic csale)

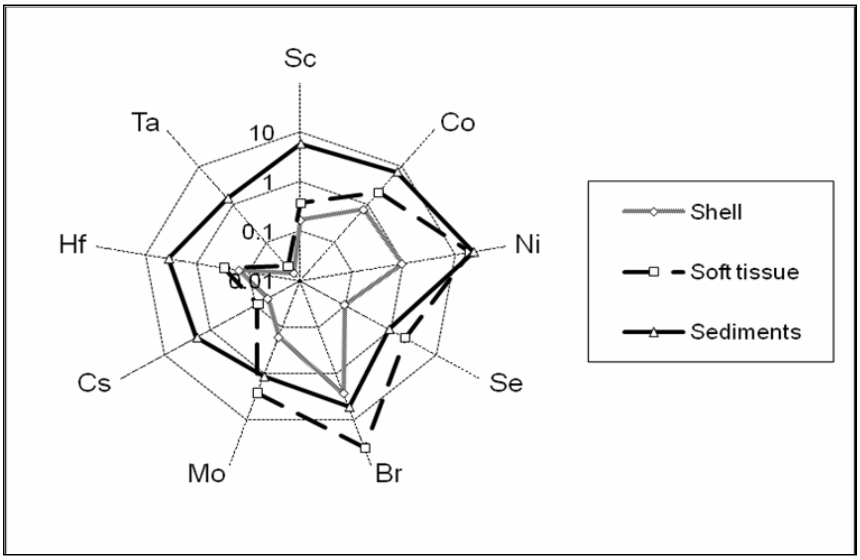

Fig. 3. Concentrations of some elements in the shell, soft tissue of the mollusks and bottom sediments (logarithmic csale)

This means that most elements consumed by the mollusk are not accumulated, but cleared from its body (Wiesner et. al., 2001). Such elemental pattern also demonstrates physiological importance of the above-mentioned elements being not toxicants but essential macro and micro components for the mollusk organism. However, it is well known that under strong anthropogenic contamination microelements can accumulate in an organism in concentrations exceeding their physiological levels. In such conditions the organism cannot control the processes of element consumption and excretion. Thus it may be suggested that the high concentrations of Zn, Co, Ni in the mollusk body are explained by the influence of Cherepovets metallurgical complex.

No significant spatial differences were revealed in shell and soft tissue concentrations for the majority of heavy metals except for zinc and cobalt, whose concentrations in the shell and soft tissues sampled in close vicinity of Cherepovets exceed those from the other sampling points (Fig. 4). Though absolute metal concentrations in soft tissues are higher than those in shells, the latter reflects anthropogenic contamination much better. Trace metal content in the mollusk body depends very much on numerous varying extraneous and intrinsic factors. As the element turnover in the shell is much slower, the shell reflects long-term input trends.

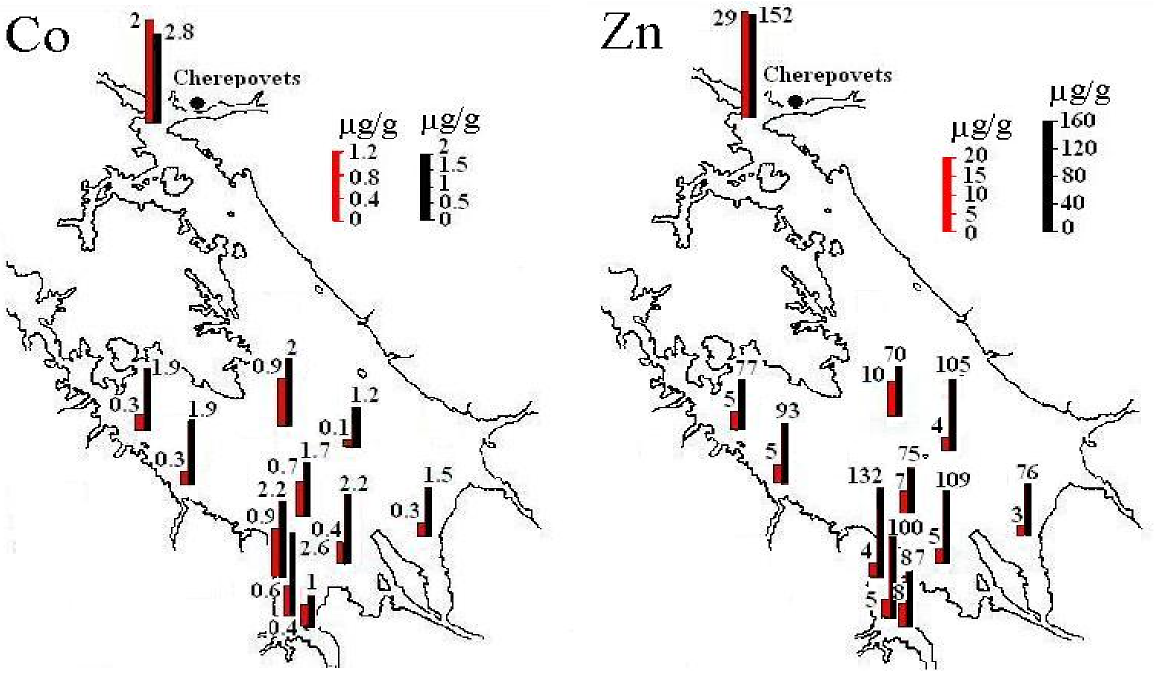

Fig 4. Spatial distribution of Co and Zn in the zebra mussel showing the element content in the soft tissue (left) and in the shell (right)

To establish the spatial distribution of heavy metals in the reservoir sediments cluster analysis was performed (Fig. 5). Clusterization was carried out on the basis of the concentrations of cobalt, nickel, zinc, antimony and tungsten normalized to scandium as a conservative element.

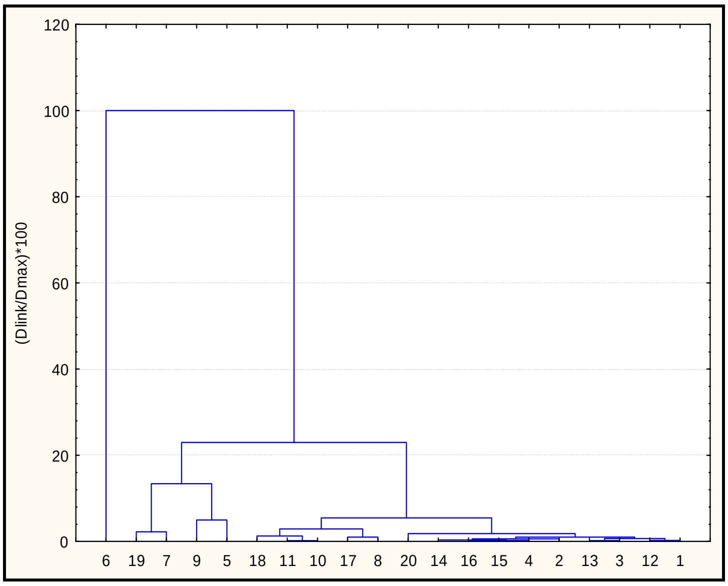

Fig. 5. Cluster analysis of bottom sediments. Hierarhical tree plot

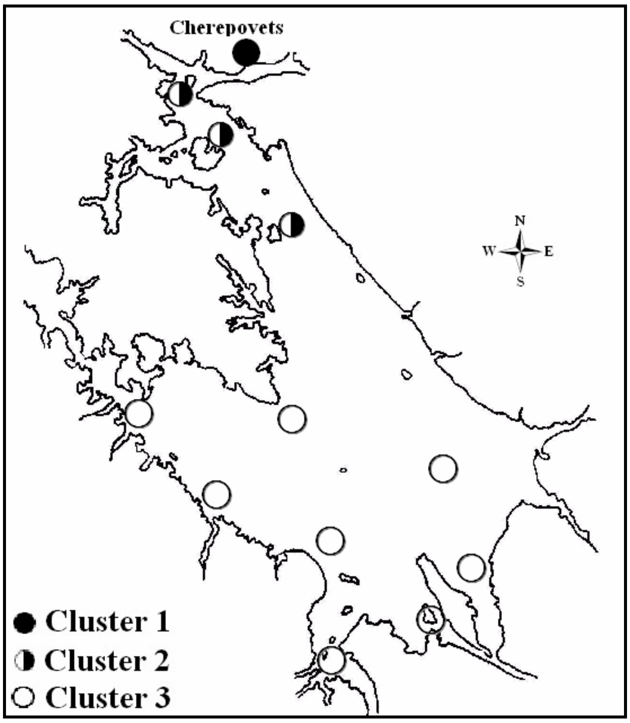

Fig 6. Results of clusterisation for some trace metal concentrations normalized to scandium in sediments from the Rybinsk Reservoir

The first cluster, represented by one sampling point, is characterized by extremely high heavy metal concentrations (Tab. 1). It is located in the Serovka River which is directly exposed to Cherepovets steel producing plant effluents. The second cluster is characterized by moderate heavy metal concentrations and the third cluster corresponds to relatively clean sites (Table 1). As it is evident from the map (Fig. 6), the area of the Cherepovets industrial complex influence is confined to the northeastern part of the reservoir whereas in the central part it is negligible.

Table 1. Mean concentrations of some metals in different sediment cluster (μg/g)

Cluster	Co	Ni	Zn	W	Sb
1	27.0	392.0	1870.0	18.0	6.0
2	10.0	31.0	198.0	3.0	0.8
3	3.2	8.3	27.5	1.0	0.1

4 Conclusions

Our study confirmed that the steel producing complex in Cherepovets exerts negative influence on the reservoir ecosystem. Bottom sediments are reliable objects for monitoring heavy metals and rare earth elements in fresh water ecosystems. Mollusks and dreissenids, in particular, may serve as contamination indicators. Nonetheless, the shell composition reflects permanent source of anthropogenic pollution better than the soft tissue composition does. The feasibility of ENAA for freshwater monitoring has been shown.

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