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THE INFLUENCE OF THE PHYSICAL-CHEMICAL FACTORS ON THE DISTRIBUTION OF HEAVY METALS IN THE DELTA ECOSYSTEMS

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ABSTRACT

Recognized to the influence of micropollutants, heavy metals represented on the ecological status of surface waters, including delta ecosystems, the paper aims to study the impact of environmental factors (temperature, pH, electroconductivitity, total salt content, dissolved oxygen content) the presence of heavy metals in the aquatic ecosystems of the Danube Delta Biosphere Reserve.

In this paper special attention is given to the conservation of sampling and water samples, sediments, plankton and plant material, to the specific methods for the determination of heavy metals and physical-chemical indicators, and to the specific methods for quality assurance of chemical analysis.

It presents a wide range of data on the concentration levels of heavy metals, both in terms of spatial distribution, and bioaccumulation in water samples, sediments, plankton and morphological parts of species that characterize the Reservation of aquatic ecosystems of the Danube Delta Biosphere, in terms of the levels and effects of heavy metal pollution.

KEYWORDS: aquatic ecosystems, heavy metals, environmental factors, sediments

1. Introduction

Heavy metals are part of the persistent pollutants in the environment and is an additional argument for research activities dedicated surveillance levels of heavy metals in the delta ecosystems and assess the effects of these contaminants on aquatic ecosystems are exercised [1, 2].

To assess the influence of physical-chemical factors on the distribution of heavy metals in aquatic ecosystems were taken into account the following physico-chemical parameters: water temperature, water pH, electroconductivity, dissolved oxygen content and total content of salts. The heavy metals have selected cadmium, chromium, nickel, lead, manganese and zinc [3-5].

Increasing water temperature increases metal concentrations in water and sediment. The pH affects the toxicity of heavy metal salts, at a low level (at the upside value of heavy metal toxicity).

The practical value and theoretical significance of the results and conclusions arising from the work on the impact of environmental factors on heavy metals delta ecosystems [6, 7].

The physico-chemical analyses were performed in the chemistry laboratory of the National Institute for Research and Development Danube Delta, a laboratory accredited to EN ISO / IEC 17025: 2005 by the Accreditation Association of Romania, RENAR

2. Experimental procedure

The main topic addressed in this paper is related to the problems and damage to ecosystems due to heavy metals and toxic pollution effects of which are developed both directly and indirectly.

In an aquatic ecosystem metal toxicity can be influenced by variations of abiotic environmental factors such as oxygen, water hardness, pH and transparency.

The temperature, in particular, is an important factor influencing metal toxicity, because most aquatic organisms are poikilothermic.

Although hardness is widely recognized tot affect the aquatic toxicity of metals, the pH is often the biggest effect on metal toxicity.

Some studies show that low levels of pH in water reduce the toxicity of cadmium in seaweed and fish. It has also been suggested that the toxicity is low due to the competition between ions H + and metal cations free transport mechanism.

Other factors that may play a role are: the organic matter, the carbon dioxide, the metabolic activity, the period (time) of halving the metal, the suspended solids, the total organic carbon (TOC), the interaction between pollutants, the stage of development and intraspecific bodies changes of the of metals. The influence of these factors on the distribution of physical-chemical properties of metal, occurs either through direct action on the physiological activity of the body's metabolic processes changing intensity or acting on the microclimate by changing the physico-chemical or pollutant concentration.

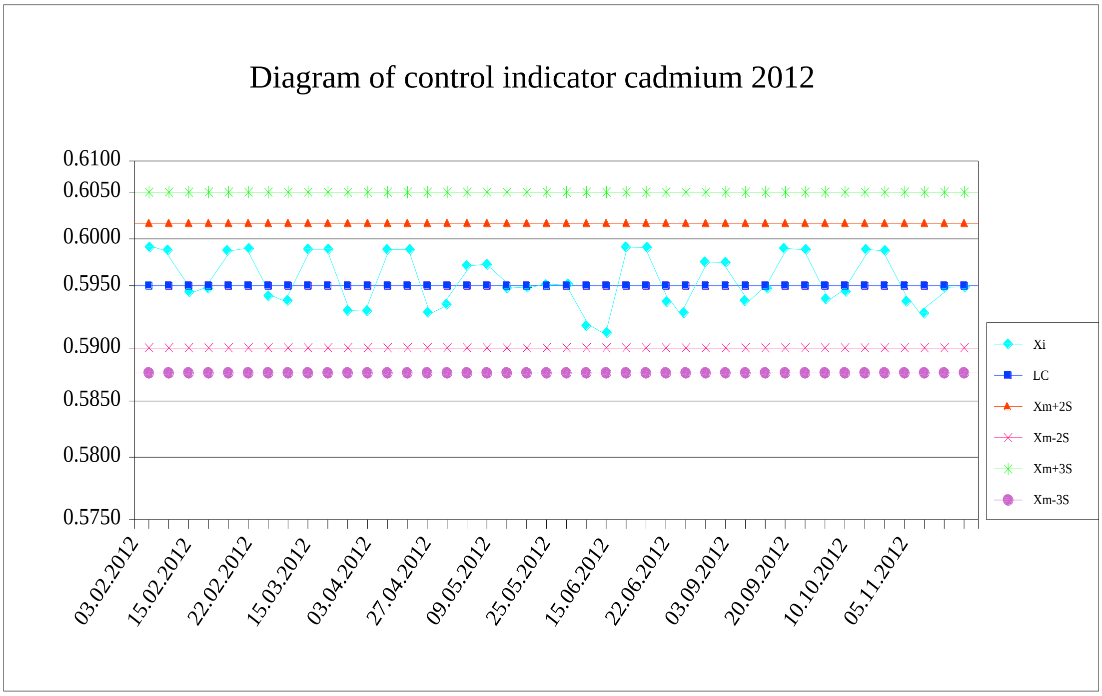

***Fig. 1.** Diagram of control indicator cadmium*

Determining the pollution gradient and the degree of accumulation of inorganic pollutants on substrates (water, mineral, vegetable) and for the purposes set out in this paper, we consider the aquatic complex Razim-Sinoe as representative of the Danube Delta Biosphere Reservation.

The types of samples are: samples of surface water, sediment samples, samples of plant material (Phragmites australis (reed) Typha angustifolia (rush). Water samples were collected quarterly in 2012-2015. Sediment samples were collected annually in 2012-2015. Aquatic vegetation samples were collected quarterly in 2012-2015.

The samples were mineralized in the Anton Paar. Microwave. The step mineralization is performed differently depending on the type of sample, in compliance with applicable standards and recommendations suggested by the Anton Paar oven manufacturer.

The determination of heavy metals by atomic absorption spectrometry. Atomic absorption may be used to determine very low concentrations of ions in solution.

This method is widely applied in biological samples, metallurgical, geological or to determine pollution. Figure 1 represents the diagram of the cadmium control indicator. Values with concentrations in the control charts are determined to be valid measurements, respectively in Xm +/- 2 S, (mean +/- standard deviation of all measurements).

For comparative extraction and analysis tests of the same type of sample, two systems of extraction and analysis were established:

1. Skalar mineralizer and atomic absorption spectrometer VARIAN AA100.
2. Anton Paar microwave oven and mass spectrometer with inductively coupled plasma ICP-MS Elan DRC.

Samples of water, sediment and reed treated by both methods were taken starting from 2014 in aquatic complex Razelm-Sinoe.

3. Result and discussions

In relation to the national quality standards for lake bottom sediment, most of the samples investigated in the period 2012-2015, had levels of manganese and zinc limits. Cadmium was the item that recorded the highest percentage of exceedances of the standard for quality, as shown in Figure 2.

To assess concentrations of metals, we considered the mean concentrations of cadmium determined in 2014 the aquatic complex Razim-Sinoe.

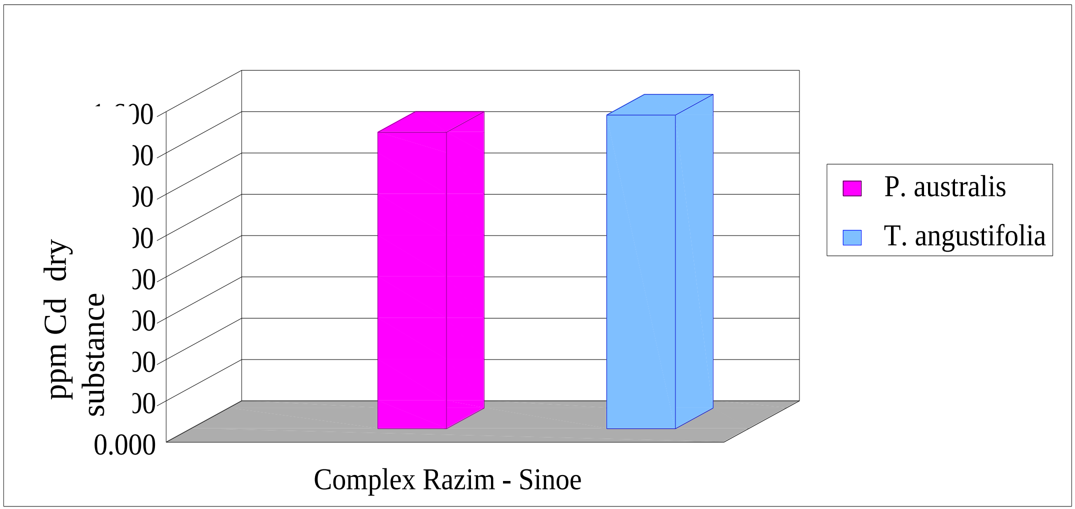

Fig. 2. *Dynamics of cadmium concentrations in samples Phragmites australis and Typha angustifolia, aquatic complex Razim-Sinoe*

Heavy metals enter into cyclic biological aquatic plants through the roots and leaves. They can directly affect plant growth, excessive intake of such elements in plants can also be dangerous for human and animal health. The chemical composition reflects the composition of the soil and plant, the plant surface contamination indicates the presence of contaminants harmful to the environment, in the air. In order to assess the accumulation of heavy metals in parts morphology of the species Phragmites australis, respectively, stalk, rhizomes and leaves, aquatic plant samples were collected at the stage of developing their most complex Razim-Sinoe water in the summer of 2014.

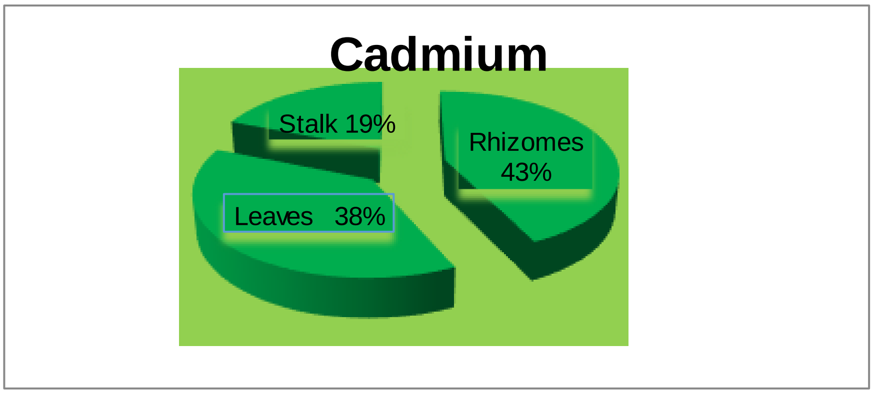

Fig. 3. *Distribution of cadmium in morphological parts Phragmites australis species of aquatic complex Razim-Sinoe*

Analysing the percentage values of the concentrations of heavy metals, we observed that all analysed metals, namely cadmium, chromium, nickel, lead, manganese and zinc, accumulate mostly in the rhizomes samples Phragmites australis (between 37% and 75%), Figure 3.

The results show that Phragmites australis leaves have a capacity to accumulate heavy metals in comparison to the roots, the reason for this is probably short-lived; leaves renew every year, while rhizomes have a longer life, so rhizomes accumulate a larger amount of heavy metals than the leaves.

Table 1. *Values factors bioaccumulation of heavy metals in aquatic vegetation in Razim-Sinoe*

No	Complex aquatic	Vegetation aquatic	BCF Cd L/kg	BCF Cr L/kg	BCF Ni L/kg	BCF Pb L/kg	BCF Mn L/kg	BCF Zn L/kg
1.	Razim-Sinoe	P. australis	120.111	90.501	759.500	2.998	8.490	360.160
		T. angustifolia	123.180	101.622	692.401	5.900	9.998	390.100

To calculate the bioaccumulation factors, the average annual values of concentrations of heavy metals in water and helofile two species, Phragmites australis and Typha angustifolia, were taken into account Table 1.

Analyzing large amounts of bioaccumulation factors obtained for these two species studied macrophytes in the aquatic complex, we conclude that both species have shown great potential for bioaccumulation of heavy metals. In general, the order growth factors bioaccumulation of heavy metals in the two species studied helofile the pool complex is as follows:

BCF Pb <BCF Mn <BCF Cr <BCF Cd <BCF Zn <BCF Ni.

Given this abundance, the distribution of these plants must be seriously taken into consideration.

In terms of the accumulation of heavy metals, the emerged vegetation is different from the submerged vegetation in that the submerged vegetation accumulated more metal than that emerged.

Heavy metals in the two types of vegetation accumulate mostly in submerged vegetation to vegetation emerged, except cadmium and lead that accumulate the same values in both types of aquatic macrophytes, Figure 4.

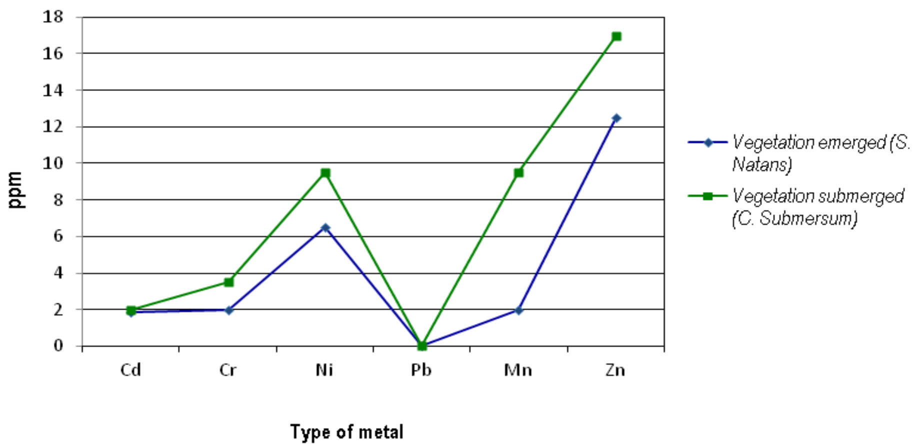

Fig. 4. *Accumulation of heavy metals in vegetation submerged and emerged*

In conclusion, the species of the selected aquatic macrophytes, i.e. Phragmites australis, Typha angustifolia, so take heavy metals from water and sediment (by-rhizome root system, highly developed) in studying aquatic complex.

Investigations on the use of the aquatic macrophytes as bioaccumulate heavy metals as well as their ability to be used in modern techniques of cleaning a water body could be very useful for environmental monitoring and health check of the water body.

To assess the influence of physical-chemical factors on the distribution of heavy metals in aquatic ecosystems were taken into account the following physico-chemical parameters: water temperature, water pH, electroconductivity, dissolved oxygen content and total content of salts. The heavy metals have selected cadmium, chromium, nickel, lead, manganese and zinc. Increasing water temperature increases metal concentrations in water and sediment. pH affects the toxicity of heavy metal salts, at a low level (at the upside of heavy metal toxicity).

Analyzing the correlations between the concentrations of metals in water samples and sediments and physico-chemical properties, we conclude that strict rules are not possible to give both positive and negative values of the indices Pearson, Table 2. This Danube Delta it is an open system that continuously circulates water so that the concentrations of metals in water and sediment undergo permanent changes.

***Table 2**. Pearson correlation index values determined for cadmium in aquatic complex Razim-Sinoe*

	Temperature (°C)	**pH**	**Ec** (µs/cm)	**O_2 disolvation** (mg O_2/L)	**Total salts** (mg/L)	**Cd-Water** (mg/L)
Cd-Water (mg/L)	0.3500	0.1801	0.1158	0.4700	-0.3110	1
Cd-Sedim. (mg/kg)	0.5010	-0.7900	0.8051	0.7998	-0.2612	-0.1161

The Pearson correlation index values were the basis for determining the influence of physical-chemical factors on the distribution of heavy metals in the delta ecosystems.

4. Conclusions

The Chemical analyses were performed by standard methods.

Aquatic macrophytes having the ability to absorb and accumulate large amounts of heavy metals, have an important role as biofilters, bio-accumulate and bio-indicators. Similar trends in the accumulation of heavy metals in the analyzed samples show the universal importance of these aquatic macrophytes in environmental clean living.

The particular capacity of these two species, Phragmites australis and Typha angustifolia, to accumulate heavy metals and that these two macrofite produce a significant amount of organic matter, which increases the potential for accumulation of toxic substances in these two species of macrophytes, make them suitable for use in environmental monitoring of water quality where they live and their role biofilters aquatic ecosystems.

Analyzing the influence of physical-chemical factors (water temperature, water pH, electroconductivity, dissolved oxygen content and total content of salts) on the distribution of heavy metals (cadmium, chromium, nickel, lead, manganese and zinc) in the lake complex Razim-Sinoe found that the influence of these factors acting on the microclimate manifests itself by changing its physico-chemical properties.

The increase of the water temperature increases metal concentrations in water and sediment, with certain exceptions; the pH affects the toxicity of heavy metal salts, at a low level (at the upside of heavy metal toxicity microclimate manifests itself by changing its physico-chemical properties.

Cadmium aquatic vegetation has resulted from a normal distribution.

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