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AQUATIC MACROPHYTES – ROLE IN MONITORING AND REMEDIATION OF NUTRIENTS AND HEAVY METALS

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Abstract:

*Monitoring of the aquatic environment by chemical analyses of dominant aquatic macrophytes from DTD (Danube-Tisza-Danube) canal indicating possible chemical contamination of water and littoral zone were surveyed. Although significant variations of concentrations as related to plant species and surveyed site were found the highest accumulations of nutrients and heavy metals, especially Fe, Mn, Ni, Zn and Cu were obtained in submerged plant *C. demersum* and *P. communis* rhizome. An extremely high P accumulation was obtained in *P. communis* rhizome at site 6 (1.83%) showing that the Krivaja river loads DTD canal complex with remarkable amounts of organic matter. Concentrations of Pb in plant tissues were below $10 \mu\text{g} \cdot \text{g}^{-1}$ and concentrations of Hg in *C. demersum* from the localities nearly Novi Sad were all but $40 \mu\text{g} \cdot \text{g}^{-1}$. The significant increase in Ni, Zn and Cu concentrations in plant tissues from Canal section nearly Vrbas were also recorded indicating a strong human impact reflecting in the presence of wastes discharged by factories and agricultural areas.*

Key words:

Aquatic macrophytes, DTD canal system, nutrients, heavy metals, accumulation

1. INTRODUCTION

Aquatic macrophytes define the ecology of water ecosystems by integrating their role in the primary production (and decomposition) of organic matter, in food chains, light regime (shading), oxygen producing. They influence nutrient, heavy metal, and pollutant cycling, sediment stability, and characteristically determine the eutrophication degree [4, 13]. Monitoring the structure (species abundance, diversity) of macrophytic communities can provide indications of environmental impacts upon aquatic ecosystems [8]. Aquatic macrophytes have no mechanisms regulating the uptake of nutrients and heavy metals. Therefore, their impact upon environment is demonstrated through the process of chemical bioconcentration and excretion while increased nutrient and metal accumulation in their tissues may be the result of increased concentrations in aquatic environment [20]. Biomonitoring of aquatic environments by plants hyperaccumulators of pollutants is based upon the

relationship between concentration of pollutants in plant tissue and in environment. A precise expression of obtained results requires precise definition of factors significantly determining the absorption and accumulation of pollutants in plant tissue like their concentration in environment, temperature, pH, physico-chemical properties of pollutants, solubility, antagonism and synergism of ions taken up, and physiological and biochemical properties of plants (permeability of cell membranes and enzyme activity during absorption) [12, 18]. Rooted submersed and floating, as well as emergent macrophytes exhibit their role in bioaccumulation and filtration mostly in shallow water, namely littoral zone of rivers, canals, and lakes, and in slow streams [3]. An evident nutrient and heavy metal bioconcentration ability significantly enlarges the possibilities of utilization of aquatic plants not only for bioindication, but, also, for the purification of water, substratum, and littoral zone. Due to rapid industrial development and urbanization, with respect to the ecological problems caused by chemical contaminants, pollution reinforces studies of the possibility of utilization of macrophytic vegetation to remediate pollutants from environment, namely water detoxification [5]. Utilization of aquatic plants for a biological clean-up technique in various polluted ecosystems is highly acceptable due to their high biomass production resulting in a high uptake of macronutrients (N, P, K, S) and heavy metals. In addition, the ability of most of aquatic plants to highly tolerate a specific metal is of a great importance [14].

By determining nutrient and heavy metal concentrations in tissues of dominant aquatic macrophytes of certain sites along the DTD canal section Novi Sad – Bezdán undergoing a strong human impact, the aim of the survey was to show the ecological status, namely chemical contamination of water and its littoral zone. The obtained results should also point out the role of macrophytic vegetation in pollutant phytoremediation.

2. MATERIAL AND METHODS

Plant sampling was done by using a randomized block system at 9 sites of the DTD canal section Novi Sad – Bezdán during 2002 summer. Sampling sites were chosen according to plant abundance. For a more accurate result comparison, wherever it was possible, the same plant species from different sites were sampled. In the laboratory, plants were rinsed several times in tap water to remove the adherent periphyton and detritus. After the final rinsing in distilled water, material was dried and prepared for analyses following Standard methods for the examination of water and wastewater APHA [1]. Total N concentration in the dry matter was determined by standard microkjeldahl method [15]. After dry ashing at 450 °C and treatment with HCl, concentrations of heavy metals (Cu, Pb, and Cd) were determined by atomic absorption spectrophotometry (AAS). Concentrations of P, K, Ca, Mg, Na, Cl, Fe, Mn, Zn, Co, Sr, V, and Hg were determined in the Institute of Nuclear Research, Dubna, Russia, in dry plant material by neutron activation analysis (NAA).

Study area: The DTD canal complex includes canals connecting the Danube and the Tisza with Vojvodina canal network totaling 960 km. The Novi Sad – Bezdán section is undergoing a strong human impact due to wastewaters of food industry and fertilizer factories and also oil refinery wastewaters emptying into this section. The chosen sites include Bezdán – canal emptying into the Danube (1), Sombor – surrounding municipal area (2), Prigrevica – arable land (3), Vrbas – upstream (small impact of food industry wastes) (4), Vrbas – downstream (strong impact of food

industry wastewaters (5), Turija – Krivaja river mouth (6), Backi Petrovac (7), Novi Sad – lock (8), and Novi Sad - fertilizer factory and oil refinery (9).

3. RESULTS AND DISCUSSION

Unlike terrestrial species, aquatic plants absorb macro (N, P, K, Ca, Mg, S) and micronutrients (Fe, Mn, Cu, Zn, Mo, Co, B) from water through their leaves while from sediments through roots and rhizomes. Although indispensable for plant life cycle, greater amounts of nutrients, N, P, and K, in particular, provoke a high primary production, namely, eutrophication of aquatic ecosystems. Such a high primary production affects all the remaining physico-chemical water and sediment properties, oxygen content in particular. When present in higher concentrations and as free ions, metals – micronutrients may cause toxification of plants. The content of nutrients and heavy metals in sediments rely upon the rate of organic matter decomposition while an important role in detoxification of bottom and littoral zone belongs to rooted submersed, floating, and emergent species due to their roots and rhizomes taking up significant amounts of these elements in soluble form [16].

Test plants in this investigation were the species *C. demersum* and *P. communis*. Species *C. demersum* occurred in all surveyed sites except site 5 where no individual was found due to an extremely high water and bottom pollution (Tab. 1). The lowest N accumulation (1.83%) was recorded in tissue of this species at site 7 while a rather high N concentration (4.03 and 4.21%) was found at sites 6 and 9, respectively. Concentrations exceeding 3% were recorded at sites 8 and 3. Such N content distribution points out an elevated organic load of site 8 polluted with industrial wastewaters and site 6 where the Krivaja river empties significant amounts of this nutrient from surrounding arable land. The site 3 where also a higher N accumulation in *C. demersum* tissue was recorded confirms that arable land areas are remarkable pollutants of streams.

Table 1. Concentrations of nutrients in *Ceratophyllum demersum* tissue (%)

| Locality | N | P | K | Ca | Mg | Na | Cl |
|----------|-------|-------|------|------|-------|-------|------|
| 1 | 2.791 | 0.062 | 8.05 | 1.03 | 0.589 | 0.642 | 3.18 |
| 2 | 2.847 | 0.044 | 6.93 | 0.55 | 0.430 | 0.633 | 2.18 |
| 3 | 3.182 | 0.618 | 5.36 | 1.48 | 0.603 | 0.745 | 1.97 |
| 4 | 2.205 | 0.034 | 5.74 | 0.69 | 0.572 | 0.735 | 2.13 |
| 6 | 4.033 | 0.445 | 4.90 | 2.49 | 0.768 | 0.712 | 1.63 |
| 7 | 1.828 | 0.084 | 5.44 | 1.40 | 0.729 | 0.689 | 2.53 |
| 8 | 3.098 | 0.053 | 6.88 | 1.17 | 0.603 | 0.843 | 3.06 |
| 9 | 4.214 | 0.317 | 6.89 | 1.63 | 0.536 | 0.868 | 1.83 |

N concentration in the emergent species *P. communis* was lower than in submersed species *C. demersum*, amounting up to 2.46% (emergent part at site 2) (Tab. 2). A specific distribution of this element by organs was evident, namely N content in rhizome was smaller than in emergent part, on the average. The smallest values were recorded at site 6 and 7. Lower N concentrations concurrent with elevated P content in rhizome tissue of the species *P. communis* at site 6 and 7 show an antagonism between these ions. In other words, concentration of Cl^- , K^+ , SO_4^{2-} , and PO_4^{3-} significantly influences N uptake by plants [10]. Concentration ratio of N to P has a great impact upon plant metabolism, sometimes greater than absolute concentrations [2].

Table 2. Concentrations of nutrients in *Phragmites communis* tissue (%)

| Locality | | N | P | K | Ca | Mg | Na | Cl |
|----------|-------|------|-------|------|-------|-------|-------|-------|
| 1 | ag. | 2.20 | 0.021 | 2.84 | 0.195 | 0.076 | 0.045 | 0.919 |
| 2 | ag. | 2.46 | 0.016 | 2.92 | 0.194 | 0.052 | 0.013 | 0.746 |
| 4 | ag. | 1.56 | 0.036 | 2.03 | 0.313 | 0.139 | 0.046 | 0.827 |
| 4 | rhiz. | 1.45 | 0.186 | 1.19 | 0.442 | 0.135 | 0.139 | 0.454 |
| 5 | ag. | 2.27 | 0.027 | 3.02 | 0.228 | 0.110 | 0.161 | 0.788 |
| 5 | rhiz. | 1.94 | 0.043 | 3.00 | 0.067 | 0.020 | 0.298 | 0.993 |
| 6 | ag. | 1.52 | 0.028 | 1.74 | 0.207 | 0.111 | 0.031 | 0.662 |
| 6 | rhiz. | 1.00 | 1.830 | 1.43 | 1.75 | 0.751 | 0.380 | 0.262 |
| 7 | ag. | 1.46 | 0.025 | 1.88 | 0.116 | 0.063 | 0.042 | 0.760 |
| 7 | rhiz. | 0.93 | 0.967 | 1.29 | 0.387 | 0.353 | 0.141 | 0.412 |

ag.– aboveground part

rhiz. - rhizome

Although tissue N concentration is ten times as high as P concentration, diagnostic studies of water ecosystems indicate phosphorus as a limiting nutrient for plant growth. Generally, rooted aquatics satisfy their demands for P from sediments, thus interfering biomonitoring due to nutrient concentration, water depth, light regime, and pH limiting their distribution. Despite that, P is often chosen as a critical element to control nutrient loading rate [19]. Aquatic plants play an important role in taking out excessive P from wastewaters, which cause pollution when present in greater amounts. P amounts taken out rely upon plant species and P from water and substratum while, frequently, a main P source for macrophytes is the surface mud layer [11]. For that reason P accumulation is higher in rhizome than in emergent part and by comparing P content relying upon plant species, one may conclude that submersed species *C. demersum* accumulated few times higher P in its tissue than emergent part of *P. communis*. An extremely high P accumulation was obtained with *P. communis* rhizome at site 6 (1.83%) showing that the Krivaja river loads DTD canal complex with remarkable amounts of organic matter. Also, littoral zone of site 7 showed organic pollution.

Potassium (K) also assembles the group of main macronutrients responsible for plant growth, namely primary production where higher K and N accumulation is reported [6, 7]. Recorded K concentrations at site 1 were extremely high, amounting even up to 8%. Also high K concentrations were recorded at site 8 and 9.

Calcium (Ca) enters aquatic environment primarily from the sediment, because it is mineral that dissolves easily in water. As a result of extensive use of calcium-containing chemicals in agriculture and industry, Ca can be deposited in water environment in excessive levels and influence the growth of aquatic plants and animals. Submersed aquatic macrophytes accumulate higher Ca concentrations than emergent due to the CO₂ exchange in the processes of photosynthesis and dark respiration in aquatic environment concurrent with CaCO₃ deposition on plant surface. This is also confirmed by our results clearly showing the hyperaccumulation ability of submersed species *C. demersum*. Recorded concentrations of Ca in *C. demersum* are significantly lower than those already reported elsewhere [17]. The highest Ca concentrations in both analyzed aquatics were recorded at site 6 – Turija (Tabs. 1 and 2).

Concentrations of Na and Cl in *C. demersum* were also few times as high as those of *P. communis* (Tabs. 1 and 2). Higher concentrations of these two elements frequently defined as useful nutrients, were recorded at Novi Sad and Vrbas sites after wastewater loading.

Plants require trace amounts of some heavy metals, as Fe, Mn, Ni, Zn, Cu, Co, Mo, V and Sr, which are essential micronutrients. Non-essential heavy metals being of particular importance when ecosystem pollution is discussed are Pb, Cd, Hg, and Cr. Excessive levels of heavy metals in environment, and consequently in plant tissues can be detrimental to the development of vegetation. However, many species developed special physiological mechanisms that allow their survival in contaminated conditions. Nutrient uptake and tissue storage of nutrients as well as heavy metals are major issues that have been identified in utilization of macrophytes as clean-up techniques of polluted water ecosystems [9]. Our results showed that purification efficiency and nutrient assimilation depended on plant species. With respect to the investigated heavy metal accumulation, *C. demersum* showed significantly the highest concentration values of almost all the surveyed elements except some elements in *P. communis* rhizome. From the heavy metal concentrations which were measured, Fe showed the highest values followed by Mn, Zn, Cu, Sr, and so on. Sites that might be distinguished due to their highest heavy metal load in aquatic macrophytes are Prigrevica, Turija and Novi Sad – nearby fertilizer factory and oil refinery. Also chemical contamination of littoral zone of these sites was recorded judging by the highest concentrations of metals recorded in rhizome of *P. communis*. In addition, rather high concentrations of mercury (Hg) (11.2 and 36.8 $\mu\text{g} \cdot \text{g}^{-1}$) were found in tissues of *C. demersum* in the surroundings of Novi Sad – lock, fertilizer factory and oil refinery.

High concentrations of heavy metals recorded in plant species of the surveyed sites additionally favor the conclusion that the canal water of these sites was remarkably loaded with the analyzed pollutants, so Turija, Novi Sad and Vrbas may be distinguished as potentially highly threatened regions.

Pb was recorded in *C. demersum* and in rhizome of *P. communis* at all the surveyed sites. Although the recorded concentrations were below 10 $\mu\text{g} \cdot \text{g}^{-1}$, it may be concluded again that the canal water was loaded with the heavy metals.

Our results clearly show that biomonitoring enforcement as the analysis of chemical composition of test – species might be essential for the protection of areas experiencing a strong human impact.

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