Macrophytic nutrient and heavy metal accumulation ability as a parameter of pollutant remediation in aquatic ecosystems

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Introduction

An important physiological property of aquatic vegetation, in general, is the ability to accumulate chemical elements unselectively. Therefore, numerous novel investigations of aquatic ecosystems are associated with the possibility of water purification by employing aquatic vegetation to remediate nutrients, heavy metals, and other pollutants (DeBusk et al., 2001; Scholz, 2003). Very influential is the role of aquatic flora in heavy metal accumulation taking into consideration the fact that heavy metal concentration in macrophytic tissue can be several ten to several thousand times higher than concentration in aquatic environment (Pajević et al., 2002; Samecka-Cymerman et al., 2005). Bioaccumulation ability of metals relies upon plant species, plant organ, and abiotic factors like temperature, pH, and concentration of chemical elements (Matagi et al., 1998). This particular ability and also the fact that macrophytes have powerful production of organic matter in water ecosystems make them suitable for ecological monitoring of water quality (Janauer, 2001; Samecka-Cymerman and Kempers, 2002). When the number of macrophytic species and their spatial and temporal distribution are used to evaluate the status of aquatic ecosystems, it is very important to employ also data on chemical composition of plants as biological parameters since bioconcentration of chemical elements in macrophytic tissue is a reliable parameter for the assessment of the environmental chemical load.

By determining the concentration of nutrients and heavy metals also in tissue of aquatic macrophytes originating from sites undergoing human impact, along the section of the Danube-Tisza-Danube (DTD) canal complex (Banat region), the aim of our study was to show potential chemical contamination of canal water and littoral zone using acquired content of nutrients and heavy metals in tissue of dominant aquatics. The obtained results will serve as the base of promoting the role of macrophytic vegetation in phytoremediation of pollutants, heavy metals and nutrients in particular.

Methods

Randomized block system was employed to take samples at 11 sites characterized by the highest density and cover of the analyzed aquatics. The same species were collected from different sites whenever it was possible to facilitate the comparison of obtained results. Dominant aquatics used as indicator species were *Ceratophyllum demersum* L. and *Phragmites communis* Trin. Certain sites were dominated by *Hydricharis morsus ranae*, *Potamogeton natans*, *Myriophyllum spicatum*, and *Trapa longicarpa* that were also taken as indicators of water status. Plant material

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was classified, rinsed in distilled water, and dried at 105ºC. A standard procedure for water and aquatic plants was used to prepare plant material for chemical analysis (APHA, 1995). Heavy metal concentrations (Mn, Ni, Cu, Pb, and Cd) were determined from stock solution by atomic absorption spectrophotometry.

Study sites: The DTD canal complex totalling 960km covers the canals connecting Danube and Tisza and also the canals in Vojvodina Province. Main canals in the Bačka region and their natural and artificial tributaries were included in the investigation (Figure 1).

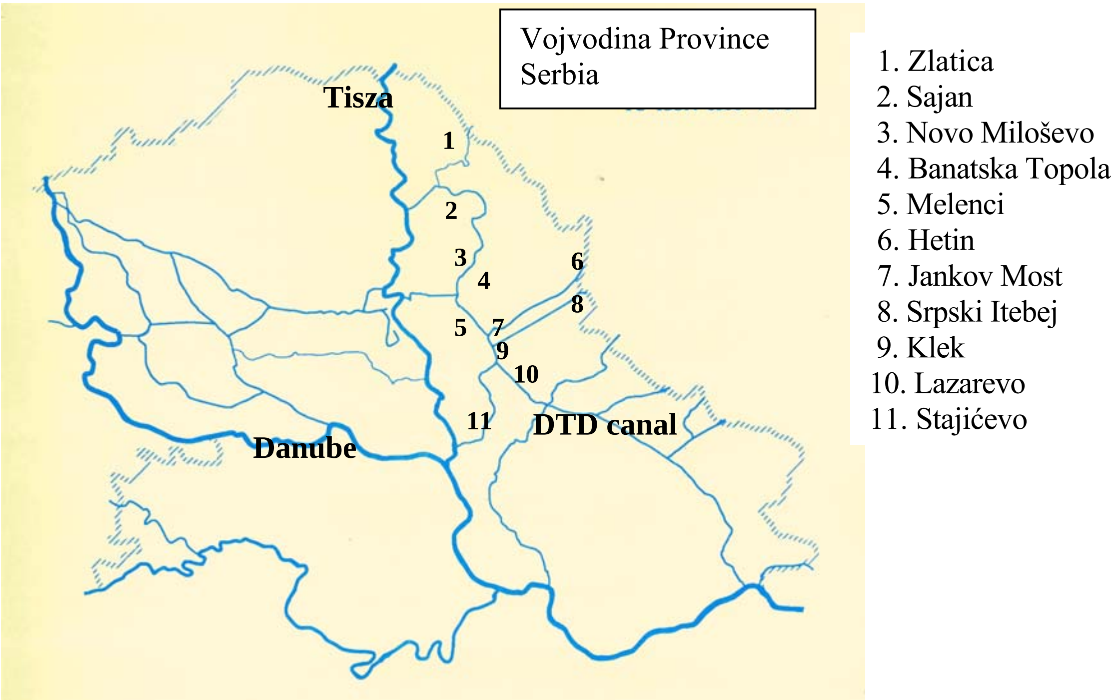

Figure 1. DTD canal complex section and tributaries with investigated sites

1. Zlatica- a stream formed in Rumania undergoing no serious contamination in Vojvodina Province; **2.** Sajan- a site at the Kikinda canal in the very vicinity of the mouth of the Zlatica stream; **3.** Novo Miloševo- a site at the Kikinda canal loaded with industrial and municipal waste waters effluents; **4.** Banatska Topola- a site at a smaller canal empting into the Kikinda canal downstream the city, loaded with industrial effluent; **5.** Melenci- a site at the Banatska Palanka-Novi Bečej canal in the vicinity of the Kikinda canal mouth; **6.** Hetin- a site at the beginning of the Stari Begej stream in Vojvodina Province, loaded with waste waters contamination from Rumania; **7.** Jankov Most- termination of the section of Stari Begej stream, immediately before its empting into the Banatska Palanka-Novi Bečej canal; **8.** Srpski Itebej- a site at the beginning of the Plovni Begej stream in Vojvodina Province, loaded with municipal and industrial waters of city Timişoara in Rumania; **9.** Klek- section termination of Plovni Begej stream, immediately prior to empting into the Banatska Palanka-Novi Bečej canal; **10.** Lazarevo- a site at the Banatska Palanka-Novi Bečej canal, after empting of Stari Begej and Plovni Begej streams; **11.** Stajićevo- a site at the Begej canal, undergoing the influence of municipal and industrial waters of the City of Zrenjanin.

Results and Discussion

Macronutrients in aquatic macrophytes: The species *C. demersum* characterized by the highest accumulation of macronutrients was the test plant of the majority of investigated sites (Table 1).

The highest nitrogen (N) concentration was recorded in *C. demersum* tissue at Novo Miloševo and Klek sites. Concentrations exceeding 3.5% show an extremely high organic load of surrounding water possibly due to empting of municipal and industrial waste waters of the

Kikinda city (Novo Miloševo site) and a high pressure of waste waters coming from Rumania (Klek site).

Table 1. Concentration of macroelements in tissue of *Ceratophyllum demersum*

Site	**Total ash**	**N**	**P**	**K**	**Na**
	%	mg·100g^{-1} d.m. (mg %)			
Zlatica	23.3 **B**	1589.3 **F**	392.3 **A**	3084.0 **F**	746.0 **BC**
Novo Miloševo	20.5 **CD**	3907.0 **A**	394.3 **A**	4750.7 **B**	1058.3 **A**
Banatska Topola	19.6 **D**	2843.3 **D**	394.0 **A**	3834.0 **DE**	679.0 **C**
Melenci	20.4 **CD**	3457.3 **C**	388.3 **A**	5473.0 **A**	1083.3 **A**
Hetin	27.5 **A**	2691.0 **D**	337.7 **B**	3667.0 **E**	740.7 **BC**
Jankov most	20.6 **CD**	2141.3 **E**	395.3 **A**	3667.0 **E**	812.7 **B**
Klek	16.7 **E**	3689.3 **B**	393.3 **A**	4195.0 **CD**	590.0 **D**
Lazarevo	21.4 **C**	3483.0 **C**	385.7 **A**	4362.0 **BC**	729.3 **BC**

Values with the same letter within the same column do not differ significantly at p=0.05

The lowest N-concentration (1.5%) was recorded at the Zlatica site. Lower concentrations of the other analysed nutrients recorded at the above site show a minor threat to this section of the Zlatica stream by macronutrients. A great number of studies dealing with the monitoring of the ecological status of aquatic ecosystems points to phosphorus as a limiting nutrient for plant development (Sondergaard et al., 2001). The concentration ratio N/P has also a great impact upon plant metabolism, sometimes more effective than the absolute concentrations.

Table 2. Concentration of macroelements in rhizome of *Phragmites communis*

Site	**Total ash**	**P**	**K**	**Na**
	%	mg·100g^{-1} d.m. (mg%)		
Zlatica	9.5 **B**	85.3 **F**	1874.7 **A**	127.7 **D**
Sajan	5.4 **DE**	80.3 **FG**	1110.0 **C**	111.3 **D**
Novo Miloševo	7.2 **CD**	87.3 **F**	708 0 **D**	75.0 **E**
Banatska Topola	5.0 **DE**	102.7 **E**	680.3 **D**	111.0 **D**
Melenci	5.8 **CDE**	67.7 **GH**	347.0 **E**	136.0 **D**
Hetin	7.9 **BC**	192.7 **B**	1041.3 **C**	141.7 **D**
Jankov most	7.1 **CD**	63.7 **H**	333.0 **E**	618.0 **A**
Srpski Itebej	6.8 **CD**	218 **A**	1958.0 **A**	150.0 **D**
Klek	21.1 **A**	166.3 **C**	1805.0 **A**	133.0 **D**
Lazarevo	4.6 **E**	105.3 **E**	625.0 **D**	528.7 **B**
Stajićevo	6.8 **CD**	142.0 **D**	1471.7 **B**	216.7 **C**

Values with the same letter within the same column do not differ significantly at p=0.05

Lower concentrations of macronutrients in the rhizome of P. *communis* in comparison to concentrations of the aboveground part of the same species and other floating and submersed macrophytes are in agreement with data obtained from other sites. The role of emergent aquatics in remediation of pollutants is also important due to their rhizomes and roots densely spreading through the littoral zone of aquatic ecosystems.

Variability of P-concentration was site dependent and more expressed in *P. communis* than in *C. demersum* (Tables 1 and 2). Significantly the highest P-accumulation in rhizome of P. *communis* was recorded at Srpski Itebej and Hetin sites, therefore showing organic load of mud due to the deposition of various organic matter (Table 2).

Potassium (K) also belongs to the group of major macronutrients responsible for plant growth, namely primary production, where higher accumulation of K and N is recorded in aboveground part of emergent plants. According to our results, K-concentrations in *C. demersum* were up to ten times higher than those in rhizomes of *P. communis*, relying upon the investigated site. The highest K-concentrations (exceeding 5%) were obtained with *C. demersum* at the Melenci site. An extremely high K- and P-accumulation recorded along almost the whole investigated section of the DTD canal complex points out a great organic load continuously decomposing to stimulate eutrophication. By comparing the obtained values with those of the Provala Lake site where K concentration in *C. demersum* amounted 1700mg% (Pajević et al., 2001), it was quite apparent that the investigated section experiences high nutrient load. Nutrient concentration in the remaining analysed aquatics was lower than in *C. demersum* while higher than in rhizome of *P. communis*. An extremely high accumulation of sodium (Na) was obtained with the floating leaves of aquatic macrophytes. It was confirmed also by our results showing the highest Na-concentration of about 2% (1902.7 mg%) in *Hydrocharis morsus ranae* at the Banatska Topola site.

Heavy metals in aquatic macrophytes: The process of phytoremediation is the most important biotic factor used in outlining the programme of the macrophytic role in purification of aquatic ecosystems (Karpiscak et al., 2001). Our results show that the purification efficacy, uptake and accumulation of nutrients relied upon the analysed plant species. Concentration of the majority of heavy metals, micronutrients in particular, in tissue of *C. demersum* was several tenth times higher than that of rhizome of *P. communis* (Table 3). When metal itself is discussed, the highest accumulation goes for manganese (Mn). Accumulation degree of nickel (Ni) and copper (Cu) relied upon plant species and investigated site.

Table 3. Concentration of heavy metals in rhizome of *Phragmites communis*

Site	**Mn**	**Ni**	**Cu**	**Pb**	**Cd**
	$\mu g \cdot g^{-1}$ d.m.				
Zlatica	63.3 **C**	0.0 **C**	3.1 **BC**	3.2 **B**	0.0 **D**
Sajan	83.7 **B**	0.0 **C**	3.1 **BC**	3.3 **B**	0.3 **BC**
Novo Miloševo	130.0 **A**	1.9 **B**	4.2 **BC**	0.0 **C**	0.3 **BC**
Banatska Topola	125.3 **A**	0.0 **C**	5.1 **BC**	0.0 **C**	0.2 **C**
Melenci	52.7 **C**	1.8 **B**	2.4 **C**	0.0 **C**	0.3 **BC**
Hetin	51.3 **C**	0.0 **C**	9.8 **A**	0.0 **C**	0.3 **BC**
Jankov most	61.7 **C**	0.0 **C**	2.3 **C**	0.0 **C**	0.0 **D**
Srpski Itebej	23.0 **D**	1.2 **B**	8.7 **A**	4.1 **B**	1.1 **A**
Klek	54.7 **C**	4.0 **A**	8.1 **A**	17.7 **A**	0.0 **D**
Lazarevo	49.3 **C**	0.0 **C**	4.0 **BC**	3.0 **B**	0.0 **D**
Stajićevo	21.0 **D**	0.0 **C**	2.7 **C**	3.5 **B**	0.4 **B**

Values with the same letter within the same column do not differ significantly at $p=0.05$

The Klek site exhibited the highest load with heavy metals, namely high concentrations of lead (17.7 $\mu g \cdot g^{-1}$) were recorded in rhizome of *P. communis*. The same site was characterized also by the presence of Pb in the tissue of *C. demersum* (5.9 $\mu g \cdot g^{-1}$). Judging by the presence of Pb in rhizome of *P. communis* at the Srpski Itebej site, the Plovni Begej stream undergoes high pollution events. The same is true of the Lazarevo site. Extremely high Mn concentrations (12561 $\mu g \cdot g^{-1}$) were obtained with *C. demersum* at the Novo Miloševo site. This site is also distinguishable from the remaining analysed localities judging by the highest Mn-accumulation in rhizome of *P. communis* (Table 3). Therefore, the Kikinda canal experiences a high chemical threat of the industrial and municipal wastewaters of the Kikinda city. This statement may be supported by the presence of Pb (7.3 $\mu g \cdot g^{-1}$) and Cd (0.7 $\mu g \cdot g^{-1}$) in the *C. demersum* tissue. Pb-concentrations in the remaining investigated species were below 10 $\mu g \cdot g^{-1}$ while no Cd in tissue of *Hydrocharis morsus ranae* at the Banatska Topola site and *Myriophyllum spicatum* at the Jankov Most site was recorded.

Summary

The content of macronutrients (P and K) and content of heavy metals (Mn, Ni, Cu, Pb, and Cd) in rhizomes of *Phragmites communis* (emergent species), *Hydrocharis morsus ranae*, *Potamogeton natans*, *Myriophyllum spicatum*, and *Trapa longicarpa* (submersed and floating) was analyzed. Sampling was performed at several sites along the Banat section of the DTD canal complex (Vojvodina Province, Serbia). The aim of this study was to use the chemical composition of dominant plant species as indicator of the degree of chemical load of water and littoral zone and to define the role of the macrophytic vegetation in the phytoremediation process, within a comprehensive monitoring of the ecological status of this particular aquatic ecosystem. Significant differences between the analyzed aquatics in chemical composition were evident. In addition, site dependent differences were also found. On the basis of metal concentrations in macrophytes from the Srpski Itebej site (section beginning) and the Klek site (section termination), it can be concluded that the Plovni Begej stream threatened by the wastewaters from Rumania shows even higher chemical load.

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