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CONCENTRATION OF METALS (Fe, Mn, Cu AND Pb) IN SOME AQUATIC MACROPHYTES OF LAKES GRUŽA, GROŠNICA, MEMORIAL PARK-KRAGUJEVAC AND BUBANJ

Snežana Branković, Dragana Pavlović-Muratspahić, Marina Topizović and Jelena Milivojević

Faculty of Science, University of Kragujevac,
P.O.Box 60, 34000 Kragujevac, Republic of Serbia
e-mail: pavsnez@kg.ac.rs; pavsnez@yahoo.co.uk

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ABSTRACT. The results of research based on the biological-chemical approach to the problem of heavy metals (Fe, Mn, Cu and Pb) in some aquatic macrophytes sampled in the Kragujevac lakes Gruža, Grošnica, Šumarice and Bubanj are presented in this paper. The results obtained by comparing examined metals showed that in the raw water of all localities, the greatest concentrations had Fe. The concentrations of the mentioned metals in the mud fall in the next order: Mn, Fe, Pb and Cu. In the mud, there were higher concentrations of all examined metals in relation to the raw water. The concentrations of the examined metals in aquatic macrophytes depended on plant species, plant organs and investigated locality. Results of this study give an instant insight into the current ecology of the researched lakes and represent the basis for future monitoring, and systematic following of state of these water ecosystems in accordance with the ecological principle of "sustainable use".

Key words: concentration of heavy metals (Fe, Mn, Cu and Pb), aquatic macrophytes, Kragujevac lakes

INTRODUCTION

Water, with its physical and chemical characteristics, has high importance for living world, both, in physiological and ecological manner for many forms of life (STEVANOVIĆ *et al*., 2003).

The hydrophytes represent special ecological group of plants, which live in aquatic ecosystems. They are divided in relation to their size on microphytes and macrophytes. The group of macrophytes includes numerous vascular plants, seaweeds *Charales*, macro weeds *Cladophora*, peat mosses and ferns (JANAUER, 2001).

Water macrophytes populating water ecosystems represent reflection of ecological conditions, and they have important role in their formation, maintaining and function, in making and structuring of vegetation, in productive and trophic relations of water ecosystems (WETZEL, 1983), as well as in general functioning of biosphere. The aquatic macrophytes also have numerous other functions and roles, such as: organic production and the production of oxygen, role in phytofiltration of polluted water, absorption and accumulation of different substances, mineralization and oxidation, detoxication of organic and mineral pollutants, bactericide role, role in keeping temperature and in prevention of erosion, importance in phytoindication and role in phytosanation of aquatic ecosystems (JANKOVIĆ *et al*., 1988).

The aquatic macrophytes are the habitats or food source for many aquatic organisms, and they are competitors to phytoplankton, and so prevent "weed blossom", participate in maintaining the stability of the water balance of ecosystems, but they can cause secondary biological contamination of the water ecosystems.

The seasonal distribution of aquatic macrophytic communities, the distribution in terms of structure (the number of species, population density), organic production and the overall trophic status, as well as the chemical composition of plant species represent very important structural-functional characteristics of different aquatic ecosystems and they are important indicators of ecological situations in them (JANAUER, 2001).

Due to the fact that aquatic macrophytes have big capacity for nutrient accumulation, bioconcentration and high tolerance toward heavy metals, they are more and more used, except for bioindication, for the cleaning of water, soil and shore in different technologies of the phytoremediation.

Continued monitoring of chemical parameters of water and monitoring of distribution and number of aquatic plant species are important parameters in planning and defining of different cleaning and maintenance programmes, as well as in sustainable development of aquatic ecosystems.

DESCRIPTION OF INVESTIGATED LOCALITIES

The artificial lake Gruža (Fig. 1) was created by parting the middle flow of the river Gruža in order to supply Kragujevac and the surrounding villages with water, for the purpose of water supply industry, as protection from floods, for the retention of sediment, to improve the regime of small water area in the downstream river Gruža in extremely unfavorable hydrological situations (PANTOVIĆ and MADŽAREVIĆ according to ČOMIĆ and OSTOJIĆ, 2005).

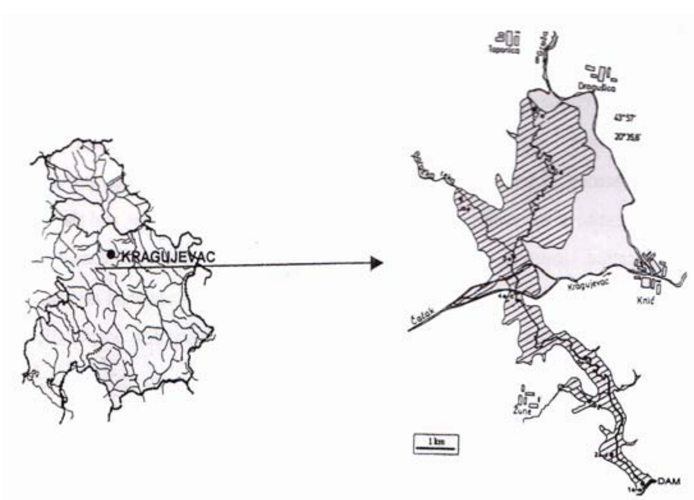

Figure 1. Locality of Gruža Reservoir

Figure 2. Locality of Grošnica Reservoir

Accumulation Grošnica (Fig. 2) is the oldest artificial lake in Serbia. This accumulation is built on Grošnica River in order to supply Kragujevac and the surrounding villages with water, as well as for the needs of industry.

Lake Bubanj (Fig. 3) is formed next to the road Kragujevac-Batočina. It is located in the alluvial plain of river Lepenica, in abandoned valley where the exploitation was being carried out for the country brick factory. This lake-pond is built in scope of the sports and recreational center, planted with fish and it is used for sport fishing and it is a significant reservoir of biodiversity with the flora and fauna of aquatic habitats.

The lake "Memorial-park Kragujevac" (The lake Šumarice) is located in the Memorial Park Kragujevački October, on the outskirts of the city of Kragujevac (Fig. 4). This accumulation was built with the intention to park irrigation, but it is not used for these purposes. It has a role in the aesthetic design of the Memorial Park, as a recreation facility for the citizens of Kragujevac, for sports, for sport fishing and maintenance of cleanliness of the city.

Figure 3. Locality of Bubanj Reservoir

Figure 4. Locality of Šumarice Reservoir

MATERIAL AND METHODS

The field work was conducted during the summer of 2004. Samples of water plants are taken from the sites with the greatest multitude on five locations: the lake Grošnica; the locality Gruža-Dragušica – near the village Dragušica; the locality Gruža-most – near the bridge, next to transit (road) Kragujevac-Knić; lakes Bubanj and Šumarice.

During the selection of plant species, dominant taxons in the populations were selected in order to create real representative sample. By reason of data comparing, the same plant species from different localities were sampled, when it was possible.

Sampled plant species were: *Myriophyllum spicatum* (whole plant), *Ceratophyllum demersum* (whole plant), *Potamogeton lucens* (whole plant), *Lemna minor* (whole plant), *Lemna minor* and *Riccia fluitans* (sampled together), *Lemna minor* and *Lemna gibba* (sampled together), *Polygonum amphibium* (stem, leaf), *Thypha angustifolia* (rhizome, stem, leaf), *Thypha latifolia* (rhizome, stem, leaf), *Phragmites australis* (stem, leaf), *Lycopus europaeus* (stem, leaf), *Bidens tripartitus* (stem, leaf), *Rorippa amphibia* (stem, leaf), *Alisma plantago-aquatica* (leaf), *Mentha aquatica* (whole plant) and *Butomus umbellatus* (whole plant).

Determination of plant material was performed in the laboratory of the Institute of Biology and Ecology, Faculty of Science in Kragujevac, with the help of standard keys for determination: Javorka & Csapody (JAVORKA and CSAPODY, 1979) and Flora of the Republic of Serbia (JOSIFOVIĆ, 1970-1980), with use binocular magnifying glass.

The identified plant material was elutriated in distilled water and then dried at room temperature. Then the plant material was dried in dryer (Binder/Ed15053), 24 hours at a temperature 105 ºC and prepared for chemical analysis by standard procedures, which is used for water and water plants (APHA, 1995).

Concentrations of a metal content in plant tissues were determined by atomic absorption spectrophotometer of company Perkin-Elmer, model 3300/96 with MHS-10 hydride system and a computer on the Agricultural Faculty in Belgrade-Zemun. Samples of raw water and mud (per 2 liters) were taken during the July 2004, at the same time when the samples of plants were taken on the same locality. Chemical analysis of raw water and mud were done by standard methods at the Institute of Public Health Division of Hygiene and Medical Ecology in Kragujevac. The metal concentrations in raw water and mud were determined by atomic absorption spectrophotometer (EPSON FX-870/P710A/2JB0012273) directly from the solution. The contents of metals in plant materials, water and mud are expressed in mg / kg. All results of these researches are shown graphically.

RESULTS AND DISSCUSION

The concentration of Fe in raw water ranged from 0.08 mg / kg on the Grošnica Lake to 0.46 mg / kg on the Gruža-Dragušica locality, and concentration of Cu ranged from 0.009 mg / kg on the Bubanj locality to 0.025 mg / kg on the Gruža-Dragušica locality. The concentrations of Mn and Pb in raw water were similar at all localities, and they were: Mn <0.05 mg / kg, and of Pb <0010 mg / kg. On all the investigated localities, in raw water the highest concentrations were recorded for Fe, by comparing all examined metals. On the Gruža-Dragušica locality concentration of Fe is above the value (0.03 mg / l) for water maximum permitted concentration (Official Gazette RS 42/98).

The highest concentration of Fe was observed in the mud, on the Bubanj locality (Fe - 478.68 mg / kg), and the lowest on the Grošnica lake (Fe – 58.482 mg / kg). In the mud on the Gruža-Dragušica locality, the concentration of Mn was the highest (572.59 mg / kg), and its the smallest concentration (199.45 mg / kg) was observed on the Šumarice lake. The greatest concentration of Cu and Pb in the mud was registered on the Bubanj locality (Cu - 29.76 mg / kg, Pb - 38.68 mg / kg). The lowest concentration of Cu (15.08 mg / kg) in the mud was registered on the Gruža-Dragušica locality. The lowest concentration of Pb in the mud was in the Grošnica Lake (17.92 mg / kg). The concentrations of Cu and Pb are in the level of MDK values for these metals (Official Gazette RS 23/94).

Distribution of metals in plants primarily depends on the plant species, plant organs and the type of metal. Some metals are accumulated only in the root, because of the existence of physiological barrier to their transport in the over ground part of plants, while the other metals in some plant species, can be easily transported to branches. As limiting factor of bioconcentration of some metals it could be ion transport from root to germ (LU *et al.*, 2004).

Comparing all investigated localities and sampled plant species, it can be concluded that the highest concentration of Fe (Graph 1) was registered in rhizome of species *Typha angustifolia* L. on the Gruža-most locality, and its the lowest concentration in leaf in the same species on the Bubanj Lake.

Translocation of Fe is metabolic process, and its distribution in plants is a specific and complex process. Iron is poorly movable in phloem, so that its redistribution from older to younger tissue is slow, which is the reason why its lacking firstly occurs on the youngest leaves. The main transport form of Fe is in chelat form, i.e. conjunct to organic acids (malic, citric), phenols, tiols or amino acids. According to GUPTA (1998) the concentration of heavy metals in aquatic plants showed the following tendency: Fe > Ni > Cr > Cu > Cd. The concentration of heavy metals depends on the plant species, and it is genetically conditioned, and tolerance to some heavy metal does not mean also tolerance to another one. The results of our research indicate that the highest amount of Fe was accumulated in rhizomes of *Typha* species, on different types of localities. This data is in favor of the above presented facts that rhizome is the main organ for adoption and disposition of Fe, and also that its translocation is complicated, so it accumulates and concentrates in organ that absorbed it.

Comparing all the sampled plant species in the researched localities, it can be concluded that the highest concentration of Mn (graph 2) was registered in the species of *Lemna minor* and *Riccia fluitans,* on the Šumarice Lake (5357.3803 mg / kg), and the lowest concentration in leaf of *Alisma plantago-aquatica* on Gruža-Dragušica locality (17.9977 mg / kg).

Distribution and mobility of Mn is determined by pH value, aeration, oxide-reduction conditions, or sediment and water redox potential (GRAČANIN, 1977). As a matter of fact the ground contained acids, in conditions of low oxide-reduction potential, leads to reduction four-valent and three-valent Mn in bivalent, that is accessible form for plants. Accumulation of a metal is not just only its simple linear bioconcentration from external environment, but on the level of accumulation of single metal, concentration and ionic form of the rest presented metals influence. Mn uptake is influenced by numerous factors, for example, Na, Ca, Cu, Fe and NH_4, which reduce its adoption due to the ion antagonism. It is difficult to explain what is really happening, which reactions occur in wet habitats, because the processes vary from one to another and make the entire mechanism of the removal of heavy metals in wet habitats very complex. Differences in the accumulation of Mn in macrophytes from different localities should be explained by differences in temperature, movement of water, ecological differences in habitats, and numerous other factors.

Comparing of the tissue Cu concentrations in plant species from the different localities showed the highest values (graph 3) in Mentha *aquatica* species on the Bubanj locality (605.1678 mg / kg), and the lowest in stem of *Bidens tripartitus* species on the Gruža-most locality (1.1215 mg / kg). Our results show that the highest concentration of Cu was recorded in emerse species *Mentha aquatica* that by its branched vegetative organs accumulates Cu at Bubanj locality, which is loaded with these heavy metals from different sources (sewage sludge, vicinity of roads, housing and industrial zone, etc.).

Copper with the organic components of xylem liquid makes complexes with a negative charge, so that it decreases its interaction with cell wall molecules of xylem, and encourages ascendant transport of Cu in plants (PUNZ and SIEGHARDT, 1993). If plants absorb Cu through leaves, almost all the copper is localized in chloroplasts of leaves (STANKOVIĆ *et al*., 2006). It was shown that increased content of Cu in the root did not cause the increase of its content in the over ground parts of plants, because Cu is a poorly movable in the plant and the most of the absorbed amounts retained in the root (MLADENOVIĆ, 1997). The most important mechanisms of plant tolerance to Cu represent compartmentation of Cu in the form of soluble and insoluble complexes in the cytoplasm and vacuole (WU *et al*., 1975).

Comparing all the sampled plant species in the researched localities it was concluded that the highest concentration of Pb (graph 4) was registered in rhizome of *Typha latifolia* species, on the Bubanj locality (52.9640 mg / kg). Lead adopted from water is in the ion form, whereas plants adopt it from the soil, water or air. The root and rhizome are primary organs of accumulation of Pb in aquatic plants, and the ability of its relocation to the over ground organs is limited and depends on the plant species. Lead, during the transportation through xylem, forms complex compounds with substances of xylem sap. They are absorbed on the walls of xylem cells, and on that way they slow down ascending transport of lead in plants (WHITE *et al*., 1981).

The results of our research point to the largest concentration of Pb on the Bubanj locality in rhizome of *Typha latifolia* (52.9640 mg / kg) and in *Ceratophyllum demersum* (25.2293 mg / kg), as well as in rhizome of *Typha angustifolia* on the Gruža-bridge locality, which indicates to the lead loading of these localities that are next to busy roads. The great accumulation capacity of root and rhizome for heavy metals, and even Pb, could be one aspect of protection of the over ground plant organs from greater concentration of heavy metals in the external environment (KASTORI, 1997).

The aquatic macrophytes through its rhizome and roots, and also by whole surface accumulate great amounts of chemical elements, especially macronutrients (nitrogen and phosphorus), but also pesticides, heavy metals, toxic salts, phenol, etc.(BRIX, 1994), and in this way contribute to the reduction of eutrophization, circuiting of nutrients, control of water quality and to the stabilization of sediments (CHAMBER and PREPAS, 1994).

The aquatic macrophytes can be applied as phytoremediators through absorption and accumulation of various toxic substances such as pesticides, derivatives of phenol, heavy metals, radio nuclides and other physiologically active pollutants. The water plants have no regulatory mechanisms regarding the adoption of nutrients and heavy metals, so they perform their phytoextraction from water ecosystems by the process of chemical bioconcentration. Increased level of bioconcentration of chemical elements in tissues of macrophyta, with the previous reasonable estimation of necessary quantity for metabolism, points to the chemical loading of environment: increased accumulation of certain elements in the tissue is the consequence of their increased concentration in the water environment (BOYD, 1970).

For a complete and comprehensive picture of changes in the ecosystem, it is necessary to combine monitoring of biological and chemical type. Researches in this paper tried to clarify the importance of macrophytes in the accumulation of toxic metals from the aquatic ecosystem and control of their pollution, and suggest which plant species are good test species for remediation for the purpose of the protection and restoration of tested lake ecosystems.

CONCLUSION

The results of our research show that in all localities, in the mud, there were higher concentrations of all metals examined in relation to the raw water. In raw water of all researched localities, by comparing all examined metals, it was recorded the highest concentration of Fe, and then concentrations of Cu, Mn and Pb followed. In the mud, the concentration of examined metals depreciated in the next order: Mn, Fe, Pb and Cu. The results show that the concentration of Fe and Mn have order - plant species > mud > raw water, and concentrations of Cu and Pb – mud > plant species > raw water. The concentrations of the examined metals (Fe, Mn, Cu and Pb) in researched aquatic macrophytes depended on plant species, plant organs and researched localities.

The aquatic macrophytes can be used in studies of ecosystem water quality and for metal and other pollutants monitoring, and with planned monitoring of the chemical composition of plants, sampled from polluted localities, the solution to the problem of protection, rehabilitation and revitalization of these areas could be reached more comprehensively.

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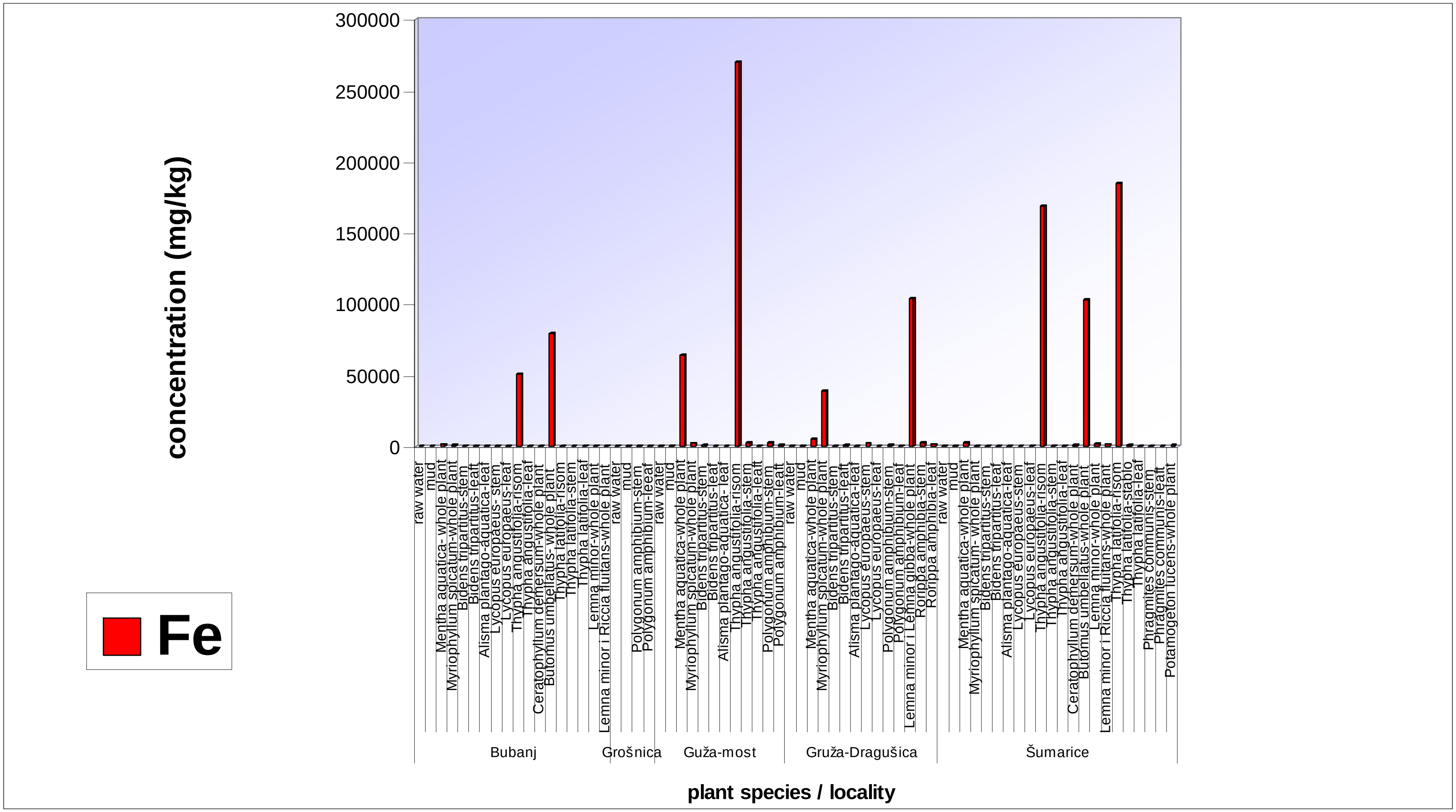
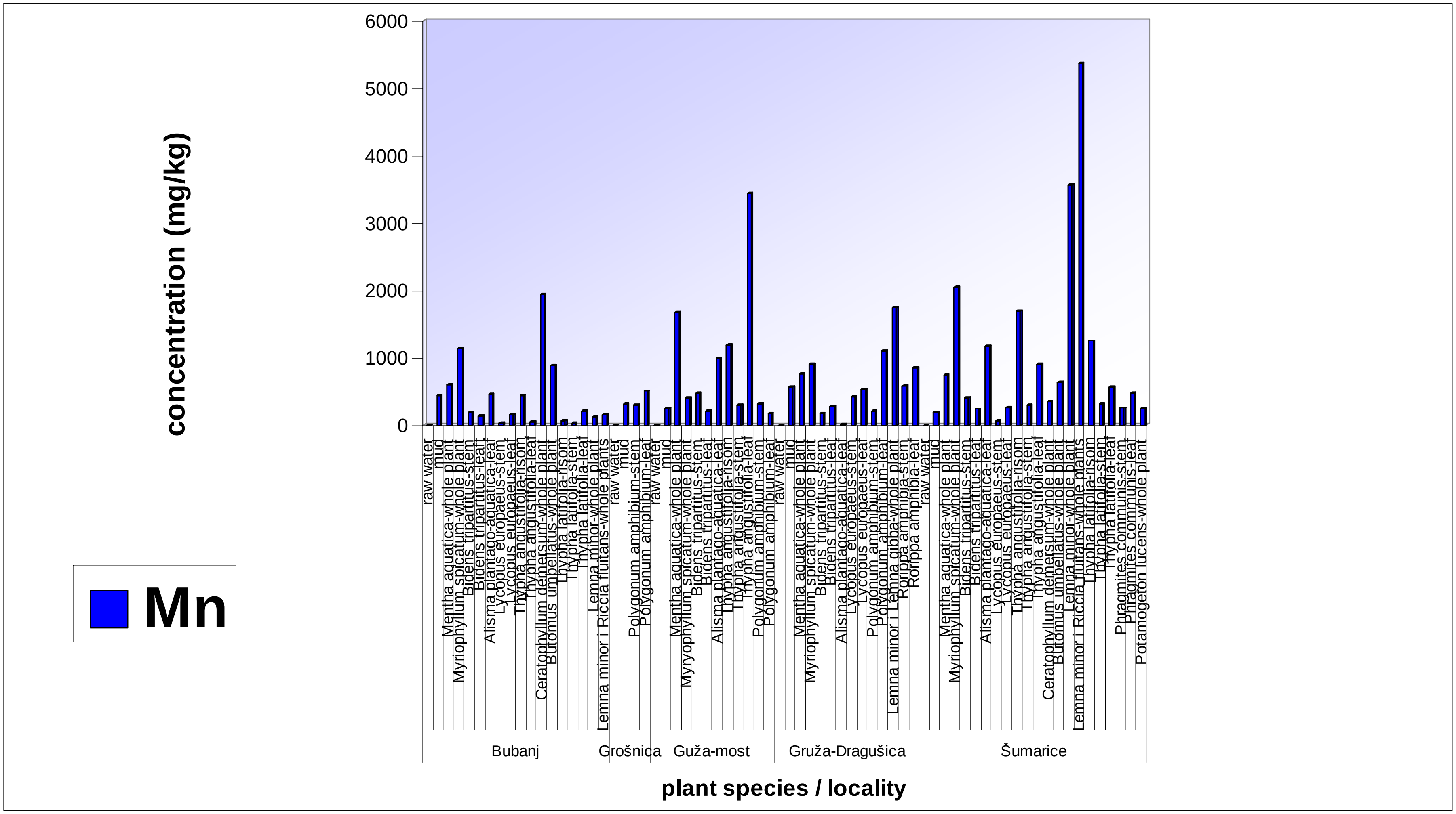
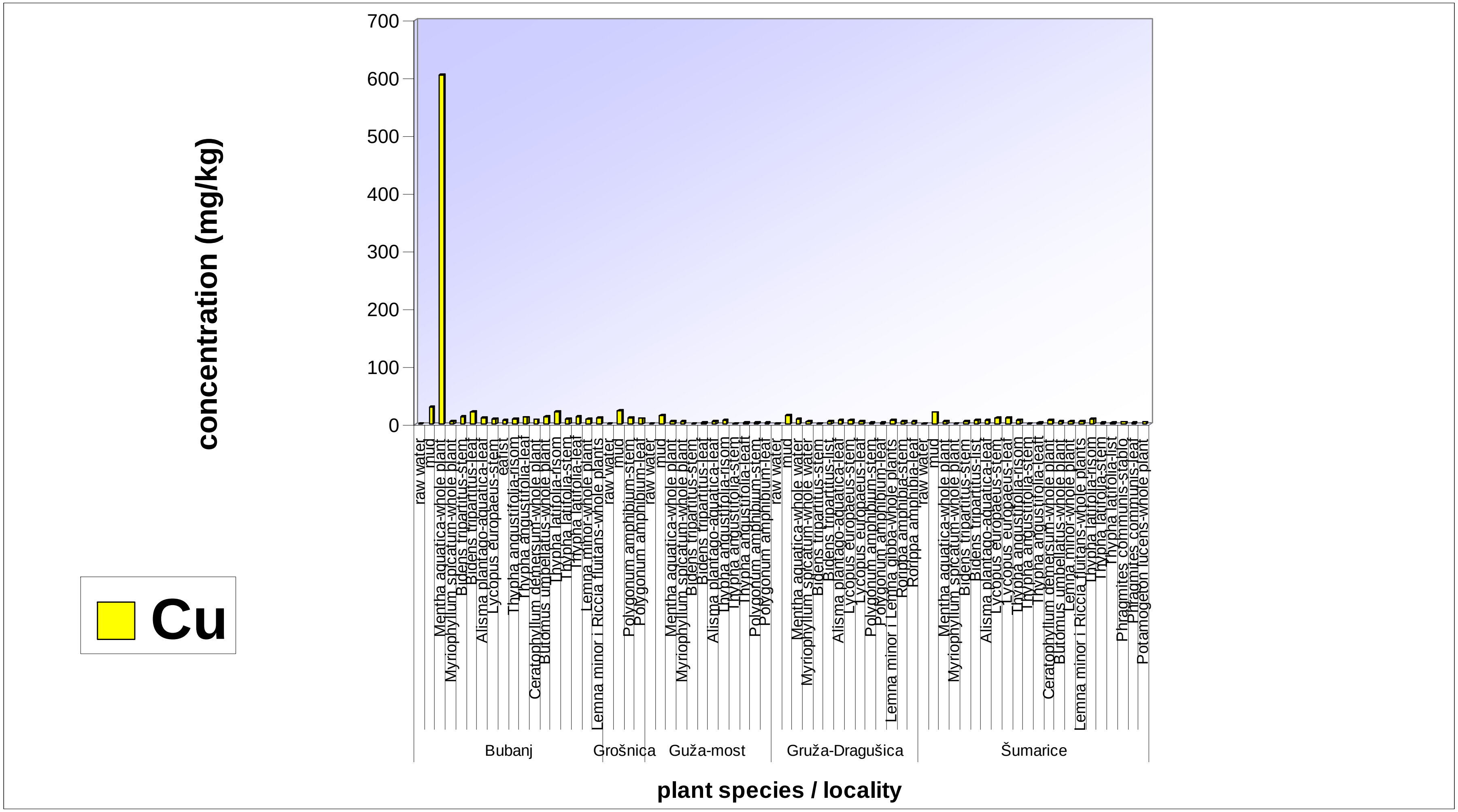


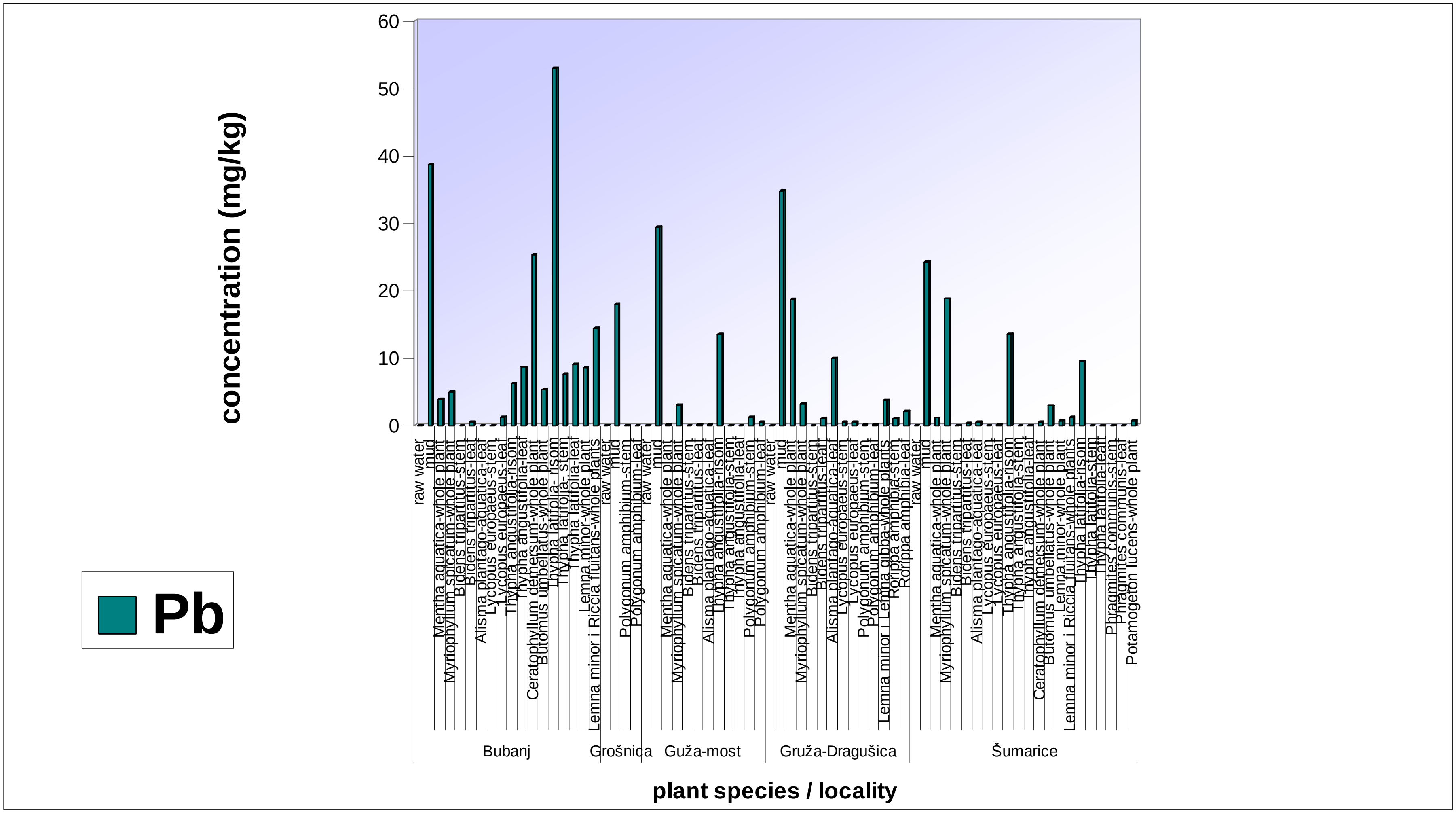
Graph 1. The concentration of Fe in raw water, mud and aquatic macrophytes in the researched localities



Graph 2. The concentration of Mn in raw water, mud and aquatic macrophytes in the researched localities



Graph 3. The concentration of Cu in raw water, mud and aquatic macrophytes in the researched localities



Graph 4. The concentration of Pb in raw water, mud and aquatic macrophytes in the researched localities