Spatial Distribution of Ecotoxic Trace Metals in Waters of "Plitvička Jezera" National Park - Croatia

D. Omanović[*], Ž. Kwokal[*], N. Cukrov[*], P. Cmuk[*], M. Mlakar[*], I. Pižeta[*], N. Pavlus[**], I. Špoljarić[**], M. Stojanovska[**]

[*] Ruđer Bošković Institute, Centre for Marine and Environmental Research, POB 180, 10002 Zagreb, CROATIA

[**] Scientific Research Center "Ivo Pevalek", Plitvička Jezera National Park, 53231 Plitvička jezera, CROATIA

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Spatial distribution of five ecotoxic trace metals (Cd, Cu, Pb, Zn and Hg) in waters of "Plitvice Lakes" National park sampled during the year of 2005 and 2006 was studied. Water samples were taken at several locations in the National Park (17 sampling sites). Cd, Cu, Pb and Zn concentrations were determined using differential pulse anodic stripping voltammetry (DPASV), while cold vapor atomic absorption spectrometry (CVAAS) was used for mercury determination. The measured concentrations of all trace metals were very low, and comparable with the concentrations obtained in unpolluted waters of other protected areas. Slightly higher concentrations of zinc and cadmium found in the "Bijela rijeka" river most likely originate from the Mesozoic dolomite. According to the water quality criteria established by the corresponding regulations of the Republic Croatia, and also according to the metal concentration parameter, the waters of National park belong to the "I class" waters.

Introduction

"Plitvice Lakes" are one of the most beautiful national parks in Europe (declared in 1949). They are situated in the mountainous region of Lika, Croatia. A total of 16 lakes, lying at different altitudes, are separated by travertine barriers and linked by waterfalls. UNESCO has declared it as the "World's natural inheritance".

As biogeochemical processes in aquatic environment take place continuously, the lakes and waterfalls are under permanent change. To preserve such sensitive areas in its original state, very thorough protection activities need to be undertaken. One of the most important part of these activities is scientific research, because it creates the core for planning, developing and coordinating different protection activities. Knowing the actual and real status of different compartments in an aquatic environment (water, sediment and biota), which are interconnected, more exact actions could be undertaken. Permanent monitoring programs are imperative in such areas. "Plitvice Lakes" is the most visited National park in Croatia, with more than 500,000 tourist during the main summer season. Hence, the monitoring of pollutants in different natural compartments within the Park is of the particular significance.

The concentration of ecotoxic metals is the parameter foreseen in water quality control. Because of very low concentration of trace metals in unpolluted natural waters (usually below 0.5 μg L^{-1}), their accurate determination requires the utilization of very sensitive methods. Unfortunately, such sensitive methods are not widely exploited by the partners integrated in water quality control programs in Croatia. For most unpolluted waters in Croatia, the actual level of trace metal concentrations is not known. Any anthropogenic influence or input in unpolluted aquatic environment is a serious risk. Therefore, it is very important to assess actual ecotoxic trace metals concentration levels in waters of protected areas, such as National Parks.

Very important parameter in the natural water quality evaluation is trace metals content and speciation (Branica, 1990). Trace metals in the aquatic environment are naturally present or introduced through various sources, including confluent and groundwater inputs, as well as fallouts, agricultural, urban runoff and domestic waste. Natural trace metals concentrations in waters depend on the type of rocks and soil in catchment areas of the river. As in the Croatian karst, natural concentrations of trace metals in waters are very low. Thus, anthropogenic input can easily elevate their concentrations significantly. Therefore, it is very important to monitor their concentration in all compartment of the aquatic.

Materials and methods

Surface water samples were collected in September 2005 and June 2006. Figure 1 shows the studied areas and sampling sites. Measurements of physico-chemical parameters (pH, dissolved oxygen, water temperature) were performed *in situ*. pH was measured by the portable instrument Mettler Toledo MP 120 (Schwerzenbach, Switzerland), dissolved oxygen by *in situ* Oxymeter Mettler Toledo MO 128 (Schwerzenbach, Switzerland), and water temperature by built-in thermometer in the Mettler Oxymeter probe.

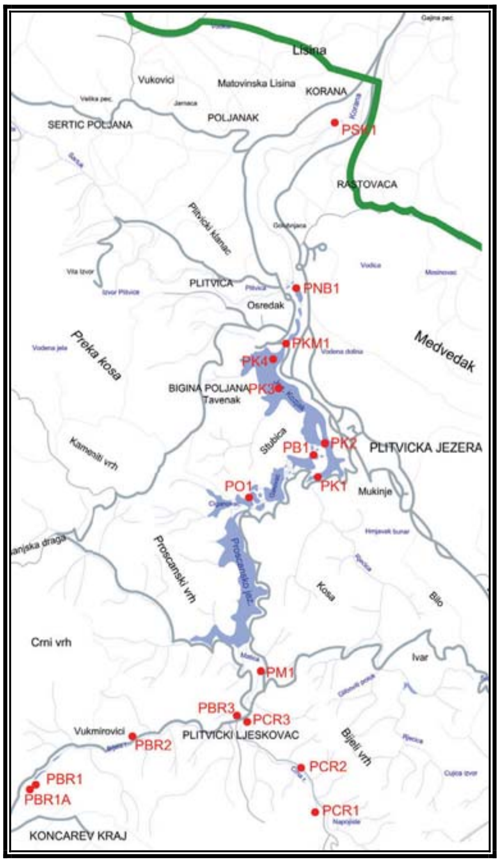


Figure 1. Overview of the investigated area with sampling sites.

Samples for the analysis of trace metals zinc, cadmium, lead and copper were taken manually (~20 cm depth) and stored in high density polyethylene (HPDE) bottles (1 L) previously cleaned with suprapur nitric acid and rinsed with Milli-Q water. Water samples for Hg determination were collected in 1 L pre-cleaned SIMAX Sklarny Kavalier borosilicate glass reagent bottles (Sazava, Czech Republic).

Analyses of total (unfiltered) and dissolved (filtered trough 0.45 μm membrane acetate filters under nitrogen pressure) trace metals Zn, Cd, Pb and Cu were carried out. Before measurements, samples were acidified to pH < 2 with HNO_3 (suprapur, Merck) and digested by UV-light (mercury lamp 150 W, Hanau, Germany) during at least 24 hours.

Trace metals concentrations were measured by a voltammetric technique, differential pulse anodic stripping, using AUTOLAB instrument (Eco-Chemie, Utrecht, Netherlands). A three electrode system was used, with a hanging mercury drop working electrode (VA stand 663m Metrohm, Herisau, Suisse), a platinum wire counter electrode, and an Ag/AgCl (saturated with NaCl) reference electrode.

Trace metals concentrations (Zn, Cd, Pb and Cu) were measured simultaneously, after adjustment of pH to 3.5 by the addition of 200-300 µL of sodium acetate buffer. Total mercury was measured by cold vapor atomic absorption spectrometry (CVAAS) with a detection limit of 0.015 ng L^{-1} (Kwokal and Branica, 2000).

Results

Figure 2 shows spatial distribution of trace metal concentrations (Zn, Cd, Pb, Cu and Hg) for samples taken along "Plitvice Lakes" during the summer and winter sampling period.

Zinc

It is obvious that the highest concentrations of zinc were measured in samples taken at the spring of the "Bijela Rijeka" river (PBR1). Furthermore, a decrease of zinc concentration in samples taken at the next two downstream stations was not observed. This suggests that the zinc was not removed from the water body, or zinc concentration was maintained by the inflow of new waters with the same level of the zinc. Comparing to the "Bijela rijeka" river, very low concentrations in samples taken at the spring of the "Crna Rijeka" river (PCR1) were measured. At the two subsequent sampling stations, an increase in zinc concentration was not observed. Taking into account the mass of water coming with the "Bijela" and "Crna Rijeka" rivers (1:3), a zinc concentration measured in samples of the "Matica" River (PM1) (which is formed by merging the "Bijela" and "Crna Rijeka" rivers) reflects its average concentration. A level of zinc concentration is lower downstream, because of its sinking through a water column in numerous lakes, and the zinc concentration is maintained at about 200 ng L^{-1} The difference between total and dissolved fraction is very small, indicating a very small quantity of suspended matter in waters of the Plitvice lakes.

The relatively high concentration of zinc in the "Bijela Rijeka" river is probably of natural origin. Namely, unusually high natural concentrations of Zn and Cd have often been associated with soils high in organic matter and sulfur (Martinez et al., 2002). These metals enter groundwaters by drainage. Another related assumption is that dolomites, which prevail in the area of the "Bijela Rijeka" spring and are often enriched with different metals, are the origin of the increased content of these two metals. A more detailed study is needed in order to answer which of these two assumptions is more probable and prevails.

Cadmium

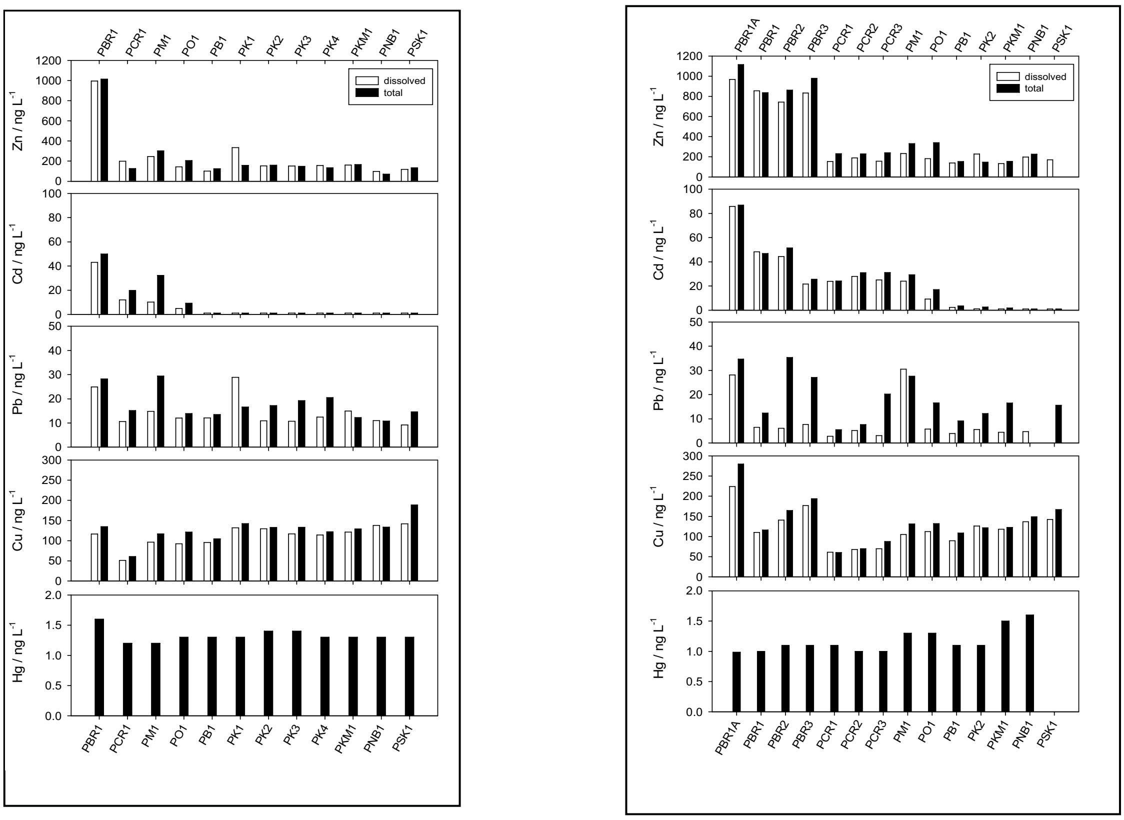
Similarly to zinc, increased concentrations of cadmium were measured in water samples collected at the "Bijela Rijeka" spring (PBR1) when compared to other locations downstream (~ 50 times). As for zinc, we assume that the increased concentration of cadmium is also of the natural origin. It is interesting to note that at the "Crna Rijeka" spring (PCR1) higher concentrations of cadmium were also measured (~ 25 times). However, no increase in zinc concentration was observed. Comparing to the area of "Bijela Rijeka", where dolomite rocks are predominant, the area of "Crna Rijeka" is mostly limestone. As mentioned above, only detailed investigations, which would include analysis of soils, rocks and waters in wider area of both springs, could give us more data for the correct interpretation of such relatively high concentrations of zinc and cadmium.

Downstream of "Lake Prošće" and "Okrugljak" (PO1), cadmium concentration decreases and remains below 3 ng L^{-1}. It is obvious that most of cadmium is eliminated in “Lake Prošće” by natural processes. To have more insight into these processes, speciation studies should be done.

Lead
A spatial distribution of lead concentrations shows very small variations. Except at few sites with slightly higher concentrations (~30 ng L^{-1}) (which could still be considered very low), an average total concentration of lead at other sites is about 15 ng L^{-1}. This is is an extremely low concentration, indicating the absence of any anthropogenic source. As it is known, lead ions adsorb more readily on particular matter than Zn, Cd, Cu. This is clearly visible by comparing concentrations of total and dissolved fraction of lead with those of other three metals.

Copper
Three different regions concerning copper concentrations along “Plitvice Lakes” could be identified. The first one is three sampling sites along the “Bijela Rijeka” river, where an increase in copper concentrations by about 70% was observed (from 110 to 180 ng L^{-1}). The second part is three sampling sites along “Crna rijeka” river where the lowest concentrations were measured (~ 60 ng L^{-1}), and the third part is the downstream site of the “Matica” river (PM1) with low copper concentration of about 120 ng L^{-1}.

Mercury
Comparing to concentrations of other four metals which show some trends in spatial distribution along the National park, the concentration profile of mercury is very uniform. Measured concentrations are extremely low (<1.5 ng L^{-1}) and are one of the lowest concentrations measured in natural waters in Croatia.



Summer period Winter period

Figure 2. Spatial distribution of trace metal concentrations.

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