Ecotoxic trace metals in waters of "Krka" National Park - Croatia

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Abstract

The Krka National Park is a large area of exceptional and multifaceted natural value, and includes one or more preserved or insignificantly altered ecosystems. It is situated entirely within the territory of Šibenik-Knin County and encompasses the area of 109 square kilometers along the Krka River. Its aquatic environment is mainly fresh water with nine tufa waterfalls and total drop of 242 meters. Therefore, the Krka River flow area is the nature and karstic phenomenon. Limestone deposits from dissolved calcium bicarbonate form tufa barriers creating waterfalls. The tufa depositing is a constant and dynamic process, including physiochemical factors and organisms present in described water ecosystem.

As protected natural areas of the Krka National Park is very sensitive ecosystems because of their substantial uniqueness it should be preserved in their original form. Spatial and temporal distributions of five ecotoxic trace metals (Cd, Cu, Pb, Zn and Hg) in waters of "Krka" National park sampled during 2004, 2005 and 2006, were studied to assess actual ecotoxic trace metals concentration levels. Cd, Cu, Pb and Zn concentrations are measured as dissolved (filtered) and total (non-filtered).

Elevated trace metal concentration levels in such vulnerable systems could be a sensitive indicator for possible anthropogenic influence. In these nature compartments of the Krka National Park any anthropogenic influence or input is serious risk for biodiversity.

Therefore, regular monitoring (periodic, field/laboratory) is necessary to distinguish elevated trace metal concentrations naturally present in the particular aquatic environment from the anthropogenic introduced ones.

Obtained results suggest complex behavior of different trace metals species investigated in the River Krka waters from the Krka spring to the Skradinski Buk waterfalls. Interesting locations are emphasized: subterranean input of clean water near Miljacka power plant and surrounding caves, and anthropogenic influence of communal waters downstream of city of Knin. Range in trace metals concentrations in Krka River water were: Zn dissolved from 59 to 3890 ngL^{-1} and total from 83 to 9410 ngL^{-1}; Cu dissolved from 20.0 to 1300.0 ngL^{-1} and total from 58.5 to 5898.0 ngL^{-1}; Pb dissolved from 3.4 to 29.6 ngL^{-1} and total from 8.2 to 275.7 ngL^{-1}; Cd dissolved from 0.5 to 7.14 ngL^{-1} and total from 1.0 to 8.4 ngL^{-1}; Hg total from 0.5 to 16.0 ngL^{-1}.

Introduction

The Krka River is a medium sized water course in the Dalmatian karst area and drains mostly carbonate terrains. Its canyon-like appearance is a consequence of the geological setting of the entire catchment area with its suite of tectonically formed faults and crevices within limestone of Cretaceous and Palaeogene age. The hydrogeologic drainage area of the Krka River is approximately 2427 km^2 (Bonacci and Ljubenkov, 2005). Average flow of Krka river at the Skradinski Buk waterfalls in last 50 years varies between 40 and 60 m^3s^{-1},with minimum flow 5 m^3s^{-1} and maximum 565 m^3s^{-1} (Bonacci and Ljubenkov, 2005). The length of the Krka River is

75 km with 9 main tufa barriers with waterfalls (Topoljski buk, Bilušića buk, Ćorića buk, Brljan, Manojlovački slapovi, Rošnjak, Miljackin slap, Roški slap i Skradinski buk). The tufa depositing is a constant and dynamic process, including physiochemical factors and organisms living in the water. The uniqueness of these tufa barriers and waterfalls is base for the National Park "Krka" proclamation in 1985.

Very important parameter in the natural water quality evaluation is trace metals content and speciation (Branica, 1990; Tesseier and Turner, 1995). Trace metals in the river environment are naturally present or introduced either in dissolved or adsorbed onto particulate matter, through various sources, including confluent and groundwater inputs,, as well as fallouts, agricultural, urban runoff and domestic waste. Natural trace metals concentrations in river waters depend on the type of rocks and soil in the catchments area of the river. As in Croatian karst waters natural concentrations of trace metals are very low, anthropogenic input can easily elevate their concentrations significantly. Therefore, it is very important to monitor their concentration in all compartment of the river ecosystem from the spring down to the estuary, taking into account river bed, groundwater and tributaries input.

Materials and methods

Surface water was sampled in November 2004, January 2005, May 2005, July 2005, May 2006 and July 2006. In these periods hydrological conditions varied considerably. In the Fig. 1 investigated area and sampling sites are presented. Sampling locations were spotted by the GPS device (Garmin GPS Map 76CSx with the accuracy of ± 5 m).

Measurements of physico-chemical parameters (pH, dissolved oxygen, water temperature, redox potential) were performed *in situ*. pH and redox potential were measured by the manual instrument Mettler Toledo MP 120 (Schwerzenbach, Switzerland), dissolved oxygen by the *in situ* Oxymeter Mettler Toledo MO 128 (Schwerzenbach, Switzerland), and water temperature by the mercury thermometer sunk for 5 minutes into the water with additional measurements by the thermometer built-in in the Mettler Oxymeter probe.

Figure 1. - Overview of the investigated Krka River area with sampling sites.

Samples for the trace metals zinc, cadmium, lead and copper analyses were taken manually (20 cm depth) into the 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 pre-cleaned SIMAX Sklarny Kavalier borosilicate glass reagent bottles (Sazava, Czech Republic) with volume of 1 L.

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, Fluka) and digested by UV-rays (mercury lamp 150 W, Hanau, Germany) during 24 hours.

Trace metals concentrations were measured by voltammetric technique using AUTOLAB instrument (Eco-Chemie, Utrecht, Netherlands). A three electrode system was used with hanging mercury drop as a working electrode (VA stand 663m Metrohm, Herisau, Suisse), with a drop surface of 0.25 mm^2, platinum wire as a counter electrode and Ag/AgCl with saturated NaCl as a reference electrode, was used.

Trace metals concentrations (Zn, Cd, Pb and Cu) were measured simultaneously, after adjustment of pH to 3.5 by the addition of 200-300 ml of sodium acetate buffer. Voltammetric technique used was anodic stripping differential pulse voltammetry and parameters were adjusted as follows: for Zn – deposition potential = - 1.3 V; deposition time = 180 s; amplitude 0.02 V; step potential 0.002 V, and for Cd, Pb and Cu - deposition potential = - 0.8 V; deposition time = 600 s; amplitude 0.02 V; step potential 0.002 V. Total mercury was measured by cold vapor atomic absorption spectrometry (CVAAS) with detection limit 0.015 ngL^{-1} (Kwokal and Branica, 2000).

Results and discussion

In the Table 1 are presented pH, dissolved oxygen and water temperature values (minimum and maximum values). Values of the pH were lowest at sampling point NPK 8 and NPK 12, because of ground water influence, and the highest at sampling point NPK 14 because of degassing of the CO_2 and possible anthropogenic influence of the city of Drniš.

Table 1. Minimum and maximum values of pH, dissolved oxygen and temperature in Krka River

Sampling sites	pH		Temperature /°C		Dissolved oxygen/mgL^{-1}	
	Min	Max	Min	Max	Min	Max
Krka Spring (**NPK 8**)	7.3	7.7	9.0	10.4	10.0	11.5
Knin (downstream)(**NPK 9**)	7.6	8.3	8.7	15.3	6.6	12.2
Bilušića buk (**NPK 10**)	8.2	8.3	8.2	15.0	9.6	13.6
Cave Miljacka IV (**NPK 12**)	7.0	7.3	12.4	13.4	7.5	11.7
Power Plant Miljacka (**NPK 11**)	7.3	7.6	12.4	14.3	9.2	12.9
Krka Monastery (**NPK 3**)	7.8	8.1	8.7	19.0	9.9	11.4
Roški Waterfall (**NPK 4**)	7.8	8.2	8.4	19.3	10.0	11.2
Visovac-West (**NPK 2**)	8.0	8.3	8.8	25.0	9.9	12.4
Visovac-East (**NPK 5**)	8.0	8.2	8.9	26.9	9.7	14.3
Čikola River (**NPK 14**)	8.5	8.6	3.6	16.3	8.5	12.2
Skradinski buk (**NPK 1**)	7.9	8.2	8.6	25.0	8.3	10.6

Range of trace metals concentrations in the Krka River water were: dissolved Zn from 59 to 3890 ngL^{-1} and total from 83 to 9410 ngL^{-1}; dissolved Cu from 20.0 to 1300.0 ngL^{-1} and total from 58.5 to 5898.0 ngL^{-1}; dissolved Pb from 3.4 to 29.6 ngL^{-1} and total from 8.2 to 275.7 ngL^{-1}; dissolved Cd from 0.5 to 7.14 ngL^{-1} and total from 1.0 to 8.4 ngL^{-1}; total Hg from 0.5 to 16.0 ngL^{-1}. Average concentration of dissolved and total Zn, Cd, Pb and Cu are shown in the Fig.2. The average concentrations of Hg ware: 0.9 ngL^{-1} NPK8; 3.8 ngL^{-1} NPK9; 1.5 ngL^{-1} NPK10; 1.0 ngL^{-1} NPK11; 1.3 ngL^{-1} NPK12; 1.7 ngL^{-1} NPK3; 2.1 ngL^{-1} NPK4; 4.3 ngL^{-1} NPK2; 3.2 ngL^{-1} NPK5; 1.3 ngL^{-1}NPK14 and 1.2 ngL^{-1} NPK1.

Elevated concentration of total and dissolved concentration of Hg, Pb and Zn downstream of the city of Knin show anthropogenic influence. In the contrary, elevated concentration of total Hg and Cu in the Visovac Lake were product of some natural phenomenon. Elevated concentration of the total Cu there may be connected with plankton bloom. Low concentration of total and dissolved trace metals near power plant “Miljacka” are result of the subterranean clean water inflow from north-west area.

Waters of the Krka River considering average ecotoxic metals concentrations are in the first category according Croatian National Regulative (W.C.D., 1998). Considering average concentration of the Pb downstream the city of Knin river water is within the second category.

It can be concluded that the Krka River is unpolluted aquatic ecosystem concerning trace metals, with the exception in the area of Knin where anthropogenic input in notable. Therefore, monitoring of trace metals concentrations in the Krka River waters on the regular basis should be performed to detect all changes and prevent any pollution that would change that precious ecosystem.

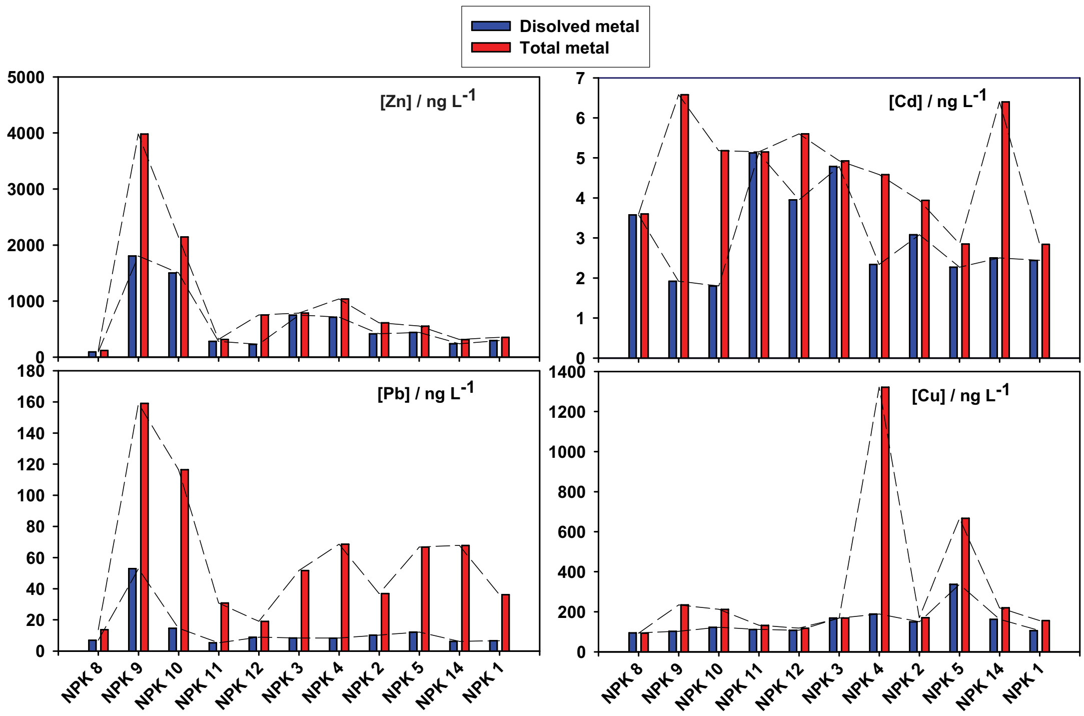

Figure 2. Average concentration of dissolved and total Zn, Cd, Pb & Cu (ngL^{-1}).

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