A PRELIMINARY STUDY OF TRACE METALS AND PHYSICO-CHEMICAL PARAMETERS IN WATER COLUMN OF ANCHIALINE CAVE ORLJAK, CROATIA

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Abstract
A preliminary study of distribution of total trace metal concentrations (Cd, Pb, Cu and Zn) and physico-chemical parameters (water temperature, pH, dissolved oxygen (DO), dissolved organic carbon (DOC) redox and salinity) in water column of anchialine cave Orljak in the well stratified Krka River estuary (Croatia) has been performed. Metal amounts and physico-chemical parameters in cave water column were compared with related column in Krka River estuary.

Keywords: Estuaries, Metals, Adriatic Sea, Organic Matter

Study area & methodology
Recently anchialine objects as a very unusual aquatic environments became target of interdisciplinary research [1,2]. The Orljak cave is unique anchialine cave at Eastern Adriatic coast because of its connection with brackish water. Anchialine cave Orljak is located in Cretaceous limestone with macro fossils 50 m from coast in lower part of the Krka River estuary. Cave is 23 m deep and 90 m long with two water bodies (2 and 7 m) probably well hydraulically connected with estuary water (tides are notable).

Physico-chemical parameters (water temperature, pH, dissolved oxygen, redox potential and salinity) were measured in situ by Hydrolab MiniSonde 4a equipped with the following sensor: pressure (depth), T, conductivity/salinity, pH (with Ag/AgCl/KCl sat as reference), Eh (Pt xire with the same ref as pH), O2 (by amperometric measurement). Samples for DOC and trace metal analyses (Cd, Pb, Cu and Zn) were taken by scuba divers, respecting a principle of a ‘clean sampling technique’ in summer 2009. Concentrations of DOC were determined using a TOC-V analyser (Shimadzu), calibrated using sodium hydrogenophtalate standard solutions, with an accuracy of 0.8 μMC. Total trace metal concentrations were measured in unfiltered, acidified (pH < 2) and UV irradiated water samples (24 h, 150W mercury lamp, Hanau, Germany). Determination of Cu, Cd, Pb and Zn concentration were performed by differential pulse anodic stripping voltammetry (DPASV) using static mercury electrode (663 VA STAND, Metrohm, Switzerland) connected to µAUTOLAB potentiostat (EcoChemie, Utrecht, The Netherlands).

Results and discussion
Values of physico-chemical parameters (water temperature, pH, dissolved oxygen (DO), from anchialine cave Orljak and the Krka River estuary are graphically presented in Figure 1 A and Figure 2 B, respectively. Total metal concentrations and dissolved organic carbon (DOC) from cave and estuary are graphically presented in Figure 1 C and Figure 1 D, respectively. Quite low and constant DOC concentrations along the cave water column profile reflect absence of autochthones DOC productivity by phytoplankton, as well as neglected anthropogenic influence (Fig. 2A). Total metal concentrations of zinc, cadmium and lead in anchialine cave’s water were higher comparing to concentrations in estuary waters, while total copper concentrations were higher in estuary waters due intensive boat traffic [3].

Fig. 1. Location of anchialine cave Orljak.

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Fig. 2. Vertical profiles of temperature, pH, salinity, redox, dissolved oxygen (DO), dissolved organic carbon (DOC) and total concentrations of Zn, Cd, Pb and Cu in Orljak Cave and Krka River estuary.

References