TRACE METALS AND DISSOLVED ORGANIC CARBON IN WATER COLUMN OF AN ANCHIALINE OBJECT IN MLJET NATIONAL PARK - CROATIA

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Abstract

Distribution of Cd, Pb, Cu, Zn and dissolved organic carbon (DOC) in water column of Bjejajka anchialine cave were studied seasonally (wet and dry periods). Metal amounts in water column were significantly higher compared to those found in seawater samples taken in near vicinity (100 m). Unusually elevated concentrations of cadmium (up to 300 ng L^{-1}) were found in water column of Bjejajka cave, which are two orders of magnitude higher than in nearby surface seawater (~ 7 ng L^{-1}). DOC amount in cave water column (up to 10.5 mg C L^{-1}) was enhanced comparing to open seawater (up to 3 mg C L^{-1}), and diminished below halocline. Elevated concentrations of trace metals and DOC in Bjejajka anchialine cave were of natural origin caused by biogeochemical processes.

Keywords: Metals, Organic Matter, Adriatic Sea

Experimental

Bjejajka anchialine cave in the remote Mljet National Park is connected hydraulically with Adriatic seawater. Tide inside the cave follows outer surface seawater level, but replenishment of the water is restricted by the karst rock. The water in the cave has a long residence time compared to a fully-flushing cave. This anchialine environment reveals a number of characteristics, such as well-developed halocline and hypoxia. Water samples for Cu, Cd, Pb, Zn and DOC determination were collected during 2009 by speleo scuba-diver. Metal measurements were performed by differential pulse anodic stripping voltammetry (DPASV), while DOC was obtained by high temperature catalytic oxidation using a non-dispersive infrared detector. Trace metals concentrations are presented as dissolved and total fractions. Total metal concentrations were measured in acidified (pH < 2), unfiltered and UV irradiated samples, while dissolved metal and DOC concentrations were obtained from filtered (0.45 µm) samples. Additionally, temperature, salinity, pH and dissolved oxygen concentration were determined directly in water column of anchialine cave. Salinity increased with depth in the range from 3 ‰ at the surface to 38 ‰ in bottom water layer, showing water column stratification.

Results and discussion

Metals concentrations throughout entire water column of Bjejajka anchialine cave were significantly higher compared to metals amount found in seawater samples taken in near vicinity (about 100 m). Total metal concentrations in cave's water column were found as follows: Pb from 0.05 to 1.4 µg L^{-1}, Cu from 0.73 to 4.82 µg L^{-1} and Zn from 0.74 to 3.05 µg L^{-1}. Moreover, cadmium concentrations in water column of Bjejajka cave were greatly elevated compared to Cd amounts found in surface seawater. In January 2009, substantial concentrations of total Cd were found in bottom water layer (300 ng L^{-1}) and in surface layer 45 ng L^{-1} in Bjejajka cave water column. However, in surface seawater samples collected in the vicinity of the Bjejajka cave, quite low total concentrations were measured, i.e. 7 ng L^{-1} Cd, 30 ng L^{-1} Pb, 200 ng L^{-1} Cu and 200 ng L^{-1} Zn. Bjejajka cave was developed in Mesozoic dolomites with limestone lenses. It has been demonstrated that dolomitic rocks can contain elevated concentrations of Zn, Pb, and Cd [1]. Mineral leaching of such lithologies is responsible for the increased Pb, Zn and particularly Cd amounts in waters of Mljet NP [2]. Cd concentrations in anchialine cave water column increase linearly with salinity (Fig. 1A). It implies mineral leaching of dolomitic rocks by seawater entering the cave, hence carrying Cd into the bottom layer of cave's water column. Also, cave's water receives considerable metal amounts by wet deposition and soil weathering. Hence, Cd, Pb and Zn contents have been enhanced in cave's upper water layers during and after rainy periods. Furthermore, a colony of bats inhabits Bjejajka cave. Cadmium concentration in guano of these flying mammals was found to be 1.8 mg kg^{-1} wet weight. Since the Cd concentration in bat guano has not been reported so far, we compared it with amounts usually reported in Eastern Adriatic Sea coastal sediments that contain significantly lower Cd content (< 0.8 mg kg^{-1} wet weight) [3]. Apparently, natural process of bat guano leaching also was the source of cadmium elevated concentrations in water column and sediment of Bjejajka cave.

DOC content in cave's water column was enhanced (up to 10.5 mg C L^{-1}) compared to seawater (up to 3 mg C L^{-1}) and generally decreases with depth and linearly with increasing salinity (Fig. 1B). It suggests that terrestrial input by soil weathering and bat guano leaching would be the source of elevated DOC concentrations.

In studied area, without considerable anthropogenic influence, natural processes of mineral leaching, soil weathering and input of terrestrial natural material were likely responsible for significantly elevated trace metals and DOC concentrations in water column of an anchialine cave.

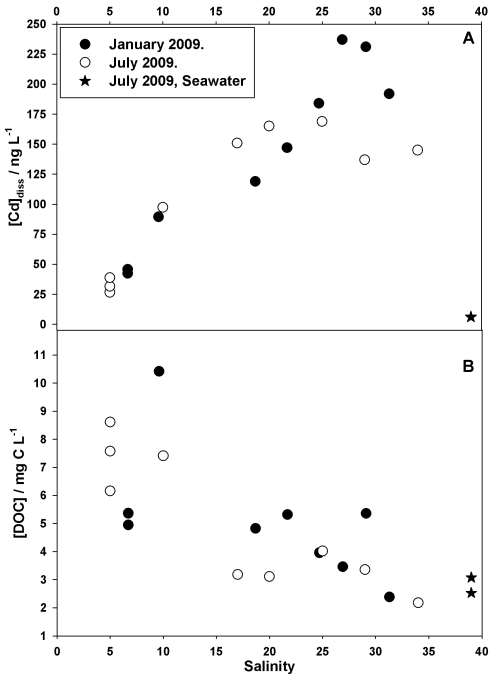

Fig. 1. Seasonal dissolved Cd (A) and dissolved organic carbon (B) concentrations vs. salinity (ppt) in Bjejajka cave water column.

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