NAT. CROAT. | VOL. 21 | Suppl. 1 | 28–31 | ZAGREB | September 30, 2012

PRELIMINARY STUDY OF TRACE METAL DISTRIBUTION IN THE WATER COLUMN OF URINJSKA ŠPILJA ANCHIALINE CAVE (CROATIAN ADRIATIC COAST)

VLADO CUCULIĆ[1,*], NEVEN CUKROV[1], DARIO OMANOVIĆ[1] & BRANKO JALŽIĆ[2,3]

[1]Ruđer Bošković Institute, Division for marine and environmental research, Bijenička 54, 10000 Zagreb, Croatia

[2]Croatian Natural History Museum, Demetrova 1, 10000 Zagreb, Croatia

[3]Croatian Biospeleological Society, Demetrova 1, 10000 Zagreb, Croatia

Temporal and vertical distributions of dissolved and total ecotoxic trace metals Cd, Co, Cu, Ni, Pb and Zn in the water column of Urinjska Špilja anchialine cave were studied by voltammetry. The physico-chemical parameters salinity (S), temperature (T) and dissolved oxygen (DO) concentration were also measured. Although the cave is situated in the vicinity of the biggest Croatian oil refinery, no anthropogenic influence was observed.

Key words: anchialine cave, trace metals, voltammetry, Croatian Adriatic karst

INTRODUCTION

Urinjska Špilja is the first anchialine cave to have been described in Croatia. This was the achievement of the Croatian geologist Josip Poljak, who reported (POLJAK, 1920) brackish water in the cave and drew a topographical map. Moreover, the first described snorkel dive (1963) in an anchialine cave was completed in the Urinjska Špilja cave by Bruno Puharić (CUKROV *et al.*, 2009).

Urinjska Špilja is 115 m long and 24 m deep (9 m dry part and 15 m of water), situated at Croatian north-eastern Adriatic coast, approximately 70 m from the sea. It is typical karst cave located in tectonic contact of upper Cretaceous limestones and dolomites. Urinjska Špilja cave is located in the close vicinity of the main Croatian oil refinery (Fig. 1) and we assumed there would be notable anthropogenic influence on the cave ecosystem.

MATERIAL AND METHODS

Water samples were collected once a month from January to March 2012 by a speleo scuba diver taking samples from progressively increasing depths in 1 L FEP (Fluorinated Ethylene Propylene) bottles previously cleaned with nitric acid and rinsed with Milli-Q® water. Total and dissolved fractions of trace metals were measured by stripping voltammetry, as described earlier (CUCULIĆ *et al.*, 2009, 2011; CUKROV *et al.*, 2006). Physico-chemical parameters (S, DO and T) were measured *in situ*.

* cuculic@irb.hr

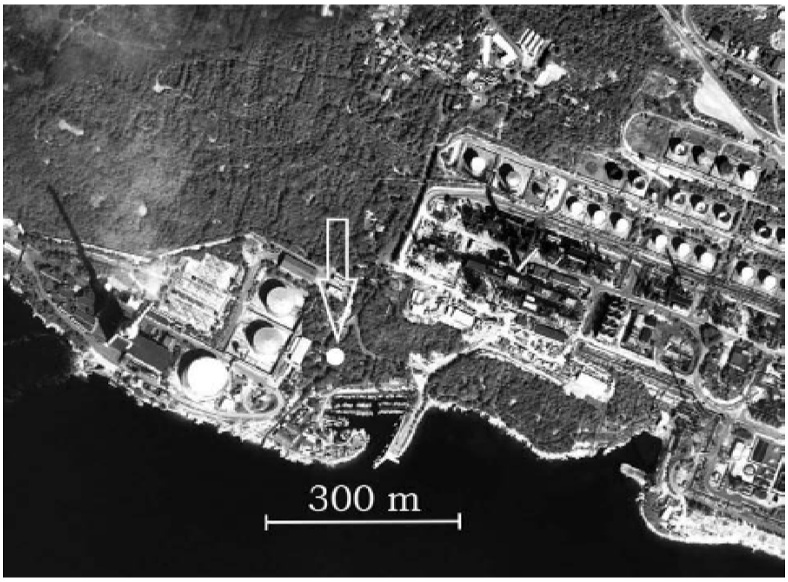

Fig. 1. Satellite photo of the study area. Arrow points at Urinjska Špilja anchialine cave.

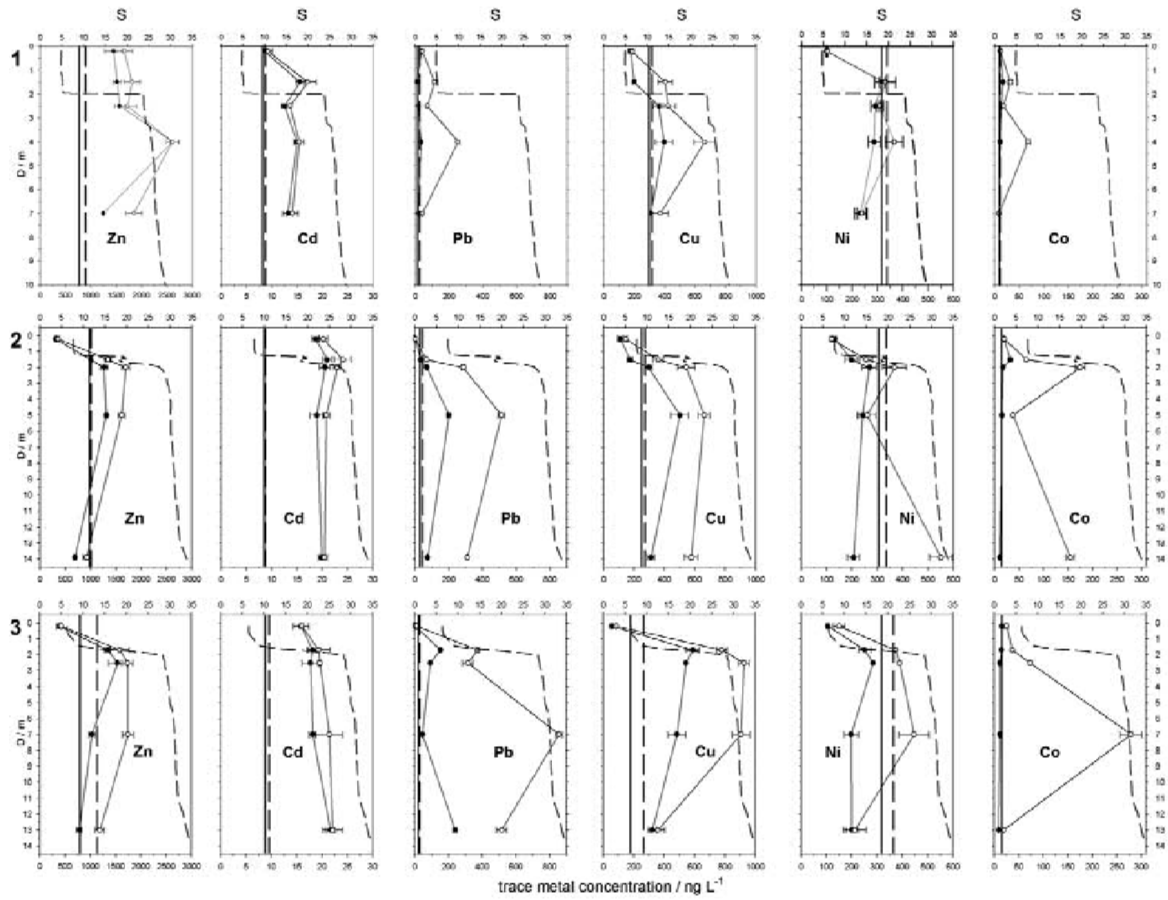

Fig. 2. Vertical distributions of trace metals in water column of Urinjska Špilja anchialine cave. Row 1 = January sampling, row 2 = February sampling and row 3 = March sampling. Concentrations are given with 95% confidence intervals. Empty circles – total metal and full circles – dissolved metal concentrations. Full line – dissolved metal and dashed line – total metal concentrations in surface seawater. Dashed curve represents halocline.

RESULTS AND DISCUSSION

Vertical distributions of trace metal concentrations and salinity in the anchialine water column in Urinjska Špilja cave are summarized in Fig. 2. Salinity follows the typical anchialine water column pattern, with the sharp halocline between 1 and 2 meters depth (S = 4–30), up to S = 30–35 at the bottom. Dissolved oxygen concentrations varied from approximately 10 mg L^{-1} in the surface water layer to a minimum of 6 mg L^{-1} at the bottom in January. Obviously, the anchialine cave is well aerated from the atmosphere. Additionally, the cave's surface water layer was flowing toward the open sea during all three samplings. Water temperatures in January varied between 10.1 at the surface and 13.7 °C at the bottom of the water column. In March, water temperature variation was smaller, from 11.2 at the surface to 12.4 °C measured in the bottom layer at 13.5 m.

Due to a considerable intrusion of fresh water (frequently rainy events before and during sampling), the cave's surface water layer was diluted. Therefore, both total and dissolved metal concentrations were below those found in the surface seawater. Only the cadmium vertical concentration range was completely above concentrations found in surface seawater (on average, twice as high). Higher levels of cadmium throughout the whole water column were probably due to Cd leaching from dolomites, which can contain higher amounts of this element (CUCULIĆ *et al.*, 2009). Generally, concentrations of all analysed trace metals (total and dissolved) in the cave's sub-surface water layers were higher than in surface seawater samples taken outside of the cave in the near vicinity (70 m).

In February and March, during and after rainy events, concentrations of total Pb, Cu and Co in the sub-surface samples of the cave were found to be significantly elevated compared to surface seawater samples and to values in the cave water column taken in January. Maximal concentration of total Pb in March was above 850 ng L^{-1}, while in January it was below 300 ng L^{-1}. Similarly, total Cu and Co in March were slightly above 900 and 280 ng L^{-1}, respectively, while in January total Cu was 660 ng L^{-1} and Co ~60 ng L^{-1}. Higher concentrations of total Pb, Cu and Co in March were mainly terrigenous; intense rainy events followed by soil weathering leached out particulate metals into the cave water body. It is known that these metals, especially Pb, have a strong capacity for adsorption onto particulate matter (BILINSKI *et al.*, 1991).

In conclusion, trace metal concentrations in the cave's water column were found to be quite low, especially when compared with the values determined in the anchialine caves of Croatian protected areas (CUCULIĆ *et al.*, 2011). Also, values were not significantly higher than those reported for the clean Croatian Adriatic coastal seawater (CUCULIĆ *et al.*, 2009). This result confirms preliminary research (CUKROV *et al.*, 2006) and comes as surprise taking into account that the cave is located in the close vicinity of the biggest Croatian oil refinery. Therefore, it is very important to study the complex and vulnerable karstic systems, such as anchialine caves and to monitor their environmental status on a regularly basis.

REFERENCES

BILINSKI, H., KOZAR, S., PLAVŠIĆ, M., KWOKAL, Ž. & BRANICA, M., 1991: Trace-Metal Adsorption on Inorganic Solid-Phases under Estuarine Conditions. Marine Chemistry **32**, 225–233.

CUCULIĆ, V., CUKROV, N., KWOKAL, Ž. & MLAKAR, M., 2009: Natural and anthropogenic sources of Hg, Cd, Pb, Cu and Zn in seawater and sediment of Mljet National Park, Croatia. Estuarine, Coastal and Shelf Science **81**, 311–320.

CUCULIĆ, V., CUKROV, N., KWOKAL, Ž. & MLAKAR, M., 2011: Distribution of trace metals in anchialine caves of Adriatic Sea, Croatia. Estuarine, Coastal and Shelf Science **95**, 253–263.

CUKROV, M., JALŽIĆ, B., OMANOVIĆ, D. & CUKROV, N. 2006: Tragovi metala u vodenom stupcu Urinjske špilje. Subterranea Croatica **7**, 25–30. (In Croatian)

CUKROV, N., JALŽIĆ, B., BILANDŽIJA, H. & CUKROV, M., 2009: Research history and anchialine cave characteristic in Croatia. Anchialine ecosystems: Reflection and prospects / W. HUMPHREYS (Ed.). Palma de Mallorca, p. 19–20.

POLJAK, J., 1920: Pećine hrvatskog krša III. Pećine Hrvatskog Primorja od Rijeke do Senja. Prirodosl. istraž. **15**, 219–266 (in Croatian).