

Ecotoxic metal concentrations in sediment from Croatians anchialine caves

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A fundamental ecological aspect of ecotoxic metals is their toxicity for living organisms and the lack of biodegradability. Once introduced into the aquatic environment, ecotoxic metals are redistributed throughout the water column, deposited or accumulated in sediments and consumed by biota. Anchialine caves are mostly small and isolated, hence, very sensitive ecosystems. Therefore, it is very important to know ecotoxic metal concentrations, because elevated metal concentrations in these systems are often considered as indicators of anthropogenic influence. In all aquatic ecosystems, sediments act as ultimate sinks for ecotoxic metals. However, sediments are not only a sink, but may act as a source of metals in the aquatic environment. In order to evaluate the metal pollution in sediments, it is very important to be able to distinguish between the natural trace element record derived from sedimentation and records that may reflect the anthropogenic impact. For this is important to know present concentrations in as many as possible anchialine caves sediments.

As a whole Croatian Adriatic coast is a karst region, there are situated numerous anchialine caves. Sediment samples were collected from 6 anchialine caves (Jama kod Komune, Urinjska špilja, Vrtare Male, Sumporna špilja mala, Sumporna špilja velika and Šipun) in the period between 2005 and 2007. Surface sediment samples were collected by scuba diving using hand-made and hand-driven Plexiglas cores.

Sediments were wet sieved using Sieve shakers AS 200 Digit with 0.063 mm standard Retsch sieves (Haan, Germany) and the fine fraction (<63 µm) was separated for future analysis. Chemical analyses were performed by ICP, ICP/MS and for Hg determination by cold vapour atomic absorption spectroscopy. The sample material was digested with aqua regia digestion (0.5 ml H₂O, 0.6 ml concentrated HNO₃ and 1.8 ml concentrated HCl).

Chemical contents were obtained for 63 elements and in this paper Hg, Cr, Mn, Co, Ni, Cu, Zn, As, Ag, Cd and Pb concentrations were evaluated.

Total metal concentrations in anchialine caves sediments varied for Hg (0.15 to 1.06 mg/kg), for Cr (29 to 234 mg/kg), Mn (215 to 684 mg/kg), Co (6.9 to 18.2 mg/kg), Ni (57 to 225 mg/kg), Cu (25 to 77 mg/kg), Zn (41 to 133 mg/kg), As (9.9 to 41.6 mg/kg), Ag (0.07 to 0.40 mg/kg), Cd (0.23 to 0.61 mg/kg) and Pb (14 to 95 mg/kg).

In order to evaluate possible toxicity, sediments were compared with Sediment Quality Guidelines from National Oceanic and Atmospheric Administration, USA (1999). ERM (effect range low) and ERM (effect range median) were calculated for 9 ecotoxic metals (Hg, Cd, Pb, Cu, Zn, Cr, Ni, As and Ag). ERL guideline represents concentrations below which effect were rarely observed, while ERM guideline represents concentrations above which toxic effect frequently occur.

The concentration levels of mercury were seriously elevated (above ERM guidelines) in Šipun and Urinjska špilja caves, and elevated (above ERL guidelines) in all other researched caves, except Vrtare Male cave. Chromium concentrations levels were elevated (>ERL) in four caves. The concentrations levels of nickel were seriously elevated (>ERM) in all researched caves. Copper concentrations level were elevated (>ERL) in all caves except Urinska špilja cave. Arsenic concentrations levels were elevated (>ERL) in all caves. The concentrations level of zinc, silver and cadmium were below ERL guidelines. Similarly, lead concentrations levels were below ERL guidelines except in Šipun cave, where are above ERM guidelines.

It is important to understand that these guidelines (ERM & ERL) were not derived as toxicity thresholds. That is, there is no assurance that there will be a total lack of toxicity when metal concentrations are less than the ERL values. Similarly, there is no assurance that samples in which ERM values are exceeded will be toxic. Toxicity, or a lack thereof, must be confirmed with empirical data from toxicity tests.

NOAA (1999). National Oceanic and Atmospheric Administration, Sediment Quality Guidelines developed for the National Status and Trends Program. (<http://archive.orr.noaa.gov/cpr/sediment/SPQ.pdf>)