TRACE METAL ACCUMULATION IN THE SEDIMENT OF THE SUBMARINE CAVE "ZMAJEVO UHO" (SOLINE BAY, CROATIA)

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Abstract

A vertical profile in a sediment core from the submarine cave "Zmajevo uho" has been analysed for granulometric composition, organic matter, carbonate contents and trace metal concentrations (Cd, Pb, Cu, Zn and Ni). The carbonate content and granulometric composition are interrelated indicating that sediments from the cave having more carbonates are usually coarse grained. The concentrations of all trace metals decreased down the sediment core and showed good correlation with the organic matter content. The surface enrichment of Pb, Cu and Zn is an indication of anthropogenic influence to the sediment. The cave acts as a trap where a significant accumulation of different contaminants may occur.

Key-words : sediments, trace elements, Adriatic Sea

Introduction

The role of sediments has been recognised to be increasingly important in determining the distribution and fate of pollutants released into water bodies. Sediments can act as both a sink and source of pollution, and diagenetic reactions can remove or dissolve contaminants (such as trace metals) producing a concentration gradient at the sediment-water interface, the direction of which determines the water fluxes of contaminants. Therefore, the determination of trace metal concentrations in sediment is important in assessing the extent to which the marine environment is contaminated. The proportions of natural and anthropogenic trace metal levels in sediments are difficult to determine, since sediments can be deposited under a wide variety of environmental conditions. Trace metal distributions in cores of nearshore sediment may reflect the natural history of anthropogenic trace metal inputs [1].

The "Zmajevo uho" submarine cave is a karst phenomena located in the karstic region near Rogoznica, Soline Bay on the Adriatic sea (Figs. 1 and 2). Its entrance is located at a depth of 1.5 m and is less than 1 m in diameter. The total water depth is 29 m. Because of the location and size of the entrance, it is assumed that the cave has not suffered anthropogenic impact.

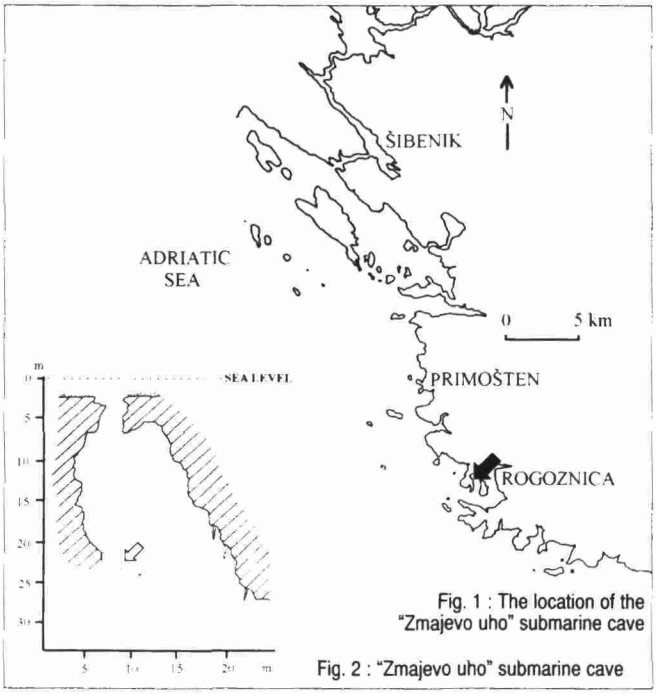

Fig. 1 : The location of the "Zmajevo uho" submarine cave

Fig. 2 : "Zmajevo uho" submarine cave

Methods

A sediment core (21 cm long) was sampled by a scuba diver using a plastic tube 3 cm in diameter. The sediment core was sliced into 2 cm long subsamples. Organic matter and carbonate contents as well as trace metal concentrations (Cd, Pb, Cu, Zn, and Ni) were determined in the subsamples. Granulometric composition of the sediment was determined by sieving and areometring (Casagrande). The organic matter content was determined as a weight loss by weighing the sample before and after H_2O_2 treatment followed by ignition at 450°C. The carbonate content was determined as weight loss after treatment with 4M HCl.

Trace metals were determined by the ET-AAS method using Perkin-Elmer 1100 B spectrophotometer. The accuracy of the analytical procedure was repeatedly checked by analysing samples of reference sediment standards (SRM 1646 estaurine sediment).

Results and discussion

Granulometric composition of the sediment core is shown in Table 1. The proportion of coarse particles (> 63 μm) increases with the sediment depth, while small particles (silt/clay grade) predominated in the upper layers of sediment. Upper sediment layers were sandy silt (1-12 cm), the middle layer was silty sand (13-20 cm) and the deepest was sand (21-24 cm).

Table 1. Granulometric composition of the sediment core (clay < 4 μm, silt 63-4 μm, sand > 63 μm).

1-12 cm	4.0 % clay	
	65.0 % silt	Sandy silt
	20.0 % sand	
13-16 cm	2.5 % clay	
	25.5 % silt	Silty sand
	48.0 % sand	
17-20 cm	1.0 % clay	
	17.0 % silt	Sand
	65.0 % sand	
21-24 cm	0.5 % clay	
	22.5 % silt	Sand
	66.0 % sand	

Carbonates (range 66.29-93.13%) were the main mineralogical component of the sediment core. Carbonate content increased with the sediment depth (Fig. 3) as the proportion of coarse particles increased. Organic matter content decreased with sediment depth as coarse particles and the carbonate content increased (Fig. 3). Linear regression between the organic matter and carbonate contents showed a significant negative correlation (Table 2).

The results obtained for the trace metal concentrations are illustrated in Figure 4. Increased surface concentrations (upper 10 cm) were observed for all the trace metals examined, especially Pb. Although the sediment originates from an area which is not considered to be polluted, the increased concentrations in the surface layer suggest some kind of contamination by these metals. While leaded gasoline would appear to be the main source of Pb, agricultural runoff may be an additional source of Cu, and domestic waste water a point source of Zn [3]. Nevertheless, the pathway in which these metals reached the cave is not clear. Namely, the entire area is karstic and the cave is very probably directly connected to ground waters. Therefore, there are two possible transport pathways for these trace metals: indirectly by sedimentation from the sea or directly by ground water.

The distribution of Pb, Cd, Cu, Ni and Zn in the sediment core is most likely controlled by the organic matter content. The trace metal concentrations in the core are correlated with the organic matter