Distribution of redox-sensitive trace elements in the water column and sediments of seawater lake (Rogoznica lake, Croatia) an unique anoxic environment on the Adriatic coast

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Position of Rogoznica Lake

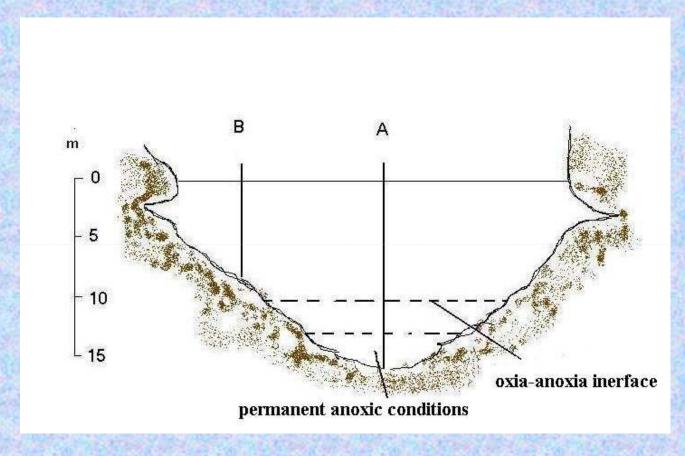Seawater lake - karstic depression filled with seawater

Area 10 276 m2

Max. depth 15 m

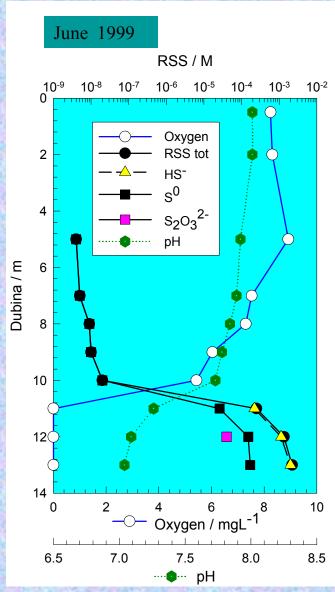-the Lake is surrounded with sheer cliffs (4 - 23 m)

- there is no visible conection with the surrounding sea but lake tides are visible on the clifs (indication of underground water conection through the porous karst)

-permanent stratification – zone of well oxygenated surface water and zone of totally anoxic deep water (the boundary is at 9-12 m depth) characterized by **high concentrations of reduced sulfur species (up to 10-3 M, mainly in the form of sulfide); nutrients (NH_4^+, up to 150 uM; PO_4^{3-}, up to 22 uM; SiO_4^{4-}, up to 400 uM) and DOC (up to 6 mg/l)**
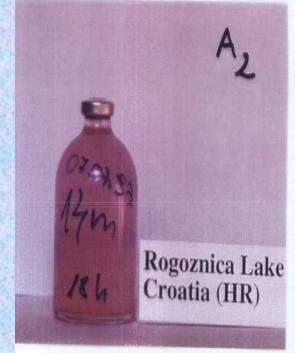
Profile of Rogoznica Lake

Eh(B)=100 mV   **Eh(A)= -420 mV**

pH = 6.98 at both sites

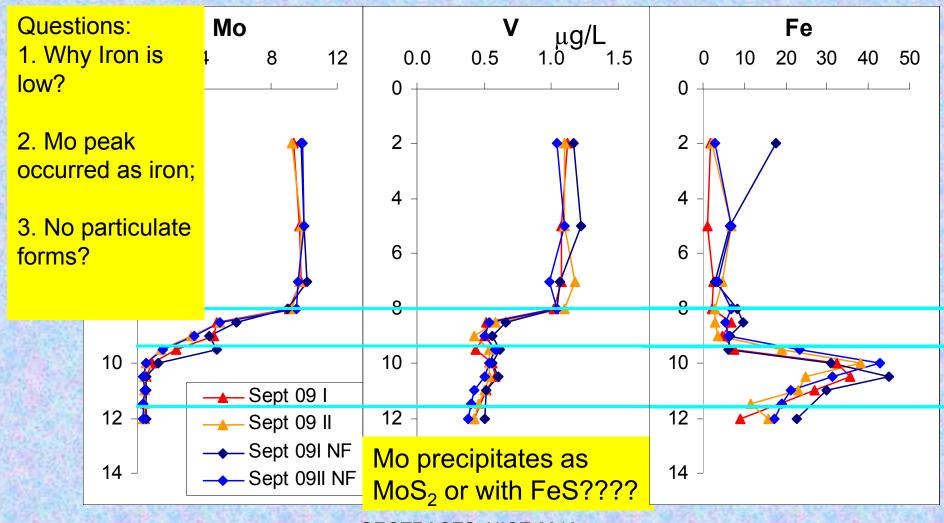GEOTRACES, NICE 2010

June 1999

RSS / M

Ciglenecki et al., Journal of Marine Systems. (2005) 56, 29-44.

E. Bura-Nakić, G.R. Helz, B.Ćosović, I.Ciglenečki,
Geochim.Cosmochim.Acta (2009) 73, 3738

GEOTRACES, NICE 2010

Rogoznica Lake

Questions:
1. Why Iron is low?

2. Mo peak occurred as iron;

3. No particulate forms?

Mo — V μg/L — Fe

Sept 09 I
Sept 09 II
Sept 09I NF
Sept 09II NF

Mo precipitates as MoS_2 or with FeS????
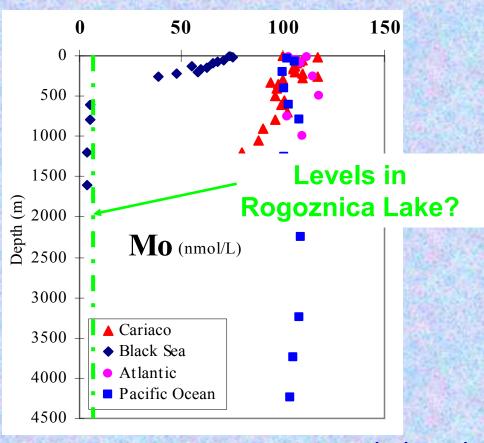
GEOTRACES, NICE 2010

Helz,Mikac,Bura-Nakic,Ciglenecki in preparation

Vertical Distribution of Mo in the Ocean

Levels in Rogoznica Lake?

Mo (nmol/L)

Depth (m)

▲ Cariaco
◆ Black Sea
● Atlantic
■ Pacific Ocean

A slight decrease at the surface of Atlantic and Pacific ⇒ **Algal uptake and particle adsorption** (e.g., Falkowski et al., 1983; Tuit and Ravizza, 2003).

Depleted in deep waters in the Cariaco Trench and Black Sea ⇒ **Reduction of Mo** are expected, but no direct measurements on speciation in seawater yet!

GEOTRACES, NICE 2010

In average world river: Mo: 5 nmol/L, (Morford, 1999).   Puzzle?   6

Sediment mineral composition

- Sediment is characterized as authigenic carbonate sediment of mainly biogenic origin with relatively high sedimentation rate (**0.093** g/cm^3/year) (*Mihelčić et al., Sci. Total Environ. 1996,182,105-115)*

- Major mineral is calcite (50-90%), followed by aragonite, quartz, dolomite and pyrite

- Traces of pyrite are detected in sediment samples from 8 (B site) and 14 m depth (A site).

Ciglenečki et al., Water, Air and Soil Polution: Focus. 6 (2006) 537-545.

GEOTRACES, NICE 2010

Concentrations of Fe, Mn and Mo in bottom water, porewater and sediments of the Rogoznica Lake at location sites A and B.

Depth/cm	A						B					
	Porewater(μgl^{-1})			Sediment (mgl^{-1})			Porewater(μgl^{-1})			Sediment (mgl^{-1})		
	Fe	Mn	Mo	Fe	Mn	Mo	Fe	Mn	Mo	Fe	Mn	Mo
Bottom water	16.8	89	2.4				1740	9	5.8			
0-5	204	278	2	5700	97	38.4	1890	597	2015	3900	59	5.71
5-10	5	142	3	5400	103	36.4	2280	162	3950	2800	26	8.05
10-15	5	149	5	4800	81	34	2295	30	5635	3100	23	17.2
15-20	5	153	5	4800	92	41.3	-	-	-	4000	121	15.9
20-25	5	147	47	4100	91	81.4	-	-	-	-	-	-

GEOTRACES, NICE 2010

Ciglenečki et al., Water, Air and Soil Polution: Focus. 6 (2006) 537-545.

Conclusions related to GEOTRACES objectives

- The main geochemical processes influencing the distribution and speciation of dissolved redox-sensitive metals in the hypoxic/anoxic environments appear to be transformations between their oxidation states, interaction with RSS and organic matter and/or formation of soluble and precipitated metalsulfide species

- Chemical speciation within the sediments tend towards equilibrium between porewaters and solid phase according the prevailing environment conditions such as redox, pH, salinity, DOC

- Regarding the sedimentary enrichment of Mo (up to 81 mg/kg) the Rogoznica lake can be characterized as a typical anoxic environment similar to well known anoxic systems like the Black Sea, Framvaren Fjord and Lake Pavin.