

## **Polysulfide dynamics in a marine euxinic environment (Rogoznica Lake, Croatia); importance of anoxygenic photosynthesis**

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Rogoznica Lake (RL) is an eutrophic and affected by climate change marine lake on the eastern Adriatic coast (43°32'N, 15°58'E). During the year the lake is strongly stratified into oxic and anoxic layers. Due to intense sulfate reduction, anoxic bottom layer is enriched in dissolved HS<sup>-</sup> (up to 5 mM). At the oxic-anoxia boundary, a pinkish colored chemocline (up to 50 cm) develops seasonally, and it is characterized by a dense population of purple phototrophic sulfur bacteria (PSB) [1]. PSB are known to store sulfur S(0) intracellularly, which by cell lysis would be released in water, and under euxinic conditions solubilized by HS<sup>-</sup> in nucleophilic polysulfides, S<sub>x</sub><sup>2-</sup>. S<sub>x</sub><sup>2-</sup> can play an important role in metal, carbon and sulfur cycles.

In this work, for the first time, differential pulse voltammetry (DPV) was used for direct determination of S<sub>x</sub><sup>2-</sup> in euxinic marine environment (RL), where total RSS (mainly HS<sup>-</sup>) varied between 0.1 and 3 mM. Concentration of S<sub>x</sub><sup>2-</sup>, as well as total RSS, varied seasonally depending on the chemocline position, light intensity and HS<sup>-</sup> concentration. During stratification in summer, when PSB reached maximum abundance, the presence of S<sub>x</sub><sup>2-</sup> was determined in the highest concentrations (up to 0.1 mM S(0)). Maximum was found approx. 1 m below the chemocline, where due to sinking of lysed PSB cells, maximum concentration of biologically S(0) would be expected.

Presence of S(0) granules in the cells and their release into water upon cell lyses, induced in laboratory conditions by acidification of the studied sample, was confirmed by AFM. The acidification as a standard methodological step in electroanalytical determination of volatile and nonvolatile RSS (RSS<sub>NV</sub>) [2] are now proved to overestimate RSS<sub>NV</sub> for 30-50% in samples enriched in PSB. Results from this study clearly prove the S<sub>x</sub><sup>2-</sup> presence in the anoxic water of RL and shed light on a crucial role of the PSB in their formation and dynamics.

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[1] M. Čanković, J. Žučko, I. Dupčić Radić, I. Janeković, I. Petrić, I. Ciglencečki, G. Collins, *Syst Appl Microbiol*, 2019.

[2] E. Bura-Nakić, G.R. Helz, I. Ciglencečki, B. Čosović, *Geochim Cosmochim Acta*, 2009.