



Biogeochemical sulfur cycling in the water column of a shallow stratified sea-water lake: Speciation and quadruple sulfur isotope composition

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Results of the analysis of concentrations of sulfate, sulfide and intermediate sulfur species, as well as quadruple sulfur isotope compositions of sulfate, acid volatile sulfide (AVS) and zero-valent sulfur (ZVS), in Lake Rogoznica (Croatia) [1] are presented.

Lake Rogoznica (Croatia) is a seawater lake located on the Gradina Peninsula (43°32'N, 15°58'E) approximately 100 m from the open Adriatic Sea with very limited water exchange with the open sea through porous karsts. The lake has an area of 10276 m² and maximum depth of 15 m. The lake is intensely eutrophicated and thermo-haline stratified from spring to autumn.

The chemocline, which was located at 8.5 – 9.5 m depth at the time of samplings, supports a dense population of purple phototrophic sulfide oxidizing bacteria from the genus *Chromatium*. Application of a one-dimensional depth-derived model of sulfide in the deep waters of Rogoznica Lake [2] showed that microbial sulfate reduction in the sediment and water column are the main sources of hydrogen sulfide. Multiple sulfur isotope composition of AVS in the chemocline of the lake is consistent with phototrophic sulfide oxidation, though multiple sulfur isotope fractionation between ZVS and AVS differs from fractionation measured for the culture of phototrophic sulfide-oxidizing bacteria *Chlorobium tepidum* during oxidation of sulfide [3].

A steep gradient of sulfide does not allow biological sulfur disproportionation in the hypolimnion at depths of more than 1 m below the chemocline without an external sulfide sink. Multiple sulfur isotope fractionations between sulfate and sulfide are also consistent with the assertion that disproportionation is not a dominant process below the chemocline.

Despite the absence of a clear signal for sulfur disproportionation in multiple sulfur isotope values, $\delta^{34}\text{S}$ fractionations between sulfate and sulfide are in the range of 43.8 - 45.2‰ which is close to an upper limit of isotope fractionation by sulfate reducers in pure and enrichment cultures in the laboratory. Results of our work agree well with recent reports which utilized a multiple sulfur isotope analysis approach to suggest that the presence of sulfur disproportionation is not necessary for fractionations as high as 54‰ in the Cariaco Basin [4] and up to 45‰ in Lago di Cadagno [5].

From the results of two samplings performed within a three days interval, we can conclude that although chemical parameters of the system may vary on a daily basis with chemocline depth fluctuations, these fluctuations do not affect the isotopic composition of AVS and sulfate, but may affect the isotopic composition of sulfur intermediates, such as ZVS.

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