

SULPHUR SPECIATION IN TWO CONTRASTING ANOXIC ENVIRONMENTS

Irena Ciglencčki¹, Elvira Bura-Nakić^{1*}, Didier Jézéquel² and Eric Viollier²

¹ Center for Marine and Environmental Research, Rudjer Bošković Institute, Zagreb, Bijenička bb, 10 000 Zagreb, Croatia

² Laboratoire de Géochimie des Eaux, Institut de Physique du Globe de Paris, 4 place Jussieu - Case 89, 7525 Paris Cedex 05 - ebnakic@irb.hr

Abstract

Sulphur electrochemical speciation techniques were applied to understand the chemistry and cycling of sulphur in two meromictic lakes: seawater lake, Rogoznica Lake (Croatia) and crater lake, Pavin Lake (France). Using a cathodic stripping cyclic and linear sweep voltammetry we aimed to make distinguish between free and metal sulphide species in the anoxic deep layers. 90% of determined sulphur species in the anoxic bottom water of Rogoznica Lake are in the form of free sulphide, while opposite result was observed in the Pavin Lake. There was no presence of free sulphide detected; all sulphur was in the form of metal sulphide species, which regarding a prevalence of Fe can be ascribed to the presence of FeS.

Keywords : Anoxia, Electrochemistry, Chemical Speciation.

The stagnant deep layers of meromictic lakes (monimolimnion), which usually exhibits an accumulation of dissolved elements, is very suitable for studies of biogeochemical processes in anoxic conditions. Anoxic environment usually produces hydrogen sulphide that can be oxidized back to sulphate by oxygen, iron (III) and manganese (III, IV) compounds. The oxidation of sulphide frequently leads to intermediate oxidation state compounds, such as elemental sulphur, polysulphide and thiosulphate which may be used by bacteria or may react with metals and organic compounds. The biogeochemical/redox cycling of sulphur is important to the function of anoxic ecosystems and has a profound influence on the distribution and speciation of other substances amongst are the most important biologically active and redox sensitive elements such as Fe, Mn, Mo, Cu.

Reduced sulphur species (RSS), including sulphide, polysulphide, thiosulphate, and thiols (or sulphhydryl compounds) have strong affinity to biologically active trace metals, changing their availability to living organisms. They could form stable complexes with most heavy metals of environmental concern. The complexation of metals with sulphide and/or polysulphide has been found to be able to control their solubility, mobility, and speciation in anoxic environments. In addition to acting as dissolved complexing ligands, RSS may exist in colloidal and particulate phases, and the interaction between trace metals and reduced sulphur may, therefore, influence the distribution of biologically active trace metals among dissolved, colloidal, and particulate fractions. On the other side H₂S is very toxic to living organisms and its removal by oxidation and/or precipitation is of great importance in maintaining the healthy state of environment.

Using different electrochemical methods it is possible to measure a variety of soluble sulphur compounds (1-3). In this work we used mercury electrode to measure different soluble and particulate sulphur species including H₂S, polysulphide, thiosulphate, elemental sulphur, thiols and metal sulphide species in two contrasting anoxic environments: seawater lake Rogoznica Lake on the east Adriatic coast and Pavin Lake in French Massif Central. Both lakes present a stable anoxic deep layer which is in Pavin Lake situated from 62 m depth to the bottom (92 m) while in more shallower Rogoznica Lake this layer is from 10 to 15 m depth (4,5). At the boundary oxic-anoxia a stable oxic-anoxic interface can be found in both lakes. This interface usually is area where major biogeochemical processes are taking place.

In the interface layer, in Rogoznica Lake the presence of elemental sulphur in relative high concentrations (up to 30 μM) as well as thiosulphate (up to 50 μM) can be found. Elemental sulphur even in the higher concentration was also determined in the anoxic water layer (up to 140 μM) where such high numbers can be explained by the presence of polysulphide. Anoxic layer in Rogoznica Lake is characterized by relative high concentration of free HS⁻, up to 10⁻² M which completely binds and precipitates almost completely metals from the water phase. In the interface layer of Pavin Lake, we found only presence of elemental sulphur (up to 2 μM), which was also in the similar concentrations determined in the anoxic deep water. Sulphur speciation in anoxic deep water of Pavin Lake was completely different than in Rogoznica Lake. A prevalence of Fe(II) in Pavin Lake, up to 1000 μM, whereas dissolved Mn was only 25 μM, indicates that Fe is the dominant metal involved in sulphur redox cycling and precipitation. Consequently, in anoxic deep layer of lake Pavin no presence of free HS⁻ was found; all sulphur detected was in the form of FeS and soluble elemental S.

In this paper for the first time the typical voltammograms of the Pavin

Lake samples with visible peaks of FeS species will be presented. Preliminary results on sulphur speciation in the interface and anoxic deep water of the Pavin Lake will be discussed.

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