

# **The impact of oxygen conditions on sulfur forms in the sediments of the Gulf of Gdańsk**

Joanna Kielczewska

The Baltic Sea, due to its location, the limited exchange of waters between the Baltic and North Sea and large river inflow, is particularly sensitive to the impact of human activities. One of the main problems is eutrophication, which leads to oxygen deficiencies on the bottom. That's why the sulfate reduction is the most important pathway of organic matter degradation in sediment and sulfate is considered to be the most important and dominant electron acceptor. As a result of the dissimilatory sulfate reduction, the concentration of ammonium, phosphate, sulfide and bicarbonate ions in the pore waters increases. Moreover, sulfate can be also the electron acceptor for anaerobic methane oxidation.

The biogeochemical transformation of organic matter in sediments is possible due to the activity of sulfur-reducing bacteria (including *Desulfobacter*, *Desulfovibrio*, *Desulfotomaculum*). The by-product of dissimilatory sulfate reduction is hydrogen sulfide, which reacts with metal ions to form insoluble salts, thus determining their bioavailability and toxicity. Some of the sulfides may react violently with dissolved iron or reactive iron minerals to form amorphous iron monosulfide subsequently converted to pyrite during early diagenesis. Pyrite is the most stable compound in anoxic environment over a wide range of pH and Eh.

The most toxic form of sulfur in the marine environments is hydrogen sulfide, which determines the distribution of marine organisms. The transformation of this compound depends on the pH, salinity and oxygen conditions. The mechanism of hydrogen sulfide oxidation has not been fully understood yet, but it is known that the intermediate sulfur oxidation state compounds, as e.g. sulfites, thionates, dithionates, and also elemental sulfur, are formed. The elemental sulfur may undergo further transformations to form polysulfides. Until 2016, there were only few scientific articles dealing with the issue of sulfur speciation in the Gdańsk Basin. Due to the changing climate, the anticipated increase in the amount of precipitation may lead to a decrease in the salinity of sea water resulting in the future in lower sulphate availability. In addition, the increasing oxygen deficiency in near-bottom water and the accumulation of organic matter in sediments will affect the biogeochemical cycling of

many elements, including carbon, phosphorus, iron, and sulfur, as well as related toxic metals, such as mercury. Changes in the hydrological and biogeochemical processes in the Baltic Sea highlight the importance of reduced forms of sulfur, which role of cannot be ignored.

The aim of the study was to optimize the method for the determination of sulfur forms and to investigate their concentration in the sediments of the Gulf of Gdańsk under different hydrodynamic and oxygen conditions in the near-bottom water.

The investigations were carried out in different environmental conditions. The selected sampling sites represented:

- the erosion bottom zone with good oxygen conditions and the permanent physical activity of water preventing the deposition of grains;
- the erosion-transportation bottom with predominantly good oxygen conditions and quite strong hydrodynamics;
- the accumulation bottom zone with relatively good oxygen conditions in near-bottom water;
- the accumulation bottom zone, which includes oxygen deficiencies or anaerobic conditions for most of the year.

The research was carried out in the area of the Gulf of Gdańsk and the Puck Bay. Generally, samples of bottom waters, sediments and pore waters from 20 sampling sites were analyzed.

Research material (sediments, pore water and near-bottom water) from the Gulf of Gdańsk was collected from 15 sampling sites in March and September 2010, March, June and September 2011, March 2012, September/October 2013. The water depth at the sampling sites ranged from 40 m to 108 m. The investigations were conducted during cruises on board the ORP "Heweliusz", ORP "Arctowski" and "Oceanograf 2". The research in the coastal zone of the Bay of Puck was conducted at 5 stations located along the Hel Peninsula - in Władysławowo, Chałupy, Kuźnica, Jastarnia, and Hel. The samples were collected in June, August, October and November 2012, as well as in March and May 2013. Additionally, at the Hel station, to study short-term changes in the chemistry of marine sediments, samples were collected daily from August 20<sup>th</sup> to August 31<sup>th</sup> 2012, with exception on August 27<sup>th</sup> 2012 due to very bad weather conditions. Intact sediments cores from the deeper part of the Gulf of Gdańsk were sampled with a Niemistö gravity corer and Rumohr Lot corer. Pore water was retrieved without contact with air using Rhizon<sup>®</sup> samplers – the samples did not require additional filtration.

The samples from the shallowest sites located in the coastal zone of the inner Puck Bay were taken using a handy corer. Pore water from sandy sediments was retrieved directly using air stones with syringes. In the laboratory, when necessary, samples were filtered through Whatman GF / F glass fiber filters with a pore diameter of approximately 0.7  $\mu\text{m}$ .

At each sampling site, temperature and salinity in the bottom water were performed using a CTD profiler, or at those site located in the coastal zone of the inner Puck Bay, a conductivity meter. At the same time, the concentration of dissolved oxygen was determined using the Winkler method, and the pH was measured with a multi-parameter meter. Sediment water content was measured by drying the samples at 105°C for 24 h. Organic matter content in the sediments was then estimated as a gravimetric loss-on-ignition (LOI) after combustion at 550°C for 6 h. Sediment samples intended for the analysis of nitrogen and carbon were dried at a temperature 60°C and homogenised in a porcelain laboratory mortar. Total nitrogen, total and organic carbon were combused in a Perkin Elmer CHNS/O 2400 analyzer. Samples for organic carbon were acidified with 1M HCl. Analysis of total sulfur, organic sulfur, and sulfate sulfur were determined by oxidation with Eschka's mixture, and then precipitation as BaSO<sub>4</sub>. Analysis of elemental sulfur, the acid volatile sulfides and total reduced sulfide were precipitated as silver sulfide. The produced Ag<sub>2</sub>S and BaSO<sub>4</sub> were determined by the gravimetric method on Whatman 42 and S&S blue ribbon 589<sup>3</sup> filter papers, respectively. Concentrations of nutrients, hydrogen sulfide and sulfates were measured by means of standard spectrophotometric methods. The population size of sulfate-reducing bacteria was analyzed by using Real-Time PCR method (fine-grained sediments), the Most Probable Number of Bacteria and HACH's SRB-BART<sup>TM</sup> biodetectors (sand sediments).

The concentration of sulfur in the sediment is strongly related to the bottom type, which is also related to the depth of the station. The lowest concentration (0.04 mg g<sup>-1</sup> s.m.) of the total sulfur was observed in a coastal zone of the inner Puck Bay (the erosion type of bottom), while the highest (22.9 mg g<sup>-1</sup> s.m.) was noted in sediments below the halocline in the western part of the Gda sk Deep (the accumulation type of bottom), which is attributed to changing hydrodynamics conditions and sedimentation regimes with depth.

Despite the presence of good oxygen conditions in near-bottom water in the shallow, coastal part of the inner Puck Bay occasional occurrence of hydrogen sulphide (max. 165  $\mu\text{mol dm}^{-3}$ ) was noted. The presence of this compound was the result of high temperature and the destruction of organic matter under stable conditions. In other cases, hydrogen sulphide was associated with the migration from deeper sediments layer to the surface as a result of resuspension.

In the 30 cm layer of sediments in the Gulf of Gdańsk excluding coastal stations along the Hel Peninsula in the years 2010-2013, the concentration of individual sulfur forms increased from sulfate sulfur (0-1.1 mg g<sup>-1</sup> d.w.), through elemental sulfur (0-2.5 mg g<sup>-1</sup> d.w.), acid volatile sulfides (0-4.4 mg g<sup>-1</sup> d.w.), organic sulfur (0.1-9.2 mg g<sup>-1</sup> d.w.), up to total chromium reducible sulfides (0-31.6 mg g<sup>-1</sup> d.w.). The most important factors on which they depend are the quality and quantity of organic matter (9.1-77.0 mg OC g<sup>-1</sup> d.w.) and variable oxygen conditions (-4.4-9.3 cm<sup>3</sup> dm<sup>-3</sup>) in the near-bottom water. Pyrite is the dominant component of the reduced inorganic sulfur pool in the solid phase of the sediments (even up to 95%). Pyrite in sediments of the Gulf of Gdańsk may be formed as a result of the reaction of iron monosulfide (AVS) with hydrogen sulfide, as well as in the reaction with polysulfides, which confirms the presence of elemental sulfur in sediments. The western part of the Gdańsk Deep (station 14) characterized by calm hydrodynamic conditions, stable sedimentation conditions and oxygen deficit, was conducive to intense pyritization. The ratio (TRS:AVS) was 10.22 and attested the high degree of conversion of AVS to pyrite. In the remaining cases, it was three to twelve times lower. This may be due to persistent oxidation processes and also may indicate that the AVS prevails over formation of pyrite.

The investigation carried out in the 30 cm layer of sediments collected at the junction of the Puck Bay and the Gulf of Gdańsk at the depth of 57 m (station 2), indicated an increase in the concentration of organic sulfur with a simultaneous decrease in the molar ratio of OC:TS in sediment profile, which indicates the formation of this forms of sulfur as a result of the reduction of elemental sulfur.

The bottom of the Gulf of Gdańsk and the coastal zone of the inner Puck Bay was inhabited by sulfate-reducing bacteria. However, the population of its size differed (even by several orders of magnitude), which determined both the direction and intensity of biochemical processes during the decomposition of organic matter. Moreover, in the shallow-water of the Puck Bay, the most abundant sulfate-reducing bacteria (2400 10<sup>5</sup> cells g<sup>-1</sup> w.m.) occurred in spring and summer in the surface layer (0-2.5 cm) of sandy sediments, which could be related to intensive primary production and decomposition of organic matter as a result of dissimilatory sulphate reduction. SRB was the most likely to synthesize lactate and acetate, and the least preferred was propionate. Additionally, an interesting situation was observed in the layer of sediments 10-12.5 cm from the western slope of the Gdańsk Basin (station 11), where the maximum number of SRB corresponded to the maximum concentration of total nitrogen. It is possible that sulfate-reducing bacteria capable of utilizing alternative electron acceptors such as nitrates (V) existed there.

The sequential extraction of sulfur forms can be difficult. Due to the multiplicity of its chemical forms, methods of their determination, extraction conditions (including time and temperature of the extraction, concentration and purity of the chemical reagents), problems with reference materials and different methods of sediment sampling, the interpretation of the results can be difficult, and their comparison with literature data may be sometimes impossible.