ABSTRACT

Iron (Fe) is a limiting factor of phytoplankton primary production, hence its availability affects ocean's productivity. The size of iron input to the open ocean depends, to a large extent, on the biogeochemical processes occurring within the continental shelves. Shelf seas are characterized by a substantial spatial gradients of environmental conditions that affect the transformation of Fe. The Baltic Sea, known for its high productivity, shallow depths, strong salinity gradient, diversified oxygenation at the bottom and spatially-variable riverine inflow coming from catchments of varying anthropogenic pressure, constitutes a perfect system to study how do environmental conditions shape iron transformations. Moreover, environmental setting of the Baltic Sea, especially the presence and the extent of the anaerobic zones, are shaped by the inflows from the more saline North Sea.

In the present work, the influence of selected physical, chemical, geological, and biological factors on the iron speciation and transformations were studied within the sediments of the deep Baltic basins. The sampling spanned diverse material (near-bottom waters, interstitial waters, sediments) collected from sites representing distinct environmental conditions. Samples were subjected to the analysis of iron speciation, and quantity, as well as the form of selected elements (carbon, phosphorus, and sulphur) were also determined.

It was found, that in the anaerobic conditions, iron retention occurs through pyrite formation within the sediment, while in the presence of a strong salinity stratification, pelagic redoxcline and an anoxic conditions of the near-bottom water, pyrite can be formed already in the water column. In areas depleted of oxygen, but with a higher salinity, pyrite formation may be limited by an insufficient availability of the iron, while in the areas of low salinity, good oxygenation, pyrite formation may be limited by the availability of hydrogen sulphide, hence leading to the iron accumulation primarily as iron monosulphides. In the presence of a high concentration of phosphates in the interstitial waters, iron retention may occur via bonding of Fe(II) with phosphorus in the vivianite.

It was also shown, that iron plays an important role in the organic matter mineralization, especially at high concentration of the fluvial-origin Fe hydroxides, low salinity and low concentration of sulphates. Reactive Fe oxides are also used in the anaerobic oxidation of methane, accompanied by the formation of iron carbonates in the sediment.

The dependence of the benthic iron flux ($F_{Fe^{2+}}$) on the aerobic conditions in the near-bottom water was also determined. The improvement of conditions, resulting from the North Sea inflow,

leads to the formation of Fe(III) hydroxides, effectively decreasing $F_{Fe^{2+}}$. Additionally, the formation of Fe(III) hydroxides decreases phosphorus release from sediments, as a result of sorption on iron compounds, what reduces phosphates availability in the water column.

Determination of the environmental conditions which intensify Fe(II) retention within the autogenic minerals, allows concluding, that expansion of the anaerobic zones in the shelf seas may lead to a decrease in the iron availability in the open ocean waters. Presented here, a unique and complex, biogeochemical, and mineralogical approach to the analysis of iron transformations, allows for a better understanding of the role of the Fe in the cycles of other elements (i.e., sulphur, phosphorus, nitrogen, and carbon) and its transformation at the water-sediment interface in the deep Baltic basins. Additionally, data collected here may be used for comparative analysis with other shelf seas and be utilized for monitoring the Baltic Sea evolution.