



Manganese and iron as indicators of the processes at the water column redox interfaces

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Investigations of the redox-interfaces structure were performed in the NE Black Sea (central and coastal parts) and Norwegian fjords (Bunnefjorden, Baerumsbassenget, Hunnbunn) in 2008-2009. Bunnefjorden is a 160 m deep anoxic basin, with flushing ones per several years, redox interface at about 90 m (aphotic zone); Baerumsbassenget is a 33 m deep permanent anoxic basin with redox interface positioned in the euphotic zone (15-20 m) subjected to the river input; Hunnbunn is a 12 m deep permanent anoxic isolated inlet with a redox interface positioned in the euphotic zone (6 m) without influence of a river.

Central Black Sea is an example of balanced redox-zone structure. Dissolved Mn(II) concentration start to increase when oxygen concentration goes down below the detection limit (<3 uM), dissolved Fe(II) – at more reduced conditions at appearance of hydrogen sulfide traces. Maximum of suspended manganese is situated at the beginning of the Mn(II) onset, maximum of dissolved bounded manganese (Mn(III)) – directly under suspended manganese. Coastal stations of the Black Sea are often characterized by irregularities of iron and manganese species distribution at normal distribution of other parameters. Such structure could arise as response to oxygen injection to this layer some time ago that is observed sometimes in coastal waters under river input, currents etc. It is known that different time is needed for different elements to return to stable equilibrium state. Perhaps such distribution is intermediate stage of system conversion to initial steady state when oxygen is already consumed and it is needed longer time for manganese/iron reduction as microbial processes.

It was shown that redox zone structure in Bunnefjorden (90 m) is practically identical to the Black Sea both for absolute content of studied parameters and for its distribution shape. Redox zone structures of shallow basins Baerumsbassenget and Hunnbunn differ significantly from the Black Sea. Wide of redox zone in Baerumsbassenget varies from 2 to 9 m (2008, 2009). Redox zones of these two basins have reduced character that lead particularly to practically total disappearance of suspended manganese in samples in one day. Distribution of dissolved bounded manganese is enough chaotic in Baerumsbassenget. In Hunnbunn this manganese form was not found. It was noted that Mn(II) concentration started to increase at 7 uM of oxygen, 14 m depth, and manganese reduction in this zone must be an aerobic process. The highly organic nature of the water column in the fjords suggests that the breakdown of humic acids may be critical in the early redox cycling of manganese. All mentioned above concerns the iron cycle too. The appearance of Fe(II) started in the Baerumsbassenget and Hunnbunn not from the sulfidic boundary as in the Black Sea. It started both in the upper part of the suboxic layer, 1 m deeper than the disappearance of oxygen and at the same depth with manganese at oxic conditions.

The primary factors influencing the redox cycling of elements in these basins are limited vertical advective-mediated mixing and the rates of microbially-mediated redox reactions across relatively stable oxic/anoxic boundaries. The flushing events, river input and increased mixing from time to time and anoxygenic photosynthesis play an important role in the formation of redox zone. These processes generally operate on time scales of hours to days to months and could have seasonal character. Response time for changes in the microbial processes involved in reduction and/or reoxidation of Mn and Fe lags behind that for oxygen injection into water. Concentrations of redox-sensitive species of Mn and Fe should thus be useful as a tracer to infer prior hypoxic/anoxic conditions not apparent from oxygen levels at the time of sampling.