



## **Electrode measurements of the oxidation-reduction potential in the Gotland Deep using medium-term moored profiling instrumentation**

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The variation of in situ redox potential (Eh) was studied in the stratified water column (30 – 185 m) of the central Baltic Sea, for a period of 56 days (November, 2010 – January, 2011) using the Gotland Deep Environmental Sampling Station (GODESS) in order to identify the processes that control Eh. During the deployment of the mooring 170 profiles of hydro-physical parameters were registered, including the oxidation-reduction potential, pH, dissolved oxygen, chlorophyll a fluorescence, turbidity, temperature and conductivity.

In general, the measured Eh (with respect to standard hydrogen electrode, SHE) ranged from – 55 to 167 mV. A comparison of the measured Eh with that calculated for the particular redox couples was carried out by applying the Nernst-equation. The standard reduction potentials were corrected for temperature and pH. Furthermore, the concentrations of the most important redox components such as Fe, Mn, N, O, C and S used for comparison were estimated by using empirical functions or were based on measurements of discrete water samples, taken at the time of deployment and recovery of the mooring. The results reveal that the reduction of Fe(III) essentially controls the electrode potential of the redox sensor in most parts of the anoxic waters. Below the redoxcline the reduction of hematite and then ferric oxyhydroxid could be related to the redox potential and somewhat deeper Fe(III)/Fe(II) was found to be the dominant redox couple. Theoretically a mixed potential theory should have been applied because in natural waters a variety of redox pairs is present but Fe couples appear to dominate all the other redox equilibria. This could be explained by the relatively high exchange current of Fe and by the high concentrations (up to 1.5  $\mu\text{M}$ ) present at those depths in the study area.

However, there are still gaps in our knowledge about the cycling of redox-sensitive elements and long-term moored profiling instrumentations may help to improve our understanding. Thus, we are pursuing the use of in situ analyzers for electro active compounds on moored systems in the future. In this case, analyzer data would be associated with chemical and physical parameters measured with high resolution in time and space, giving information on mixing processes and reaction kinetics. This approach is required to assess the relevance, for instance, of intrusions of oxygenated waters, vertical eddy-diffusion and fluctuations caused by internal waves on the cycle of redox-sensitive elements. This is particularly important as lateral transport appears to play a dominant role along isopycnal surfaces, especially in medium-sized stratified basins and yet have not been investigated extensively in the Baltic Sea with respect to the cycles of the most electro-active compounds.