



Electrode measurements of the oxidation reduction potential in the Gotland Deep using a moored profiling instrumentation



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ABSTRACT

The Gotland Deep Environmental Sampling Station (GODESS) operating between 30 m and 185 m was used to assess the variation of in situ redox potential (E_h) in the stratified water column of the central Baltic Sea, for a period of 56 days (November 2010–January 2011). The aim of this study was to acquire in-depth understanding of redox variations with the overall objective to identify the processes controlling E_h . At an interval of 8 h basic hydro-physical parameters were registered, including the oxidation-reduction potential, dissolved oxygen, chlorophyll a fluorescence, turbidity, temperature and conductivity. In total 170 profiles of all parameters were obtained. The measured E_h (with respect to standard hydrogen electrode, SHE) ranged from -0.055 V to 0.167 V. After temperature and pH correction of the standard reduction potentials, a comparison of the measured E_h with that calculated for the particular redox couples was carried out by applying the Nernst-equation. Furthermore, the concentrations of the most important redox elements 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 obtained results reveal that the reduction of Fe(III) and O_2 may be the main processes controlling the E_h potential in the Gotland basin. Below the redoxcline the reduction of hematite and then ferric oxyhydroxide could be related to the redox potential and somewhat deeper Fe(III)/Fe(II) was found to be the dominant redox couple. Although mixed potential theory could have been applied, the Fe couples appear to dominate over many other possible redox equilibria. This may be explained by the relatively high exchange current of Fe and by high Fe concentrations (up to 1.5 μ M). Finally, a close correspondence to the E_h potentials measured in the oxic/hypoxic part of the water column was found considering the O_2/O_2^- and the O_2^-/H_2O_2 couples. This suggests that one-electron transfer reactions determined the E_h under oxic/hypoxic conditions.

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1. Introduction

Oxidation–reduction (redox) reactions play a major role in the biogeochemical cycling of many major and minor elements in aquatic ecosystems (Snoeyink and Jenkins, 1980). In fact, redox reactions determine the chemical and biological behavior of most bioactive elements including mobility, availability, and toxicity (Langmuir, 1997). It is therefore of considerable interest to study the redox conditions of a given system to get a better understanding of redox transformations. Usually, this is done by in situ

potentiometric measurements of the oxidation reduction potential (ORP) using a platinum electrode. In the present study we will adopt the more widely used term E_h , which refers to the ORP referenced to the Standard Hydrogen Electrode. In natural aquatic environments a number of common chemical species undergo redox transformations and theoretically can contribute to the E_h potential. These include iron (Fe^{2+} , Fe^{3+} , $FeOOH$, Fe_2O_3 , $Fe(OH)_3$), manganese (Mn^{2+} , Mn^{3+} , MnO_2), sulfur (H_2S , HS^- , S^0 , S_2 , SO_3^{2-} , SO_4^{2-}), oxygen (O_2 , H_2O_2 , H_2O), nitrogen (NH_4^+ , N_2 , NO_2^- , NO_3^-) and carbon species (CH_4 , CO_2 , lipids, aldehydes, alcohols, carbohydrates).

However, the proper interpretation of E_h measurements is difficult, both from a theoretical and a practical point of view. Redox reactions are normally not at chemical equilibrium because electron transfer reactions are usually kinetically slow, especially if more than one electron is involved (Morris and Stumm, 1967; Hoffmann, 1981). Furthermore, most environmental systems have

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relatively low concentrations of redox elements and thus exchange currents at the electrode interface are often too low to establish a reliable E_h potential (Lindberg and Runnells, 1984). The problems associated with determining the E_h value has been the subject of much interest and has been discussed extensively over the last 50 years (e.g. Stumm, 1967; Whitfield, 1969; Thorstenson, 1984; Scott and Morgan, 1990; Peiffer and Runnells, 1992; Nordstrom, 2000; Hunting and Kampfraath, 2013). A recurring topic is the non-ideal behavior of electrode materials, particularly when affected by the presence of surface coatings (Thirsk and Harrison, 1972; Whitfield, 1974). In addition, some redox reactions are not reversible because they are microbially mediated (Cheng et al., 2007) and others do not attain an electrochemical equilibrium with the electrons of the electrode, which leads to unpredictable and spurious E_h readings (Hostettler, 1984). Thus, various redox couples are suggested to be not electro-active. In contrast, if two or more electro-active couples are present the measured potential is a function of the exchange currents of these couples and hence E_h is termed a mixed potential (Stefánsson et al., 2005). Unfortunately, the proper interpretation of a mixed potential requires kinetic information on the electron exchange rate of each couple, which is rarely available (Grundl, 1994).

On the other hand some progress has been made in overcoming the challenges of potentiometric in situ measurements. The KCl containing electrolyte gel of modern reference electrodes allows a more accurate measurement even in the presence of H_2S . The usage of adequate amplifiers for direct-potentiometers (input impedance $>10^{13} \Omega$) reduces the measurement error and minimizes possible effects of electrode polarization (Frevert, 1984; Schwan, 1992). The study of the relationship between the surface structure of a platinum electrode and its observed reactivity results in a deeper understanding of electrode processes and hence leads to an advancement of electrode production (Inzelt and Horányi, 2006). The behavior of an electrode, i.e. the amount of catalytic active Pt-sites, for instance, can be influenced by creating electrode surfaces with different roughnesses and a specific crystallographic orientation (Visintin et al., 1990). Furthermore, some E_h measurements have been successfully related to independently determined redox couples on a quantitative basis. Some studies demonstrated that both the iron and the sulfur system can give a response in a Nernstian manner (Berner, 1963; Nordstrom, 1979; Crerar et al., 1981; Grenthe et al., 1992; Ioka et al., 2011). Since these studies have mainly focused on marine sediments, flooded soils, ground-water systems or acid mine drainages, only limited data is available regarding E_h measurements in the marine water column.

In this work we present a data set, recorded throughout the stratified water column of the Gotland basin (Baltic Sea) over 56 days using the Gotland Deep Environmental Sampling Station (GODESS) (Prien and Schulz-Bull, 2011). Our objective is to determine whether in situ measured E_h can be assigned to certain redox species occurring in the environment. We attempted to identify the redox transformation processes controlling the electrode potential of the redox sensor especially within and below the redoxcline, which is a region of strong vertical dissolved oxygen and hydrogen sulfide gradients. To that end, estimated and analytically determined concentrations of the most important redox compounds were used to calculate theoretical E_h values which ultimately were compared with the potentials measured on the profiling mooring. Information gained from this approach can give us a much deeper insight even when differences are observed between computations and observations (Stumm and Morgan, 1996).

Here we demonstrate that a synthesis of a certain processing method and current analytical measurements can help to identify redox relevant compounds in the aquatic environment. The vertical and temporal resolution of the data set presented in this study is unique and was obtained by the use of moored profiling

instrumentation. Finally, experimental results and calculations show that the reduction of Fe(III) and O_2 may be the main processes controlling E_h in the Gotland basin, revealing that one electron transfer reactions are most appropriate to study E_h potential.

2. Study site

We conducted this study in the eastern Gotland basin of the central Baltic Sea (Fig. 2), where stratification separates oxygenated from anoxic waters. The separation is caused by two different features of this area, the trophical state and the hydrographical properties. As a semi-enclosed sea the Baltic Sea is connected to the North Atlantic by very narrow and shallow straits. Hence strong vertical and horizontal salinity gradients emerge as a result of the limited water exchange, the large freshwater supply from rivers and precipitation. The increased biomass production (Stigebrandt, 1991) caused by nutrient enrichment of the Baltic (Rosenberg et al., 1990) leads to an increase in sedimentation of organic material (Jonsson and Carman, 1994), and thus to oxygen depletion in the deeper basins, mainly due to sulfate reduction (Piker et al., 1998). As a result a pelagic redoxcline is existing in that area, at which a variety of redox transformation processes occur.

2. Materials and methods

2.1. Instrumentation and equipment

In situ hydro-physical parameters (ORP, dissolved oxygen, chlorophyll a fluorescence, turbidity, temperature and conductivity) were measured and recorded using the Gotland Deep Environmental Sampling Station (GODESS) for a period of 56 days (November 2010–January 2011). GODESS is a profiling instrument developed for deployments up to 3 months as described by Prien and Schulz-Bull (2011). A schematic drawing is shown in Fig. 2. Briefly, it is equipped with a conductivity-temperature-depth (CTD) probe (Sea and Sun Technology GmbH) and a fast-responding optode-based oxygen sensor, Rinko (JFE Advantech Co., Ltd.). In addition, the CTD probe was equipped with a turbidity sensor (Seapoint Sensors Inc.), an ORP-sensor (AMT Analysenmesstechnik GmbH), and a Cyclops 7 fluorometer (Turner Design). To prevent biofouling issues and also damage by ships and stormy weather, no surface buoy was used. Instead, an underwater winch (Automatic Elevator System Type 3; Nichiyu Giken Kogyo Co., Ltd.) was installed at the lower end of the mooring at 190 m depth. The profiling body, on which the sensors can be attached, is made up of a custom build titanium frame (height: 550 mm; square cross section: 200 mm). This frame is surrounded by six syntactic foam sheets with embedded glass spheres, which resulted in a net buoyancy of about 9 kgf. The overall shape of the profiler is deltoid and was chosen for hydrodynamic reasons, giving stability also in case of lateral currents. The profiler is connected to the Kevlar line of the winch using a stainless steel cable bridle. During the deployment the winch unlocked the spool of Kevlar line at a preprogrammed interval of 8 h and after the profiler ascended through the water column by its own buoyancy to a depth of 30 m the winch started to reel the line back in. The measurements were taken exclusively during the upcasts of the profiler, no connection to shore was established at any time and all registered parameters were read out at the recovery of the mooring. As there is no communication link between the winch and the CTD-probe of the profiler the synchronization of the two units was realized by their real time clocks (RTC). All sensor data were logged by the CTD-probe at about 4 Hz.

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