LOICZ-Affiliated Activities

Boknis Eck Time Series Station (SW Baltic Sea): Measurements from 1957 to 2010

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Abstract

Salinity, temperature, and O_2 have been recorded on a monthly basis at the Boknis Eck Time Series Station (BE; Eckernförde Bay, SW Baltic Sea) since April 1957 with only two major breaks (1976-78 and 1983-1985). Chlorophyll a measurements started in 1960 and nutrient data (NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, SiO_4^{2-}) are available since March 1979. Here we present a short introduction to the long-term trends observed at BE and selected results of ongoing projects covering different topics from the surface microlayer and the water column to the sediments at BE. On the basis of a preliminary analysis of the long-term records of surface water temperature, oxygen in 25m, and dissolved nutrients we conclude that BE is affected by both regional processes and global processes detectable as eutrophication and warming of the surface water, respectively. The number of events with extremely depleted O_2 concentrations (hypoxia/anoxia) in the bottom layer has been increasing during the last 25 years. Moreover, BE is site of significant emissions of climate relevant trace gases such as methane.

1. Introduction

The Baltic Sea is one of the largest brackish water systems of the world. Moreover, the Baltic Sea is surrounded by highly-industrialized countries with intensive agricultural activities. Therefore, the Baltic Sea is affected by both natural changes as well as changes triggered by anthropogenic activities. Time series measurements on a regular basis are a valuable tool to understand biogeochemical cycles and ecosystem behaviour and can help to decipher ongoing environmental trends.

The Time Series Station Boknis Eck (BE) is located at the entrance of the Eckernförde Bay (54°31'N, 10°02'E, Figure 1) in the southwestern Baltic Sea and has a water depth of 28m.

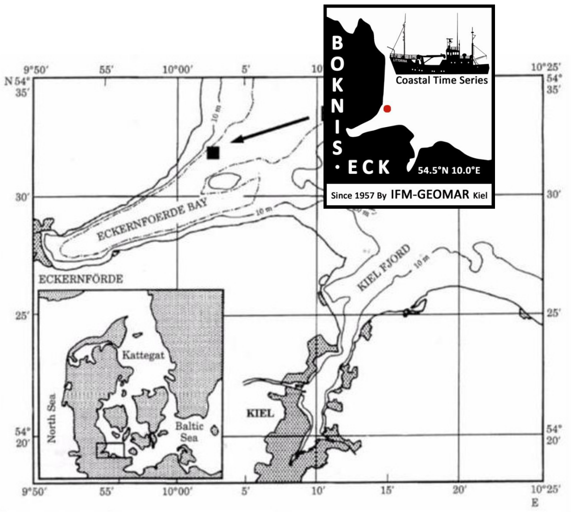

Figure 1: Location (black square) of the Boknis Eck time series sampling site (BE). More information about BE can be found under www.ifm-geomar.de/index.php?id=bokniseck. (Map H.P. Hansen, IFM-GEOMAR)

Riverine inputs are negligible in the Eckernförde Bay and thus the overall hydrographic setting at BE is representative for the southwestern Baltic Sea which is dominated by the regular inflow of North Sea water through the Kattegat and the Great Belt. Because the inflowing North Sea water has a higher salinity compared to Baltic Sea water, a pronounced summer stratification occurs which leads to the development of a pycnocline at about 15 m water depth. The seasonal stratification occurs usually from mid-March until mid-September. During this period, vertical mixing is restricted and bacterial decomposition of organic material in the deep layer causes pronounced hypoxia (O_2 < 90 µmol L^{-1}, no H_2S) and sporadically occurring anoxia (O_2 = 0 µmol L^{-1}, occurrence of H_2S) during late summer (Hansen et al., 1999) (Figure 2).

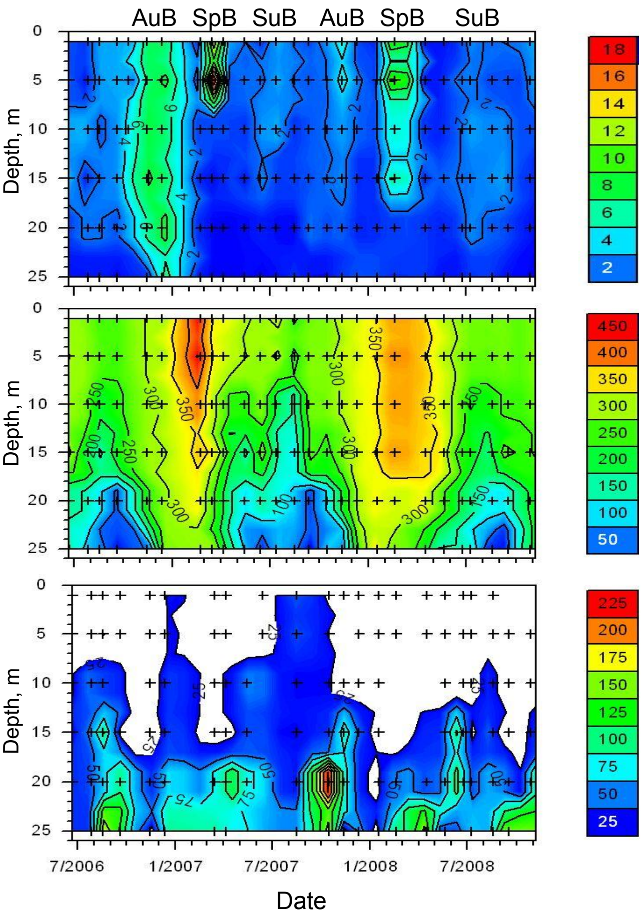

Figure 2: Time series of chlorophyll a in µg L^{-1} (upper panel), O_2 in µmol L^{-1} (central panel) and CH_4 in nmol L^{-1} (lower panel) at the Boknis Eck time series station from May 2006 to November 2007. Crosses mark the available measurements. Phytoplankton blooms are indicated: AuB, autumn bloom; SpB, spring bloom; SuB, summer bloom. On the x-axis the date is given as m/yyyy (e.g., 1/2007 stands for 1st January 2007). Figure is taken from Bange et al. (2010).

Pronounced phytoplankton blooms occur regularly in autumn (September-November) and spring (February/March) and to a lesser extent during summer (July/August) (Figure 2). The autumn and spring blooms are followed by pronounced sedimentation of organic material with >75% (autumn) and >50% (spring) of the total production being sedimented (Smetacek et al. 1984). The summer blooms can be associated with a short period of pronounced sedimentation as well, however, sedimentation during the summer months is generally lower (<25% of the total production) compared to the sedimentation events in autumn and spring (Smetacek et al., 1984).

Monthly sampling at BE started in April 1957 and samples are taken from six standard depths (Bange, 2010). The location of BE is ideal (i) to study a coastal ecosystem under the influence of pronounced changes of salinity and (ii) to study biogeochemical processes sensitive to changes of dissolved oxygen. Here we present a short introduction to the long-term trends observed at BE and selected results of ongoing projects covering different topics from the surface microlayer and the water column to the sediments at BE.

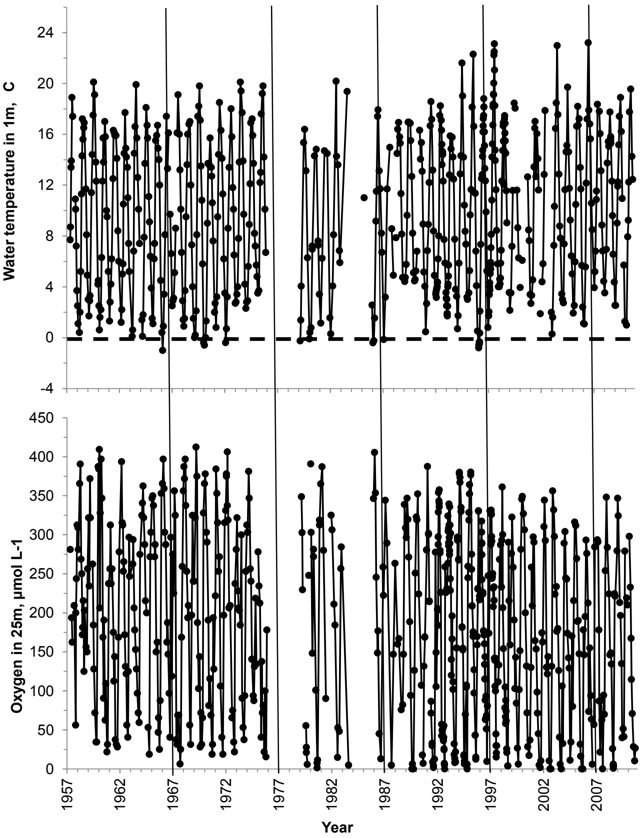

Figure 3: Sea surface temperature (SST) in 1m (upper panel) and dissolved O_2 in 25m (lower panel) at BE from April 1957 to October 2010. Please note that BE has not been sampled from January 1975 to February 1979 and September 1983 to March 1985.

2. Long term trends

Figure 3 shows the time series of surface temperature (SST) and O_2 concentrations in the bottom layer (25m) at BE from April 1957 to October 2010. SST show a trend to warmer temperatures especially during the last decade which is illustrated by the fact that cold events with winter SST below 0°C have not been recorded during the last 14 years. Besides the obvious warming of the surface layer there is a trend to increasing number of anoxia, here defined as O_2 below the detection limit of the Winkler method (i.e. ~2 µmol L^{-1}): During the period 1957-1983 only one anoxic event (1980) has been recorded, whereas during the period 1986-2010 10 anoxic events (1989, 1991, 1992, 1994, 2001, 2002, 2003, 2005, 2007, 2008) have been recorded. The long-term trends of the winter means (DJFM) of dissolved inorganic phosphate (DIP = PO_4^{3-}) and total dissolved inorganic nitrogen (tDIN = $NH_4^+ + NO_2^- + NO_3^-$) in the surface layer (0-10m) are shown in Figure 4.

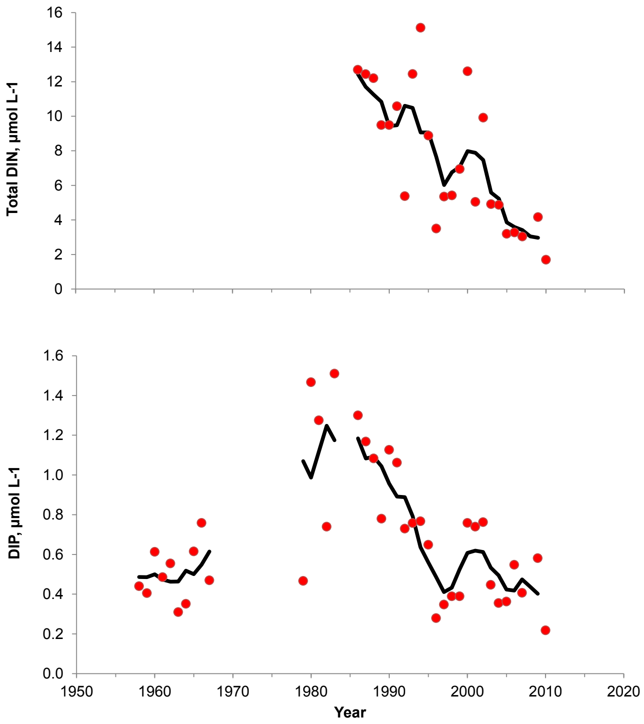

Figure 4: Mean winter (DJFM) concentrations (red circles) of dissolved inorganic phosphate (DIP = PO_4^{3-}) (lower panel) and total dissolved inorganic nitrogen (tDIN = $NH_4^+ + NO_2^- + NO_3^-$) (upper panel). The black solid lines indicate 5-year moving averages. Please not that (i) no DIP measurements are available from 1978 to 1988 and (ii) no tDIN measurements are available before 1986.

There is a pronounced trend of decreasing DIP and tDIN which started in the mid-80s. DIP concentrations seem to have reached a plateau since about 10 years. In contrast the decrease of tDIN seems to continue until today. Interestingly the present DIP concentrations are comparable to those concentrations observed at time when the BE time series has been started back in 1957. Unfortunately, comparable data for tDIN are not available because DIN measurements were started not until January 1986.

In summary, the long-term trends for SST, O2 and nutrients at BE are in general agreement with the trends observed in other coastal areas of the various basins of the Baltic Sea (Feistel et al., 2008; HELCOM, 2009; BACC Author Team, 2008). The increasing frequency of anoxic events might in part result from (i) the warming of the surface waters which leads to enhanced stratification during summer and (ii) the shift of strong wind events from autumn to winter and early spring detected for the period 1988-2007 (Lehmann et al. 2011) which, in turn, could delay the termination of the stratification period by wind-induced ventilation. Additionally, the mean winter SST (December-March, DJFM) show a significant positive correlation ($R = 0.52$, $n= 40$, $p <0.01$) with the mean DJFM North Atlantic Oscillation (NAO) index. However, the correlation at BE is not as strong as observed for other basins of the Baltic Sea (Siegel et al., 2008). Despite the fact that a pronounced decreasing trend of the winter nutrient concentrations has been detected, the concentrations of DIP and tDIN remain on relatively high level. The observed minimum water transparency (measured with a Secchi disk; data are available since 1986) during the months of the spring bloom (February-March) showed a slight decreasing trend from 5m-8m (1986-1991) to 2m-6m (1991-2010). This may indicate an intensification of the spring blooms during the last two decade. We conclude that at the observed long-terms at BE are affected by both regional processes (i.e. eutrophication) and global processes (warming due to climate change).

3. Short-term variability at BE: Glider pilot study

In particular in regions with very shallow water depth, the temporal and spatial variability of physical, biogeochemical and biological parameters can be substantial. To obtain a first impression about the variability at the Boknis Eck Time Series Station a shallow (0-30m) Slocum electric "glider" was deployed in July 2010 for a one week mission to measure temperature, salinity, oxygen, fluorescence and turbidity between the surface and close to the bottom.

The Slocum electric glider is an instrument that rises and sinks in the water column by changing its volume. The shape of the vehicle extracts also a horizontal movement out of the vertical displacement. The vehicle has no propulsion. When it comes to the surface it determines position via GPS and communicate data and commands via satellite telephone. Neutral ballast was configured for a density of 1011 kg m–3 based historical data from the Boknis Eck Time Series Station. The deployment and recovery were conducted from the FK Polarfuchs of IFM-GEOMAR/CAU Kiel. The scientific payload of the glider comprises a turbidity/chlorophyll-a (fluorescence) Wet Labs ECO FLNTU Puck, AADI oxygen optode 3830, and a SeaBird SBE 41 temperature, conductivity, pressure sonde. Data was recorded with one Hertz (oxygen with 2 Hertz) and approximately 790.000 (oxygen 395.000) data points of each variable have been collected. The maximal sampling depth was 22m. During four periods the glider had stranded at the sea floor as it drifted into water that was shallow as its programmed deflection depth. During these periods the glider remain at the sea floor until a time-out triggered the pump to release ballast and to rise to the sea surface.

The summer mixed layer during the observation period was about 8m to 10m deep and well oxygenated (Figure 5).

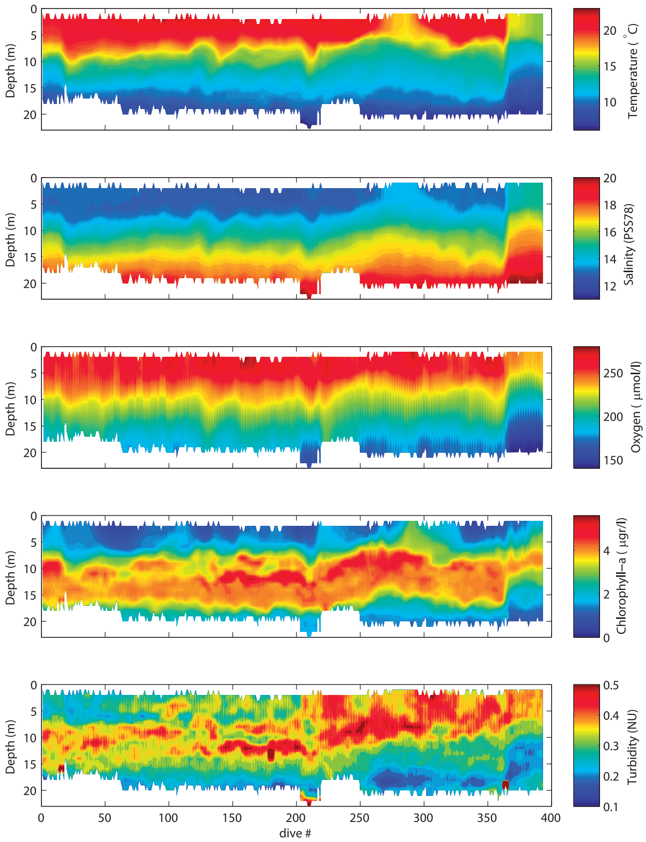

Figure 5: Temporal evolution of the vertical distribution of (from top to bottom): temperature, salinity, oxygen, chlorophyll and turbidity in relation to the dive number. First dive was 08 July 2010, 15:32 (UTC), last dive was 15 July 2010, 18:01 (UTC).

The mixed layer reflects the summer conditions with warm and less saline (compared to the deeper layer) waters that are depleted in chlorophyll and relative clear. Underneath the mixed layer a transition zone to saline and less oxygenated waters, very likely of North Sea origin, can be seen. In the transition layer the chlorophyll concentrations are highest and highest particle concentrations can be found. An upwelling event occurred between dives 250 to 300 that can be identified by a substantial cooling of the surface waters by about 5°C over a period of one day. Associated with the upwelling is an increase in chlorophyll concentrations and turbidity. Overall the variability is rather large considering the short observational period. In depth coordinates we find: 4.1°C, 1.8 PSS78, 27.7 µmol L–1, 1.1 µg L–1, and 0.06 NU for the average standard deviations of temperature, salinity, oxygen, chlorophyll and turbidity, respectively.

4. Surface microlayer measurements

The sea surface microlayer represents the uppermost, approximately 1mm thick layer of the ocean water column. It is enriched by organic molecules and, due to the availability of nutrients and sunlight, is a place of rich biology, microbial transformations, and photochemistry (see e.g. Cunliffe et al., 2011). Especially at low wind speeds, the sea surface microlayer is known to inhibit air-sea gas exchange. Various types of surface-active substances accumulate directly at the water-air interface. Often, insoluble surfactants such as lipids have been discussed to be present directly at the interface. It is this layer of merely monomolecular thickness, the nanolayer that ultimately plays a key role in air-sea gas exchange. Nevertheless, due to problems associated with sampling this tiny amount of substances, detailed knowledge about the composition and molecular structure of the nanolayer remains scarce. Sea surface microlayer samples are taken at BE Time Series Station by means of the screen sampling technique.

Basically, a stainless steel wire mesh is drawn through the water surface from below (Figure 6, left upper panel), leaving a thin water layer in the wire mesh as a consequence of surface tension. After recovery from the sampling device, the samples are transported to the laboratory. The surface nanolayer reforms due to the hydrophobicity/buoyancy of its components and can be spectroscopically investigated without further processing.

We employed and are further developing the use of vibrational sum-frequency generation (VSFG) spectroscopy as an intrinsically surface selective analytical tool for surface nanolayer analysis (Laß et al., 2010). This method relies on a second-order nonlinear optical process (Figure 6, left lower panel), in which an infrared (IR) photon and a visible photon are combined into one new photon with the sum of the energies of the two incident photons. The process is only possible directly at the interface and becomes more efficient upon resonance of one of the photons with a spectral transition of a molecule residing on the surface. In this way, by using tuneable IR light, it is possible to record vibrational spectra of surfaces and thus to detect spectral signatures characteristic for specific molecular functional groups such as alkyl chains of lipid molecules. Furthermore, VSFG spectroscopy provides insight into the molecular structure and overall order of surfaces and even allows one to determine net orientations of molecules at the interface. A drawback of the method is that bulky laser systems are needed to generate the required intense laser radiation. Consequently, to date the use of VSFG spectroscopy is still limited to laboratory work; however, this situation might change with more advanced laser technology in the future.

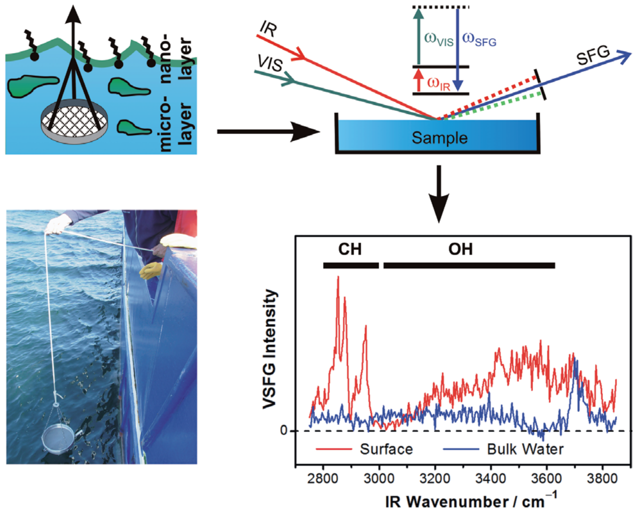

Figure 6: Left panels, surface microlayer sampling by means of screen sampling. Upper right panel, principle of surface-sensitive vibrational sum frequency generation spectroscopy (VSFG). Two intense short laser pulses are temporally and spatially overlapped on the sample surface, where a new beam is generated in a second-order nonlinear optical process. Right lower panel, VSFG spectra of BE seawater samples. In contrast to the bulk water spectrum, the surface water sample shows considerable amounts of organic material.

A spectrum taken from a BE surface layer sample and a bulk water reference spectrum is shown in the upper right panel of Figure 6. Observed peaks correspond to CH bond stretch vibrations (2800-3000 cm^{-1}), OH hydrogen bond stretch vibrations (3000-3650 cm^{-1}) and the OH dangling bond peak at 3700 cm^{-1}. The latter signal, which stems from free OH groups of water molecules pointing out of the water surface, is visible only for the surfactant-free bulk water spectrum. This peak vanishes in the nanolayer spectrum since the surface is covered with an organic adlayer. The organic adlayer itself gives rise to strong CH signals stemming from alkyl-chain bearing species. Further analysis of many samples collected during the regular sampling trips lead us to the conclusion that natural marine nanolayers are dominated by lipopolysaccharides or other lipid-like compounds embedded in colloidal matrices of polymeric material.

5. Trace gas measurements

The worldwide increasing number of coastal areas with extremely (persistent or temporary) depleted dissolved oxygen (O_2) concentrations (see e.g., Díaz and Rosenberg, 2008) is especially alarming in view of the fact that the microbial pathways of many climate-relevant trace gases such as methane (CH_4), nitrous oxide (N_2O) and dimethylsulfide (DMS) are significantly driven by the prevailing O_2 concentrations in the water column as well as in the underlying sediments. However, to what extent the ongoing expansion of hypoxia/anoxia is going to lead to an increased production of CH_4 and N2O in coastal waters which in turn may result in an enhancement of their emissions to the atmosphere is not clear (see e.g., Naqvi et al., 2010). Because of the seasonally occurring hypoxic/anoxic events, Boknis Eck provides an ideal natural laboratory to investigate the effects of extreme O_2 depletion on the formation pathways of these gases. Routine trace gas measurements in the water column at BE started in July 2005 (N_2O), June 2006 (CH_4) and February 2009 (DMS). Here we present the results of the CH_4 measurements at BE.

Sedimentary release of methane (CH_4) determines the CH_4 concentrations in the water column at BE. The water column is always supersaturated with CH_4, and therefore, BE is a year-round source of CH_4 to the atmosphere. Enhanced release of CH_4 to the atmosphere occurs when the CH_4 accumulated in the hypoxic bottom layer during summer is brought to the surface by mixing of the water column in late summer/autumn. We do not detect a straightforward relationship between periods of enhanced CH_4 in the bottom layers and hypoxic events (Figure 2). Indeed a bimodal seasonality of CH_4 in the bottom layer with two maxima in March and September was found (Bange et al., 2010) The sedimentary release of CH_4 seemed to be triggered mainly by sedimenting organic material from phytoplankton blooms. Therefore, we conclude that future CH_4 emissions from BE will be determined by the intensity of phytoplankton blooms, which in turn will be influenced by the future trends in nutrient inputs (i.e. eutrophication). Hypoxic/anoxic events have only a modulating effect on the enhancement of methanogenesis in the sediments (Bange et al., 2010).

6. Benthic geochemical modelling

During 2010, the sediments at a 28 m deep site in the Boknis Eck channel were sampled monthly and analysed for their major nutrients and geochemical constituents. The data were used to constrain a benthic model to study the benthic cycling of redox sensitive elements and investigate how the pathways of organic matter degradation and biogeochemical fluxes across the sediment-water interface respond to changing O_2 concentrations. The model includes organic matter degradation by aerobic and anaerobic respiration pathways and can be used to quantify the total rate of O_2 depletion in the sediment.

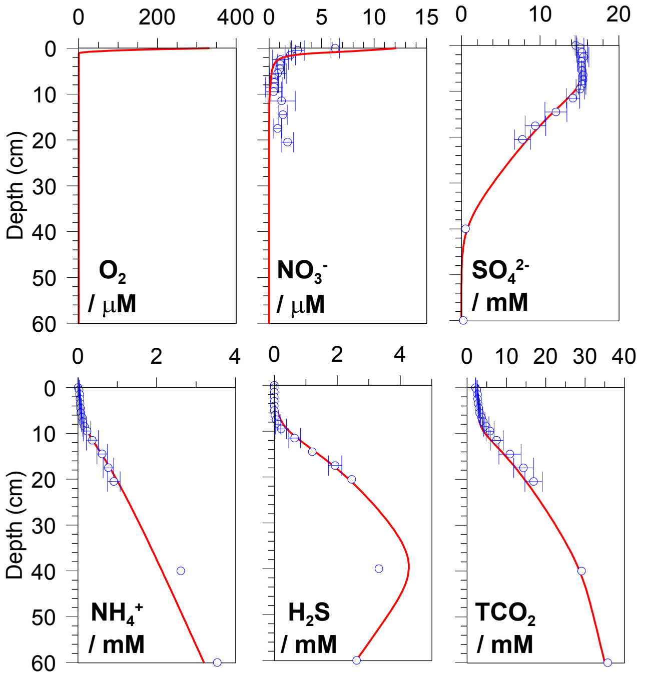

Figure 7: Modelled (lines) and measured (points) of porewater constituents in the upper 60 cm of Boknis Eck sediments during winter 2010.

An example of the model application to data from winter 2010 is shown in Figure 7, when oxygen levels in the bottom waters were high. The figure shows how the concentrations of various oxidized species (e.g. O_2, NO_3^-, SO_4^{2-}) decrease with depth in the sediment. O_2 decreases very rapidly and is exhausted by 2 cm depth, which is typical for muddy coastal sediments (Røy et al., 2004). This illustrates that the sediments are sink for these constituents due to respiration by aerobic and anaerobic microorganisms which use these compounds to oxidize phytoplanktonic organic matter (Berner, 1980). Organic matter decay releases a number of reduced species such as ammonium (NH_4+), carbon dioxide (TCO_2) and the highly toxic hydrogen sulphide (H_2S). The increasing concentration gradient of these compounds with depth indicates that they are diffusing upwards to the sediment surface where they will be eventually released to the overlying water column (Balzer, 1984). The results show that the sediments are efficient recyclers of inorganic nutrients, yet the significance of their return flux to the water column on primary production remains an open question and is a ripe area for future investigations.

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