Final report

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What controls phosphorus burial in the Baltic Sea?

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1. Summary

This report summarizes the findings of a 1-year project on the quantification of phosphorus (P) burial in the Baltic Sea. The work was funded by the Baltic Sea 2020, with additional financial support from Utrecht and Göteborg Universities and the Netherlands Organisation for Scientific Research (NWO). In the first month of the project, sediment cores with a length of 25 to 40 cm were recovered from 11 sites during a cruise to the Baltic Sea with RV Skagerak from August 31 to September 7, 2007. Here, we report on 9 sites in the Kattegat, Danish Straits and Baltic Proper. Bottom water redox conditions at our sites ranged from oxic to temporarily hypoxic (group 1: Fladen, Sound, Arkona) to nearly permanently hypoxic and anoxic sites (group 2: Bornholm basin, Northern Gotland Deep, Gotland Deep, Landsort Deep). Two additional sites for which the redox conditions are less well-defined were included (group 3; Bornholm Slope, Gotland Slope). Total chemical sediment analyses, sediment P fractionation, (organic) carbon and nitrogen contents and porewater analyses are combined to elucidate the controls on sediment P dynamics. Our results show that reactive P (i.e. potentially biologically available P) is abundantly present at depth in most cores (on average at ~ 17-20 μmol/g at group 1 and 2 sites), although the major P forms vary greatly from site to site. Detrital, non-reactive P accounts for, on average, 15% of total P, and thus is a minor phase. The variation in reactive P burial forms depends on the predominant oxygenation regime. At oxic/seasonally hypoxic sites (group 1), the major long-term P burial sink is organic-P. Fe-bound P is a major temporary sink as is evident from surface enrichment of both Fe oxides and Fe-bound P at most sites of group 1. At Arkona, late summer hypoxia leads to coupled release of Fe^{2+} and PO_4 to the porewater and a (transient) high PO_4 flux to the overlying water (~800 μmol m^{-2} d^{-1}). At permanently anoxic sites, organic P is a less prominent sink and authigenic inorganic P minerals gain importance. The Gotland Slope and Landsort Slope sites (group 3) show somewhat intermediate behaviour compared to groups 1 and 2. Fish debris is not important as a reactive P sink. Corg/Porg ratios confirm enhanced regeneration of P from organic matter with the degree of anoxia. "Sink-switching" to inorganic P phases in anoxic basins compensates for this release, leading to similar Corg/Ptot ratios compared to oxic sites. Our results indicate that long-term increased oxygenation of the deep basins will have major effects on P dynamics in the Baltic. In the long run, P burial is expected to increase because of increased permanent organic P burial. Future work will include an assessment of the expected transient effects of oxygenation on hypoxic and anoxic sites using reactive transport modelling.

2. Introduction and background

Increased terrestrial input of phosphorus (P) to the Baltic Sea due to anthropogenic activity has led to enhanced primary production and the more frequent occurrence of hypoxia throughout the basin (Larsson et al., 1985). This is negatively affecting living conditions for benthic organisms (Karlsson et al., 2002) and is leading to other water quality problems linked to eutrophication, such as increased trace metal mobility and toxic algal blooms (HELCOM, 2003). Besides the input of P from rivers and groundwater, the availability of P for primary producers in the water column of the Baltic is determined by variations in the recycling efficiency within the system and the sinks for P, which are outflow to the North Sea and permanent burial in the sediments (e.g. Wulff et al., 2001).

Many studies to date have focussed on quantifying the internal cycling of P in the Baltic Sea on various spatial scales. For example, Conley et al. (2002) have shown that annual changes in dissolved inorganic phosphate pools on a basin scale were positively correlated to the sediment area covered by hypoxic water between 1970 and 2000 and not to changes in total external P load. The changes were attributed to release of Fe-bound P upon the transition from oxic to hypoxic conditions and subsequent increased sediment retention of P upon return to oxic conditions. This is in accordance with the surface enrichments in Fe-bound P observed in the Baltic Proper by Carman and Rahm (1997) and the enhanced PO_4 release upon anoxic incubation of oxic sediment from the same region (Koop et al., 1990). Redox-dependent changes in the sediment Fe-bound P pool have also been reported for the Gulf of Finland (Lehtoranta, 2003) and have been used to explain elevated organic C/total P ratios in sediments in deep basins in the Baltic Proper (Emeis et al., 2000).

Little is known, however, about the role of sediments as a permanent sink for P in the Baltic and the processes that control this burial. Typically, burial rates for the Baltic have been calculated from surface concentrations of total P and sediment accumulation rates (e.g. Hille, 2005). Thus, changes in total P with depth in the sediment due to diagenetic processes and variable contributions of detrital, non-reactive P (i.e. non-biologically available; e.g. Ruttenberg, 2003) are commonly disregarded. In a recent budget calculation for 1991-2000, Savchuk (2005) estimated the net sediment P burial in the Baltic to be $\sim 20 \times 10^3$ ton P/yr from mass balance considerations. This is comparable in magnitude to the net outflow through the Skagerrak, which was estimated at $\sim 17 \times 10^3$ ton P/yr. During this period, the Baltic Proper likely acted as a net source for P, while the Kattegat, Danish Straits and the coastal subbasins acted as a net sink. An earlier phosphorus budget for 1975-1991 suggests that P burial in the Baltic proper (here including the Gulf of Riga and Gulf of Finland) was responsible for a net sink of $\sim 16 \times 10^3$ ton P/yr (Wulff et al., 2001). Given the residence time of P of 14 years in the water column, changes in net burial of P could significantly alter the P availability in the Baltic on decadal time scales.

Based on studies in other brackish and marine basins, permanent burial of P is expected to occur largely in the form of organic P and calciumphosphate (Ca-P) minerals. The Ca-P minerals can form in situ ("authigenic Ca-P") in the sediment or, under low-oxygen conditions, may also consist of the remains of fish hard parts ("biogenic Ca-P"). Where authigenic Ca-P is formed through precipitation of dissolved P released from either organic P (Ruttenberg and Berner, 1993) or Fe-bound P (Slomp et al.,1996a), this redistribution of sediment P phases with depth is called "sink-switching". In fully anoxic settings, authigenic Ca-P formation is often limited by the availability of dissolved PO_4 since most release of P from organic matter or Fe-oxides occurs at the sediment-water interface and porewater concentrations will remain low. This has been demonstrated for anoxic low sedimentation rate environments in the Mediterranean (Slomp et al., 2002) and Arabian Sea (Schenau et al., 2005). In contrast, preservation and burial of biogenic P is enhanced under anoxia and fish debris can become a major P burial sink (Schenau and de Lange, 2000; Slomp et al, 2002). Both

organic P and Ca-P were important sinks for P in the Bornholm Basin prior to ~2400 BP (Westman, et al., 2003). No information is available on their role as a permanent sink for P in modern Baltic sediments, however.

In this study, porewater and sediment data for 9 sites in the Baltic Sea are used to assess the redox-dependence of the burial of various P forms and their role as a temporary and permanent sink for P. We also specifically focus on identifying the diagenetic processes active in the sediments, since these ultimately control the fate of P (e.g. Ruttenberg, 2003; Canavan et al., 2006a and b; Lehtoranta et al., 2008). Corg/Porg and Corg/Ptot ratios are used as an indicator of enhanced recycling of P from organic matter and possible sink-switching of P to other phases (e.g. Ingall et al., 1993; Anderson et al., 2001; Slomp et al., 2002; Algeo and Ingall, 2007).

Our recent work (Kraal et al., 2008) has shown that storage of sediment samples may greatly affect sediment P speciation due to artefacts related to pyrite oxidation under oxygenation. This made it essential to focus only on freshly collected cores and samples that were processed and stored under oxygen-free conditions. As a consequence, we could not use existing cores as outlined in the original project proposal and thus relied completely on sediment material collected during a new cruise in 2007.

3. Objectives of this project

The major objectives of this project are (1) to quantify the temporary and permanent burial sinks of phosphorus (P) in various sub-basins of the Baltic Sea (the Kattegat, Danish Straits and Baltic Proper, including the Bornholm basin and Gotland and Landsort Deep) and (2) to use these data to obtain a preliminary assessment of the factors controlling sediment P burial in these areas.

4. Materials and methods

4.1 Sample collection

An 8-day cruise funded by Baltic Sea 2020 was carried out with RV Skagerrak from August 31 to September 7, 2007 (see Appendix I; Shipboard Report for details on the Sampling). Sediment cores from 10 sites (Fig. 1; Table 1). were recovered using a multicorer (10 cm i.d.) or boxcorer and analysed in this project. Each core contained up to 40 cm of sediment and between 10 and 30 cm of overlying water. Bottom water was collected with a syringe and closed with a 3-way stopcock and processed with the porewater samples as described

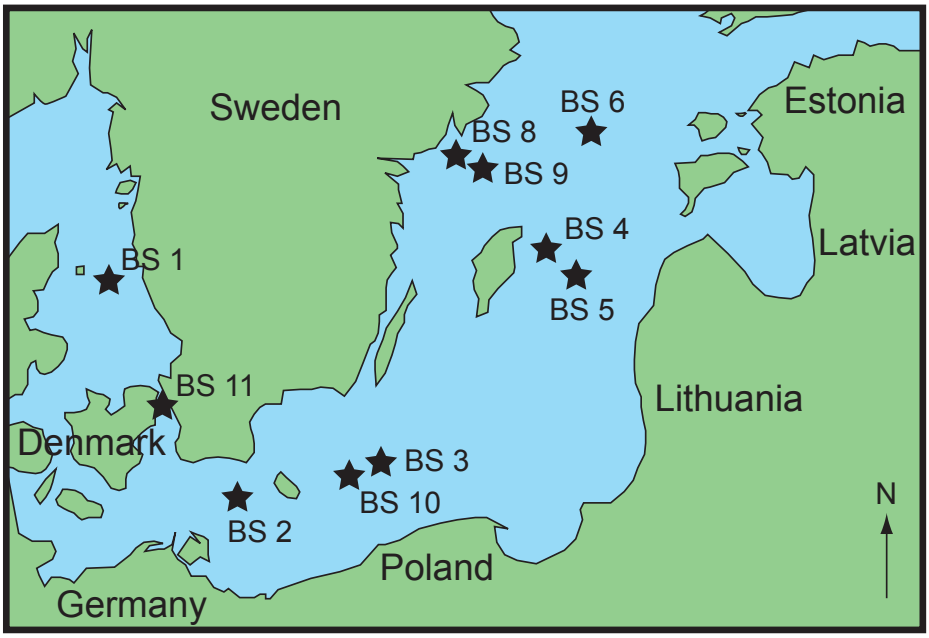


Figure 1. Locations of the sampling sites in the Baltic Sea.

Table 1. Position, bottom water oxygen conditions at the time of sampling (early September), salinity, temperature and depth at the 10 study sites. Different colours refer to the separation of sites made in the report (Group 1: blue = oxic/seasonally hypoxic, Group 2: orange = anoxic and Group 3: yellow = other). *Redox conditions are classified in terms of dissolved O2 concentrations as follows. Oxic > 2 ml/l, hypoxic > 0 - < 2 ml/l, anoxic = 0 ml/l.

Site Name	Position	Redox*	Salinity	Temperature (°C)	Water Depth (m)
Group 1					
BS1 Fladen	57°11.573 N 11°39248 E	Oxic	34.2	10.7	82
BS 11 Sound	55°52.538 N 12°44.460 E	Hypoxic	32	10	53
BS 2 Arkona (BY2)	54°58.504 N 14°05.937 E	Hypoxic	12.2	13	47
Group 2					
BS 6 Northern Gotland Deep (BY29)	58°52.759 N 20°18.569 E	Anoxic	11.4	5.7	175
BS 10 Bornholm Basin (BY5)	55°15.160 N 15°59.160 E	Hypoxic	16.2	9	89
BS 5 Gotland Deep (BY15)	57°19.413 N 20°01.928 E	Anoxic	13	6.5	240
BS 9 Landsort Deep (BY31)	58°35.314 N 18.35.556 E	Anoxic	11.2	4.7	466
Group 3					
BS 4 Gotland Slope (BY15O)	57°26.718 N 19°40.718 E	Hypoxic	11.2	5.7	115
BS 3 Bornholm Slope (BY5O)	55°24.459 N 16°22.820 E	Oxic	14	5.5	66
BS 8 Landsort Slope (BY31O)	58°37.578 N 17°56.768 E	Oxic	7.4	4.5	54

below. At each site, one multi-core or subcore from the boxcore was immediately sectioned in a N_2-purged glovebox on board the ship in a temperature controlled laboratory. A small section of each slice was stored anoxically at 4°C for sediment analyses. For 9 sites, the remaining sediment was centrifuged at 2500 g for 10 to 30 minutes in polyethylene tubes to collect porewater. A lithological description of each core was made during sampling (Fig. 2). At the Northern Gotland Deep site, porewater was collected using rhizon samplers (Seeberg et al., 2005).

4.2 Porewater and bottom water analyses

After centrifugation, tubes were transferred to a N_2 purged glove box or glove bag, with the corresponding bottom water samples. Both the pore water and bottom water was filtered through 0.45 µm pore size filters, and pH was measured immediately with an ion selective field effect transistor electrode (ISFET, Sentron). The samples were then sub-divided and preserved for analysis in the laboratory. Sub-samples for PO_4, Si, NO_3^-, NH_4^+, Cl^-, and SO_4^{2-} were stored frozen until analysis: NO_3^- and NH_4^+ were determined colorimetrically on a nutrient auto-analyzer (Bran and Luebbe), Cl^- and SO_4^{2-} were determined by ion chromatography (Dionex DX-120). Sub-samples for total dissolved Mn, Fe and Na and additional minor and major elements (see Appendix III) were acidified with HNO_3 (50 µl conc. suprapur HNO_3 per ml) and stored at 4° C until analysis by ICP-OES. Alkalinity was measured on board by automatic titration. For the rhizon samples from the Northern Gotland Deep site, only porewater PO_4 was analysed. Dissolved oxygen microprofiles were obtained on board at 3 sites where the bottomwater was oxic (Fladen, Sound and Bornholm Slope) using a Unisense oxygen sensor attached to a micromanipulator in perspex cores (4.2 cm

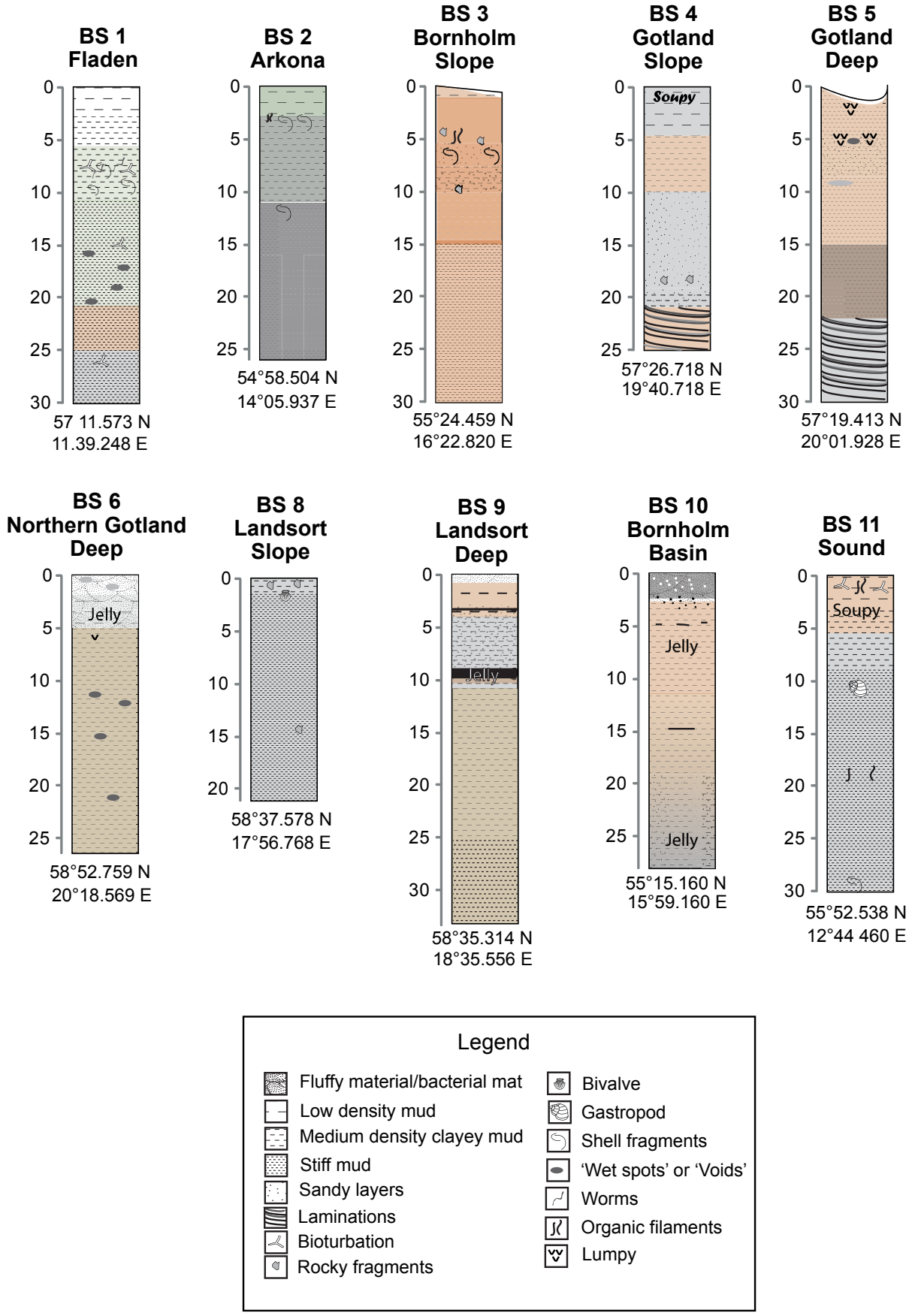


Figure 2. Lithological descriptions of the sediment cores used for sediment and porewater analyses.

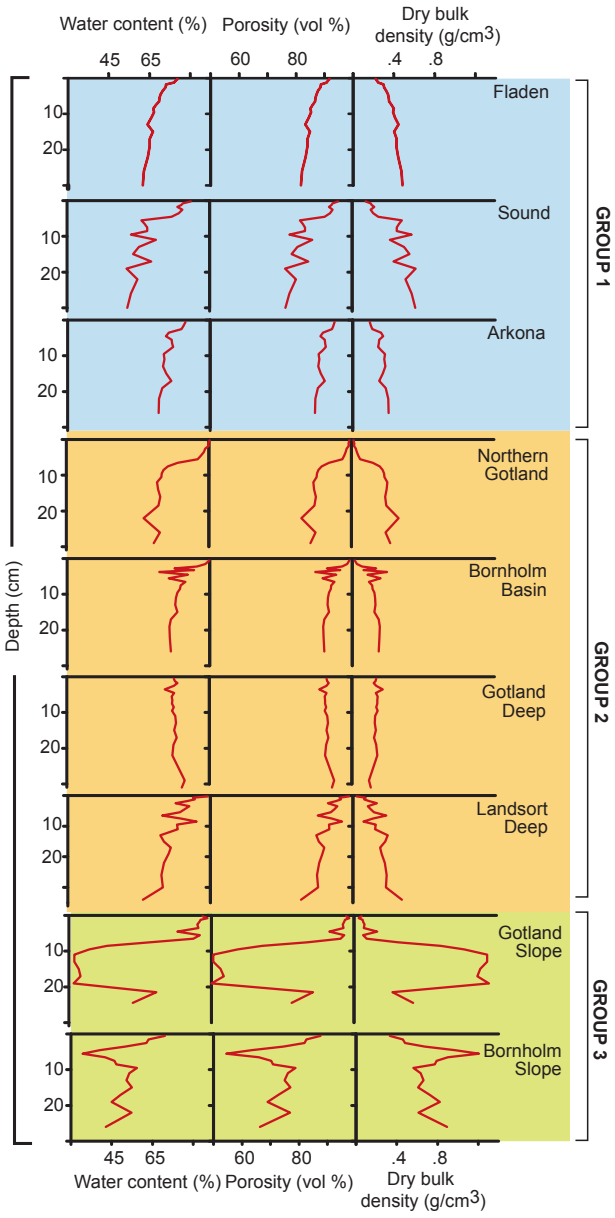


Figure 3. Depth profiles of water content (%), porosity (%) and dry bulk density (g/cm3) for 9 sites. Group 1 (oxic – seasonally hypoxic), Group 2 (mostly/permanently anoxic) and Group 3 (other). See text for details.

i.d.) with 10 cm sediment and 5 cm overlying water collected from a box core.

4.3 Solid phase analyses

The water content, porosity and bulk density were determined from the weight loss of sediment upon freeze drying. Total carbon and organic carbon and nitrogen (following carbonate removal with 1 M HCl) were determined using an elemental analyser (Fison Instruments, model NA 1500 NCS). Total Al, Ca, Co, Fe, Mn, Mo, P, S and V were determined by ICP-OES after HF-HlO_4-HNO_3 digestion of freezedried sediment. Sediment P was fractionated into exchangeable P, Fe-bound P, authigenic Ca-P (this includes CFA, biogenic Ca-P and $CaCO_3$-bound P), organic P and detrital Ca-P using the SEDEX extraction procedure (Ruttenberg, 1992) as modified by Slomp et al. (1996a; for details, see Appendix II). An 8 step 1 M NH4Cl extraction (Schenau and de Lange, 2000) was performed on selected samples from all the group 2 stations to test for fish debris. The Fe and Mn extracted in Step 2 of the SEDEX procedure was used as a measure of the Fe- and Mn oxides in the sediment, respectively. $CaCO_3$ contents were calculated from total sediment Ca concentrations. Samples from Arkona, Bornholm anoxic and the Gotland Deep sites were analysed for the activity of ^{210}Pb, ^{226}Ra and ^{137}Cs via gammaspectrometry at the Gamma Dating Center, Institute of Geography, University of Copenhagen. CRS modelling was applied to obtain sediment ages and accumulation rates with depth (Appleby, 2001).

5. Results

5.1 Bottom water oxygen conditions

In order to facilitate the presentation of the data, we separated the sites into three groups (Table 1), based on the prevailing oxygen conditions throughout the year as determined in regular monitoring cruises (SMHI, 2008) and as known from earlier work (e.g. Kullenberg, 1981). Note that the actual oxygen conditions at the time of sampling were sometimes different from yearly average conditions (Table 1). Fladen, Sound and Arkona are classified as 'oxic – seasonally hypoxic' (**Group 1**) as they are oxic throughout at least 9 months of the year. While Fladen remains oxic continuously, the latter 2 sites are prone to hypoxia during the late summer. The Bornholm Basin, Northern Gotland Deep, Gotland Deep and Landsort Deep are termed 'semi-permanently anoxic' (**Group 2**) since they are almost continuously hypoxic or anoxic, with the exception of periodic flushing events from oxygenated North Sea water (e.g. Fonselius, 1985). The Gotland Slope and Bornholm Slope sites are classified as 'other'

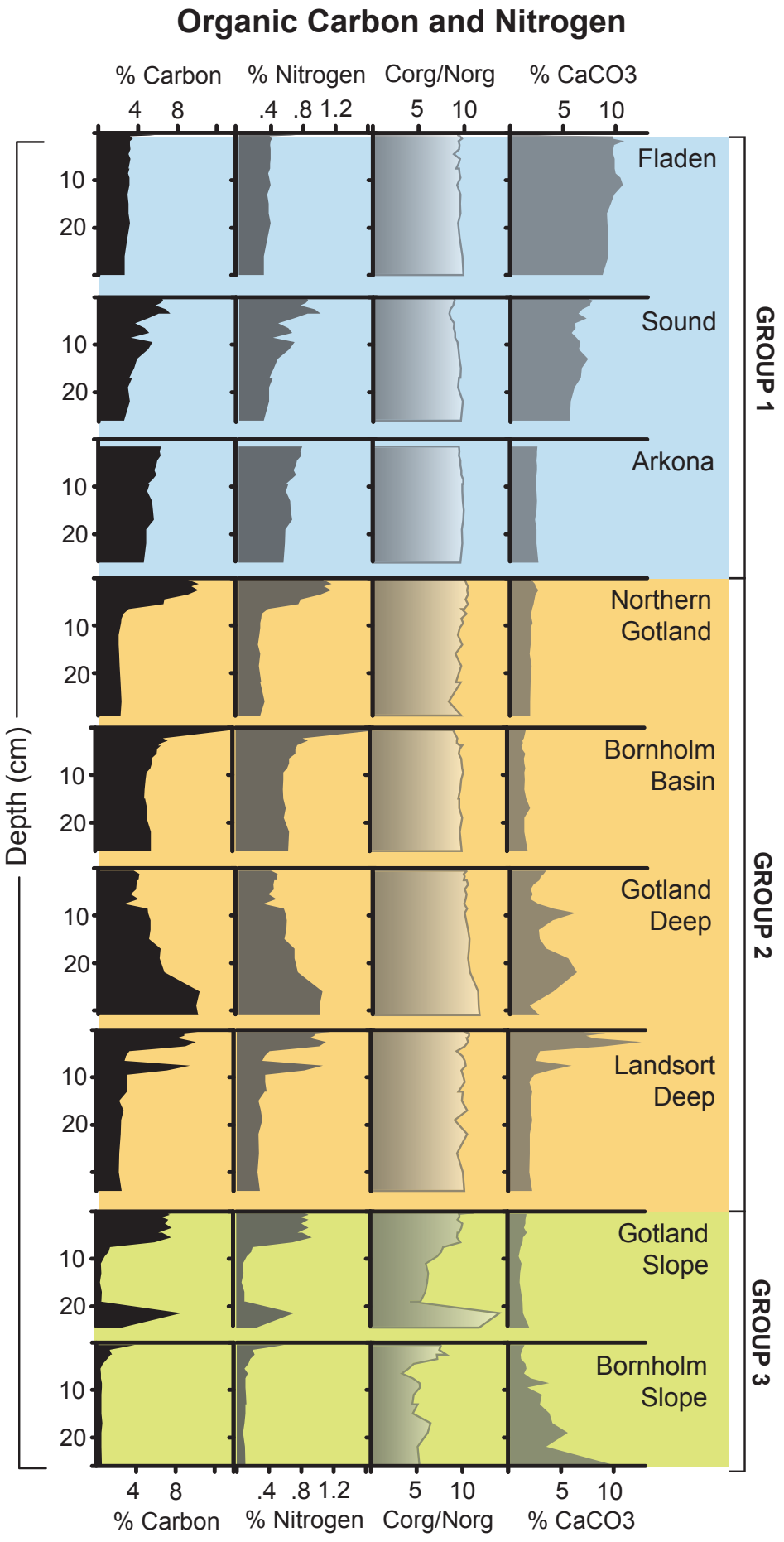


Figure 4. Depth profiles of organic carbon and nitrogen (in wt%), corresponding organic C/Nratios (mol/mol) and $CaCO_3$ (wt%). Classification: see caption of Figure 3.

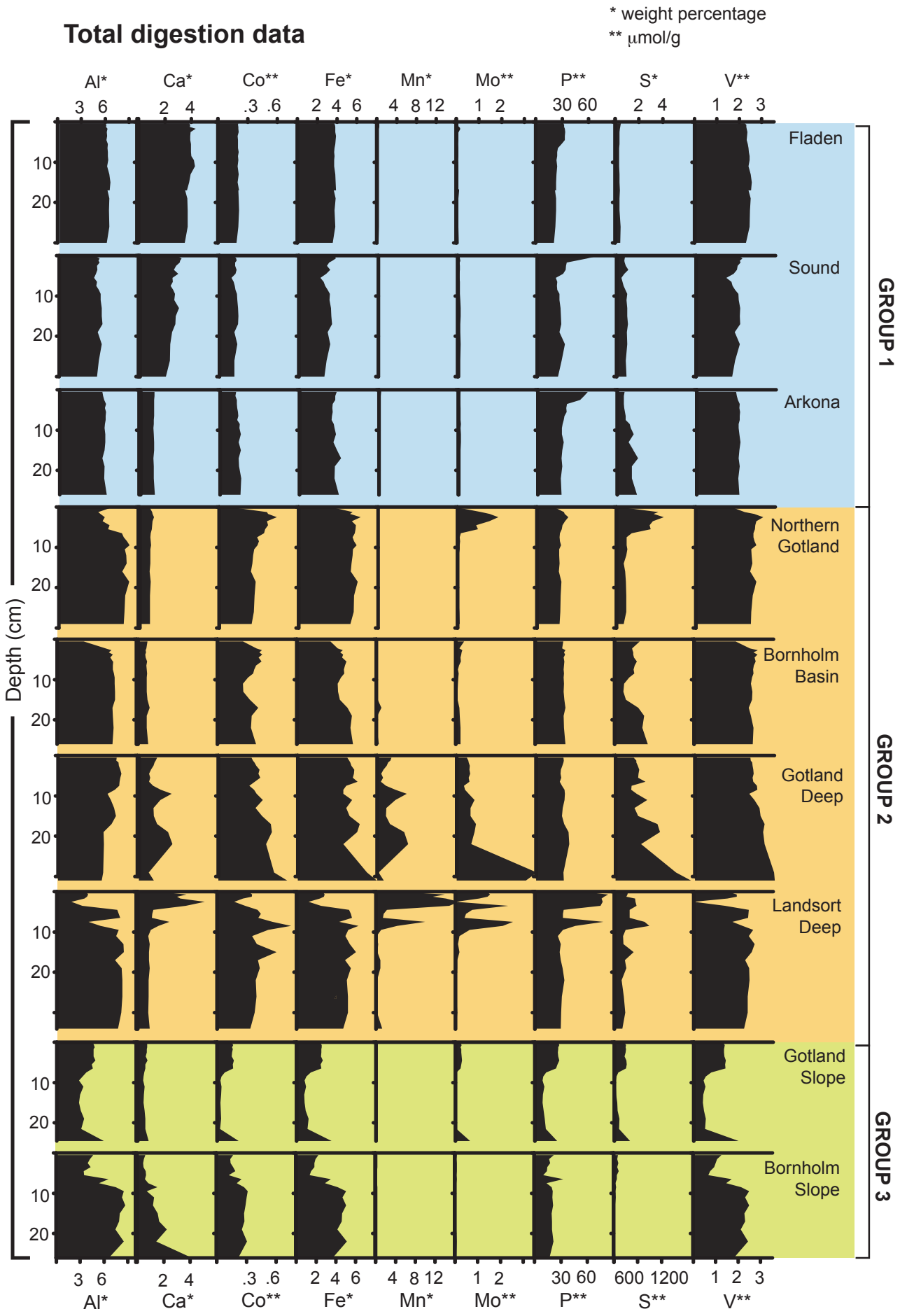


Figure 5. Depth profiles of total Al, Ca, Co, Fe, Mn, Mo, P, S and V (either as wt% or µmol/g). Classification: see caption of Figure 3.

(**Group 3**) since their oxygenation states (and depositional settings) are not well known. The oxic Landsort Slope site is included in this "other" group also, but its results are not discussed further in this report, since, based on its lithology and porewater chemistry and sediment composition (not shown), it is evident that this is a glacial clay in a non-depositional environment with limited active diagenesis.

5.2 General sediment characteristics

The sediments at all sites are highly porous (Fig. 3) and rich in organic C and N but relatively poor in $CaCO_3$ (Fig. 4). Organic C/organic N ratios are relatively constant with depth at values of ca. 9 to 10, with the exception of the Bornholm Slope site where organic C/N ratios show a maximum in the surface layer and then decrease to values of ca. 5. At the group 1 sites ("oxic/seasonally hypoxic"), both porosity and organic C and N gradually decrease with depth. The Fladen and Sound sites are relatively rich in $CaCO_3$ compared to the other stations. At the group 2 sites ("semi-permanently anoxic"), similar trends are observed for the Northern Gotland and Bornholm basin sites. At the Gotland Deep site, in contrast, sediment porosity is constant with depth, while organic C and N contents increase with depth and are highest in the laminated interval at the bottom of the core (Fig. 2 and 4). At the Landsort Deep site, simultaneous peaks in $CaCO_3$ and organic C and N are observed in the surface sediment, suggesting a common origin (Fig. 4). At the slope sites of group 4 ("other"), only a relatively thin surface layer of the sediment is highly porous and enriched in organic C and N.

Total concentrations of Al are typically relatively constant with depth (Fig. 5), with the exception of the Ca-rich layers at the Landsort Deep site, the high porosity surface layers at the Northern Gotland and Bornholm basin sites and the Slope sites below 10 cm depth. Redox sensitive metals (Co, V, Mo), total Fe and total S are relatively enriched in the anoxic sediments of group 2 compared

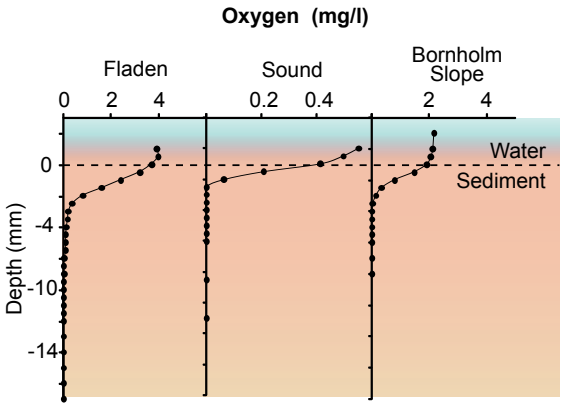


Figure 6. Oxygen porewater profiles for three sites where oxygen was detectable in the bottom water (group 1: Fladen, Sound; group 2: Bornholm Slope).

to other sites. In general, Mn concentrations are low, but are enriched in Ca-rich layers in the Gotland Deep and Landsort Deep. Total P profiles show enrichments in surface layers at the oxic/seasonally hypoxic sites of group 1, at the Landsort Deep (group 2) and Gotland Slope sites (group 3). Surface enrichments of Fe- and Mn-oxides are also observed for group 1 sites (Appendix III).

5.3 Porewater chemistry

Oxygen concentrations rapidly decreased to zero within the upper 2-4 mm of the sediment at the Fladen and Sound (group 1) and Bornholm Slope (group 3) sites in September 2007 (Fig. 6). Porewater profiles of Fe^{2+}, Mn^{2+}, PO_4, NH_4, SO_4 and alkalinity show significant variations within and between groups (Fig. 7). In general, alkalinity and NH_4 production are closely coupled, with highest concentrations being observed at the Sound (group 1) and Landsort Deep (group 2) sites. SO_4 concentrations are highly variable, with bottom water concentrations tracking salinity (Na^+) and concentrations decreasing with depth at most sites. Dissolved Fe^{2+} is only present in the porewater of groups 1 and 3. In contrast, dissolved Mn^{2+} is most abundant in the porewater of group 2. Dissolved PO_4 concentrations show an increase with depth at all sites. A close coupling between porewater Fe^{2+} and PO_4 is observed in the surface sediment of Arkona.

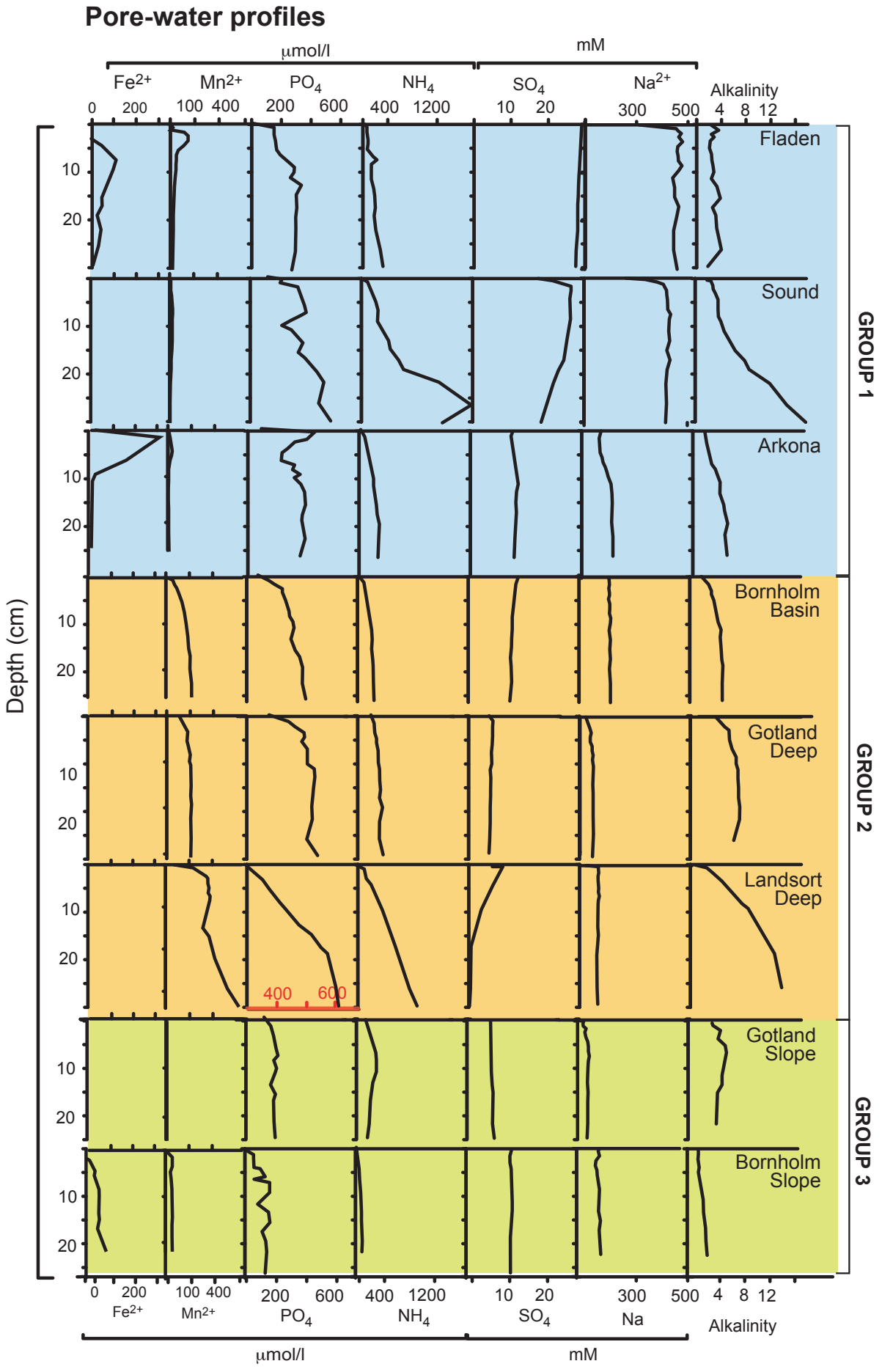


Figure 7. Porewater profiles of Fe^{2+}, Mn^{2+}, PO_4, NH_4 (all in uM), Na^+ and SO_4 (in mM) and alkalinity (in mM). Classification: see caption of Figure 3.

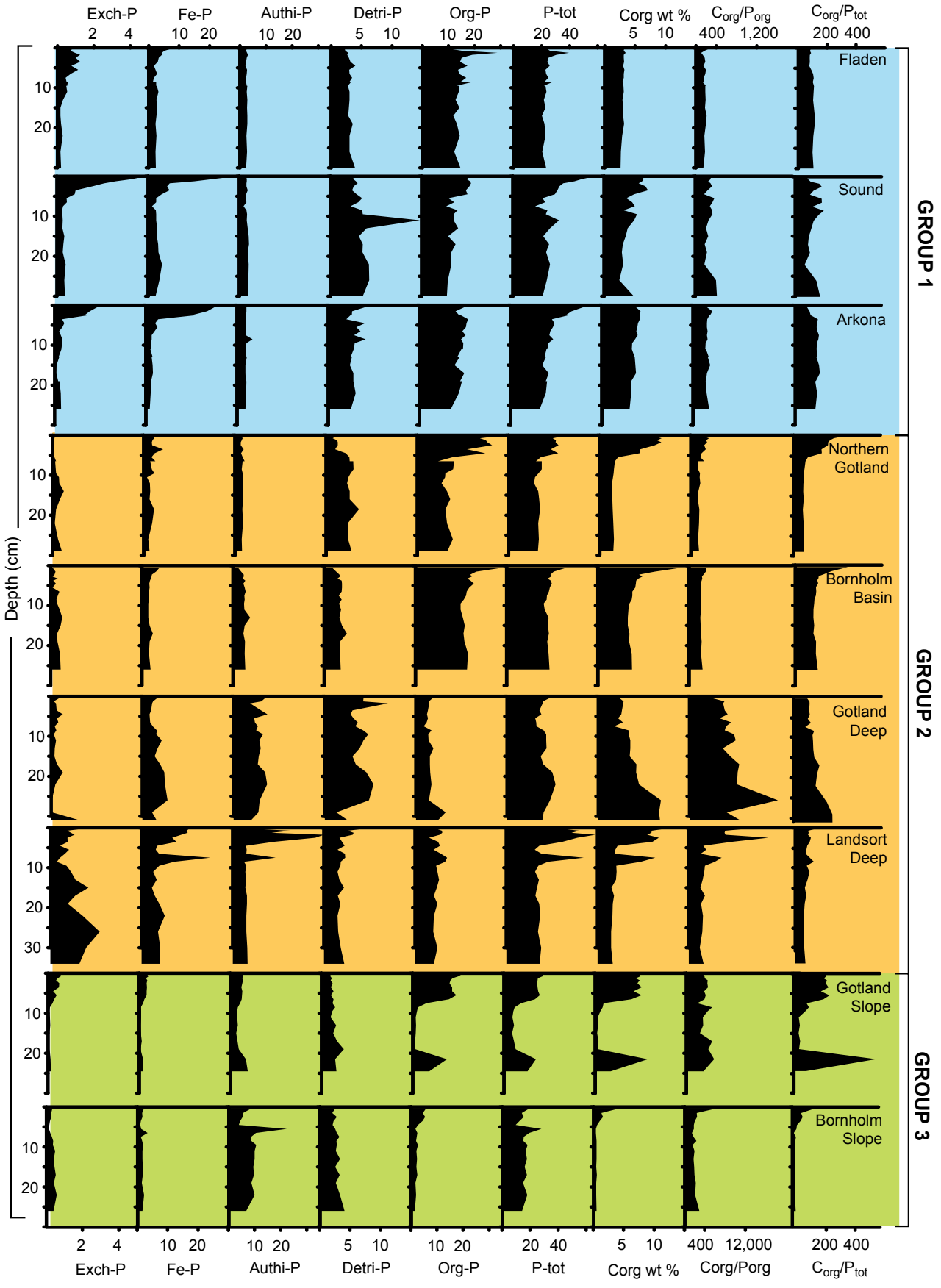


Figure 8. Solid phase profiles of exchangeable P, Fe-bound P, authigenic Ca-P, detrital P, organic P (Porg) and total P (all in umol/g) and organic C (Corg in wt%), Corg/Porg and Corg/Ptot (both in mol/mol).

5.4 Phosphorus speciation

Total concentrations of P at depth in the sediment are, on average ~22 μmol/g, despite the wide range in ambient redox conditions (Fig. 8). All Group 1 sites show surface enrichments of exchangeable and Fe-bound P and Fe-oxides. This Fe-bound P is not an important burial sink, however, since at depth Fe-bound P concentrations are negligible. Authigenc Ca-P concentrations are very low and constant with depth, suggesting little in-situ formation. Organic P is the major burial sink for P at these sites. The same holds for the group 2 stations Northern Gotland and Bornholm basin. The other group 2 stations show different patterns for P: at the Gotland Deep site, authigenic Ca-P is an important sink for P, while organic P is of less significance. Detrital Ca-P is also a quantitatively important phase. An inverse correlation is observed between reactive P and Al burial. At the Landsort Deep site, peaks in Fe-P and authigenic Ca-P are observed that coincide with maxima in organic C and Ca (Fig. 4). The group 3 sites show signatures of both groups 1 and 2, with organic P being the dominant phase in the surface layer of the Gotland Slope site and authigenic Ca-P being dominant at depth at the Bornholm Slope site. Biogenic Ca-P concentrations were negligible in sediments from the Bornholm basin and Gotland Deep and at depth at the Landsort Deep site. ~6 μmol/g of P was extracted with NH_4Cl from the surface sediment of the Landsort Deep, but this may not necessarily be fish debris, since this extractant also dissolves carbonates.

5.5 Corg/Porg and Corg/Ptot ratios

Ratios of organic C/organic P (Corg/Porg) in sediments of the deepest anoxic basins (group 2) are significantly higher than the Redfield ratio (106; the average C:P ratio for primary producers) and than values for group 1 locations, indicating enhanced release of P from organic matter under anoxia (Fig. 8). For example, average Corg/Porg ratios for the anoxic Gotland and Landsort Deep are 780 and 480, respectively. At the oxic Fladen site, in contrast, the average Corg/Porg ratios is 120, while an intermediate value of 290 is observed for the seasonally hypoxic Arkona site. Corg/Ptot ratios show less pronounced differences between group 1 and 2 stations suggesting that increased burial of inorganic P at the anoxic sites largely compensates for this enhanced loss from organic matter.

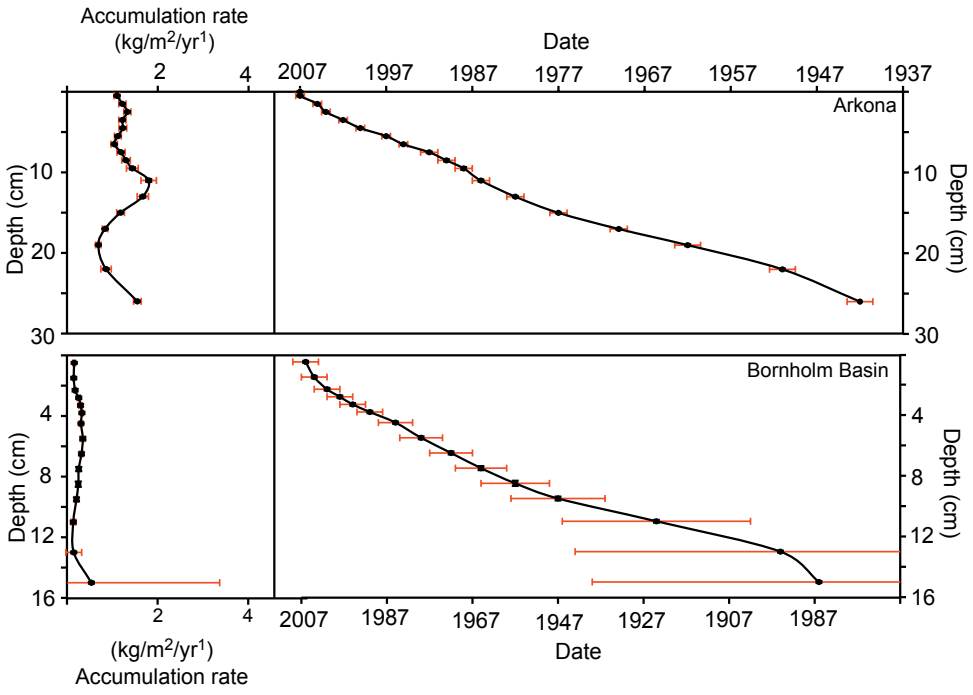


Figure 9. Age profiles and sediment accumulation rates for the Arkona and Bornholm anoxic sites (based on ^{210}Pb and ^{137}Cs profiles).

5.6 Age dating and sediment accumulation rates (Arkona, Bornholm basin, Gotland Deep)

Age dating based on ^{137}Cs and ^{210}Pb profiles indicates significant sediment burial at the Arkona and Bornholm sites (average of 0.4 cm/yr and 0.12 cm/yr respectively). At both sites, the surface sediment is subject to slight mixing. No reliable dating was possible for the Gotland Deep core due to very low contents of unsupported ^{210}Pb and ^{137}Cs. This site is probably experiencing erosion and based on these profiles, it is safe to say that sediments below 8 cm depth are older than 120 years.

6. Discussion

6.1 Diagenetic processes in Baltic Sea sediments

Phosphorus dynamics in aquatic sediments are largely driven by primary and secondary redox reactions related to organic matter and mineralization. As a consequence, predictions of the response of the sedimentary P cycle to environmental change (e.g. oxygen conditions, sediment mixing, salinity) require detailed insight in the prevailing diagenetic processes (Canavan et al., 2006a and b). Many detailed studies on selected diagenetic processes and products have been carried out for the various subbasins in the Baltic Sea (e.g. Boesen and Postma, 1988; Jakobsen and Postma, 1989; Piker et al., 1998; Rysgaard et al., 2001; Tuominen et al., 1998) including assessments of the role of sediments in P dynamics (e.g. Jansson, 2001). However, a comprehensive and quantitative understanding of organic matter mineralization, iron cycling and sulphate reduction in the various subbasins, their relation to the sedimentary P cycle and their response to perturbation is still lacking.

Recently Lehtoranta et al. (2008) suggested that sulphate reduction is the major pathway for organic matter mineralization in sediments of the Baltic Proper. In general, the trends in our porewater and solid phase data confirm this major role for sulphate reduction in the anoxic basins (group 2). This is evident, for example, at the Gotland Deep site where porewater Fe^{2+} is absent due to Fe scavenging by hydrogen sulphide (H_2S) and burial as pyrite (also see Boesen and Postma, 1988). Other pathways, such as oxic respiration, denitrification and dissimilatory Mn- and Fe-oxide reduction, may be of additional importance at the group 1 and group 3 sites. Note that secondary redox reactions (e.g. reduction of Mn and Fe-oxides by H_2S, oxidation of Fe^{2+} and Mn^{2+} with oxygen) may in fact play a dominant role in controlling Fe and P cycling in these organic rich sediments. (Wijsman et al., 2002; Canavan et al., 2006b).

At the Landsort Deep and Gotland Deep sites, a close correlation between burial of Ca, Mn and carbonates is observed. This has been shown to be due to formation of Ca-rhodochrosite minerals in these basins (Jakobsen and Postma, 1989). At the Landsort Deep site, burial of organic C and P is also enhanced in these layers, suggesting possible enhanced formation of authigenic Ca-P during rhodochrosite and calcite precipitation in the sediment or, possibly, the formation of mixed Ca-Mn-P-Fe minerals.

A critical issue for the interpretation of the solid phase and porewater profiles is the sedimentary regime at the sites (erosional, depositional), the dating of the cores and the transient changes in bottomwater chemistry. Preliminary dating results show that the Arkona and Bornholm sites can be considered as depositional, whereas the Gotland Deep site has undergone erosion. Further dating of 4 additional cores is in progress to resolve these issues. Based on the large variations with depth in total elemental concentrations at the two slope sites of group 3, these likely also may have undergone periods of erosion/ lack of net accumulation.

6.2 Temporary burial of P and the internal source of P in the Baltic Sea

Variations in P availability in the water column of the Baltic Sea (Conley et al., 2002) have been attributed to reductive dissolution of Fe-oxides and release of associated P during periods of hypoxia. Our porewater Fe^{2+} and PO_4 and sediment Fe-bound P profiles for

Arkona (Fig. 10) demonstrate the periodic release of PO_4 from the sediment during the seasonally hypoxic period in late summer at this site (SMHI, 2008). Similar surface enrichments, although less pronounced, are observed at the Fladen and Sound sites (Fig. 8). Here, a thin oxic sediment layer is still present and is likely leading to retention of P in Fe-bound P. Although Fe-oxide profiles for Arkona closely follow the Fe-bound P profiles, average Fe/P ratios for this site are relatively high (~38) compared to what is common in most marine and brackish sediments (range from 2-20; e.g. Slomp et al., 1996b; Gunnars and Blomqvist, 1997). This suggests that the Fe-oxides at these sites have a low affinity for P.

Diffusive fluxes of PO_4 across the sediment-water interface calculated for the 9 stations (based on the porewater profiles and assuming molecular diffusion; Fig. 11) show that highest PO_4 fluxes are observed for the seasonally hypoxic sites in group 1 (Sound and Arkona). Intermediate flux values are found at the anoxic sites of Group 2 and 3 whereas lowest fluxes are found at the permanently oxic site (Fladen) and the site that was oxic during sampling (Bornholm Slope). These trends are in accordance with earlier studies showing that sediment-water exchange rates are enhanced upon a redox change from oxic to anoxic conditions (Sundby et al., 1986; Koop et al., 1990) and more efficient P retention in oxic sediments (Slomp et al., 1998). These flux values compare well to the range of 180 to 440 μmol m^{-2} d^{-1} estimated by Conley et al. (2002) based on changes in dissolved dissolved inorganic P (DIP) in the water column upon expansion of the hypoxic area. At the observed flux rate of P, it would take almost 1.5 years of continous hypoxia to achieve complete loss of the Fe-bound P enrichment at the Arkona site. Preliminary modeling of the Arkona data with a simple 1-D single component for P (Slomp et al., 1996a) has been performed and confirms the conclusions above.

6.3 Permanent burial of P in the Baltic: quantification and controlling factors

Burial forms of sediment P in the Baltic Sea are dependent on the prevailing redox conditions, as is evident from the average P speciation for the deepest sediment section for sediment cores from group 1 (oxic, seasonally hypoxic) and group 2 (anoxic) sites (Table 2). Average total reactive P concentrations are similar at 17 and 21 μmol/g for groups 1 and 2, respectively. However, organic P is a significantly more important sink at the oxic/hypoxic sites, whereas Fe-bound P and authigenic Ca-P are prominent sinks at the anoxic sites. This is also obvious

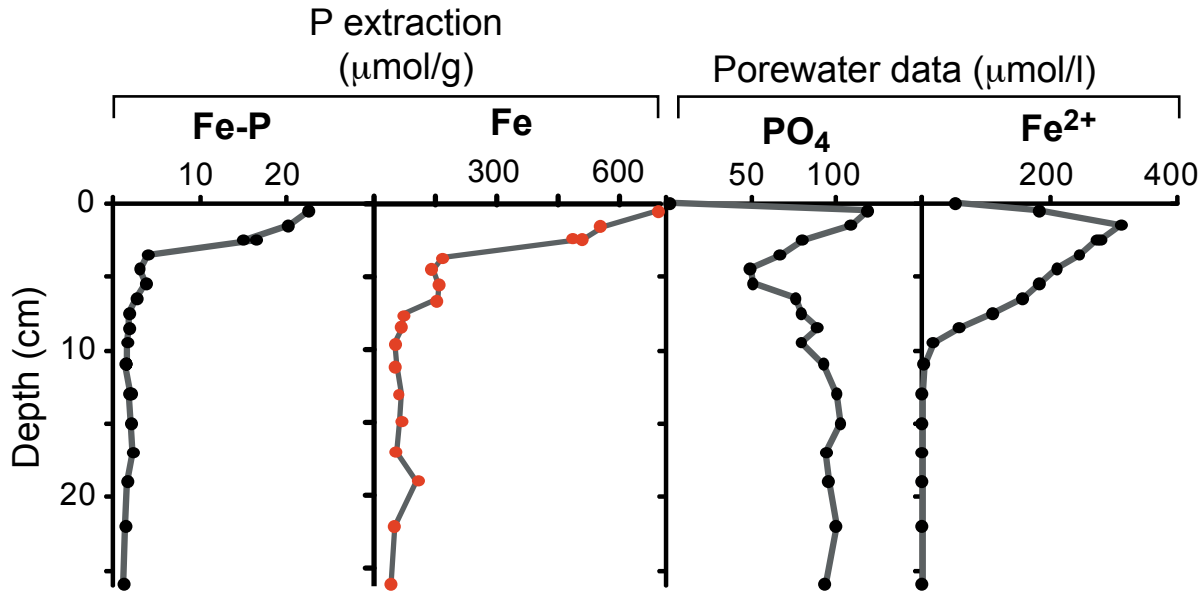


Figure 10. Depth profiles of Fe-bound P and Fe-oxide Fe and porewater PO_4 and Fe^{2+} for Arkona.

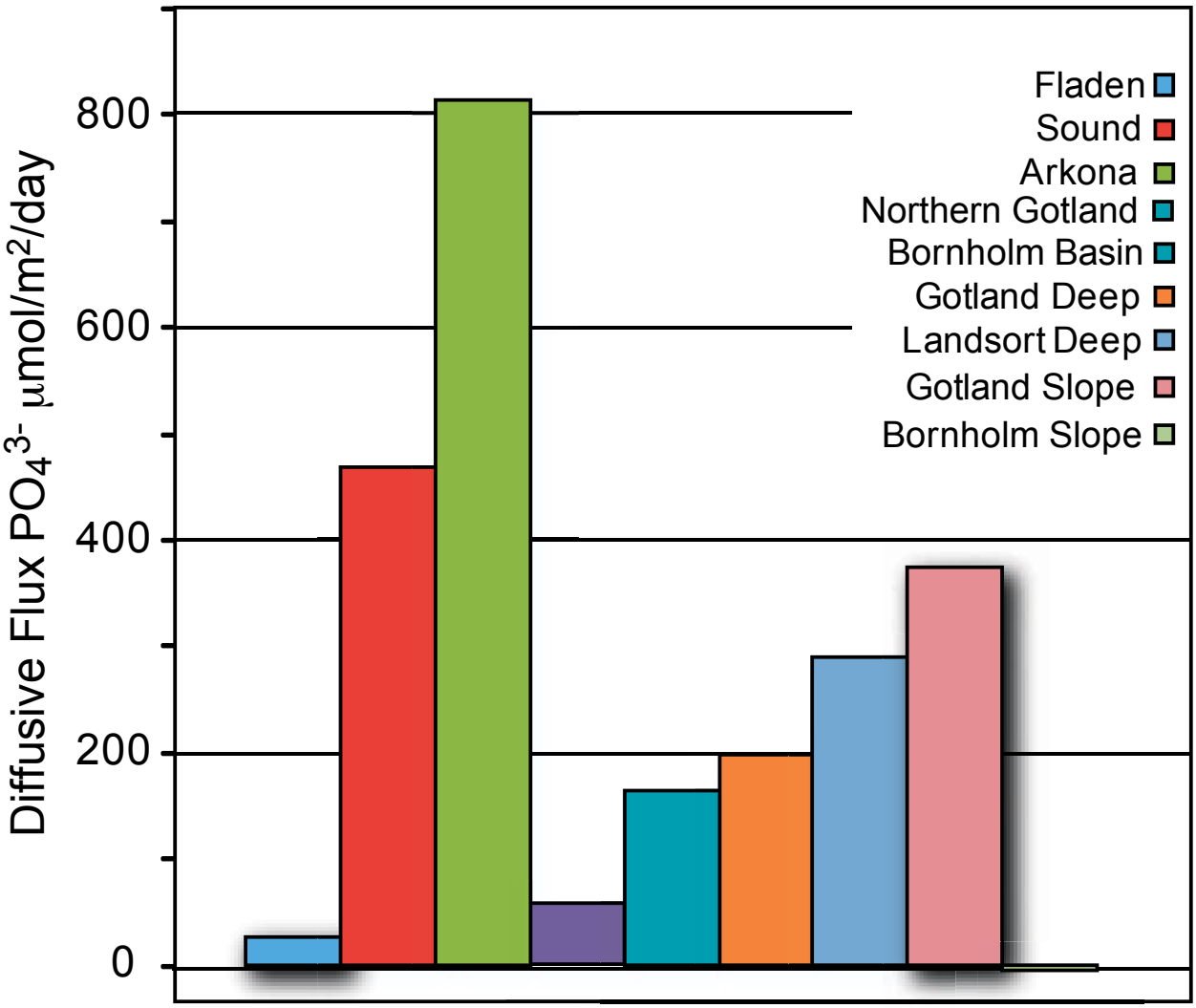


Figure 11. The diffusive fluxes of PO_4 for each station calculated from PO_4 bottomwater and porewater data (from Figure 7, except for Baltic proper for which rhizon data were used; data not shown). See text for details.

when directly comparing the P speciation and organic C contents for Fladen (group 1; oxic) and the Gotland Deep site (group 2; anoxic), (Fig. 12). Organic P accounts for 75% of the reactive P burial at the Fladen site, compared to 40% at the Gotland Deep location, despite the generally higher organic C contents at the latter site. The data for the group 3 sites (Gotland and Bornholm slopes) suggest that here authigenic Ca-P is the dominant burial phase. Dating of these cores is needed to assess whether these sites are truly depositional (see section 6.1). Fish debris is not important as a P burial sink in the Baltic.

Our results for group 1 and 2 suggest there is no (or only very limited) sink-switching of Fe-bound and organic P to authigenic Ca-P in

Table 2. Average contribution of each P burial phase to total reactive P burial (in %) for each group of sites.

Phase	Group 1	S.D.	Group 2	S.D.	Group 3	S.D.
Organic-P	69	*6*	44	12	28	*20*
Authigenic-P	17	*4*	28	3	58	*12*
Fe bound-P	12	*3*	22	7	12	*6*
Exchangable-P	2	*1*	5	4	3	*2*

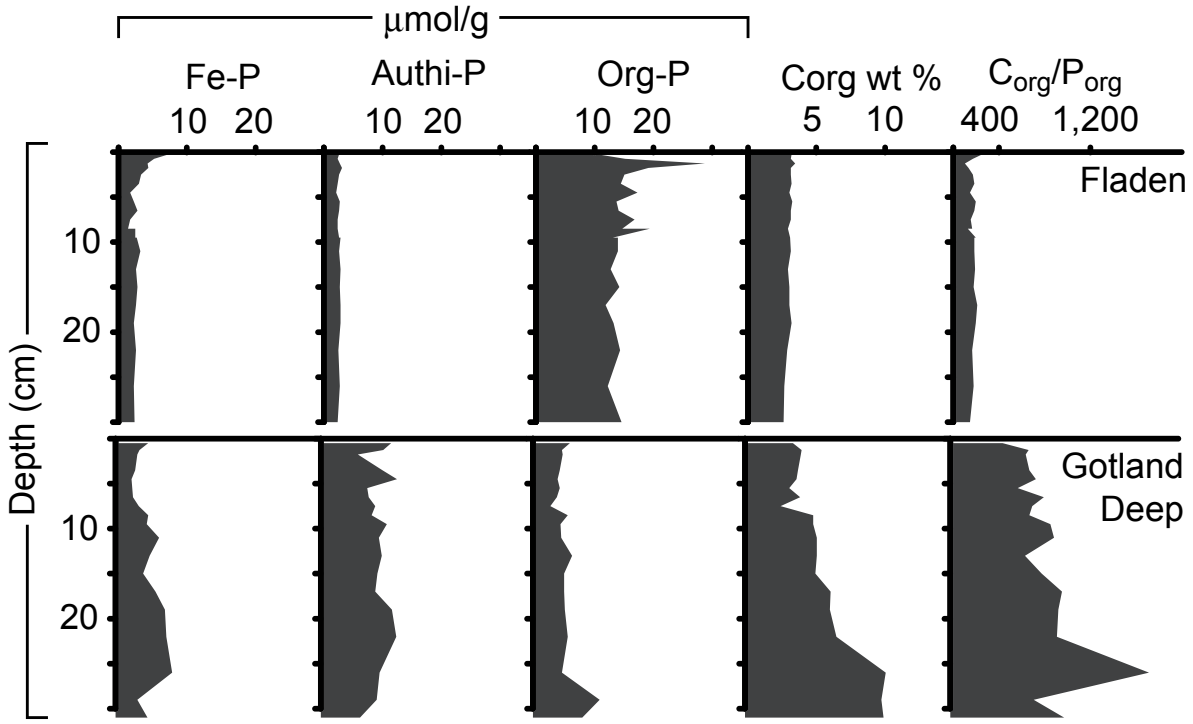


Figure 12. P speciation and organic C contents for Fladen (oxic) and Gotland Deep (anoxic) for comparison.

the oxic and hypoxic areas in the Baltic Sea (group 1). Organic P is the dominant sink for P at these sites. In the anoxic basins (group 2), in contrast, results suggest enhanced release of P from organic matter and subsequent significant retention of P in inorganic minerals that, based on our extractions, are suggested to be Fe-bound P and authigenic Ca-P. Note, however, that the actual minerals may possibly include, mixed Ca-Mn-P-Fe phases (Nriagu and Moore, 1984). The inverse correlation of P burial with Al at the Gotland Deep site suggests that sediment dilution may also play a role. Since the age dating results indicate that the Gotland basin site is undergoing erosion, it is not possible to assess whether P mineral formation is occurring in the overlying water, at the sediment-water interface or at greater depth in the sediment.

The enhanced regeneration of P from organic matter at the deep basin sites of group 2 is highlighted in Fig. 13 by the higher C_{org}/P_{org} ratios for the Landsort and Gotland Deep sites. C_{org}/P_{tot} are mostly within the same range for the oxic sites. Similar results are obtained when plotting Corg/Porg versus Corg/Preactive (with P reactive being the sum of all P phases excluding detrital Ca-P; data not shown). Figure 13 illustrates that while P is regenerated preferentially from organic matter in the anoxic basins, the overall average retention efficiency in the oxic and anoxic locations is similar due to enhanced authigenic Ca-P and Fe-P burial in the deep basins. The linear correlation between Corg/Porg and Corg/Ptot (Fig 13) for all other sites suggests that outside the deep basins, enhanced regeneration of P from organic matter leads to decreased P retention in the sediment. Again, similar results are obtained when plotting Corg/Porg versus Corg/Preactive. Note that Emeis et al. (2000) observed an increase in Corg/Ptot (to values of ca. 300 from ca. 100) at a Gotland Deep site since the early 1970s, which they related to increased anoxia in the basin.

Detrital P concentrations in Baltic Sea sediments are relatively low, accounting for on average 15% of total P. Thus, P burial estimates based on total amounts for deeper layers provide a good approximation. Note that our average total burial concentration of 22 µmol P/g is bracketed by the total P values of 16 and 30 µmol P/g used by Jonsson et al. (1990) to calculate P burial rates in the Baltic Proper of 15 and 28 x 10^3 ton/y.

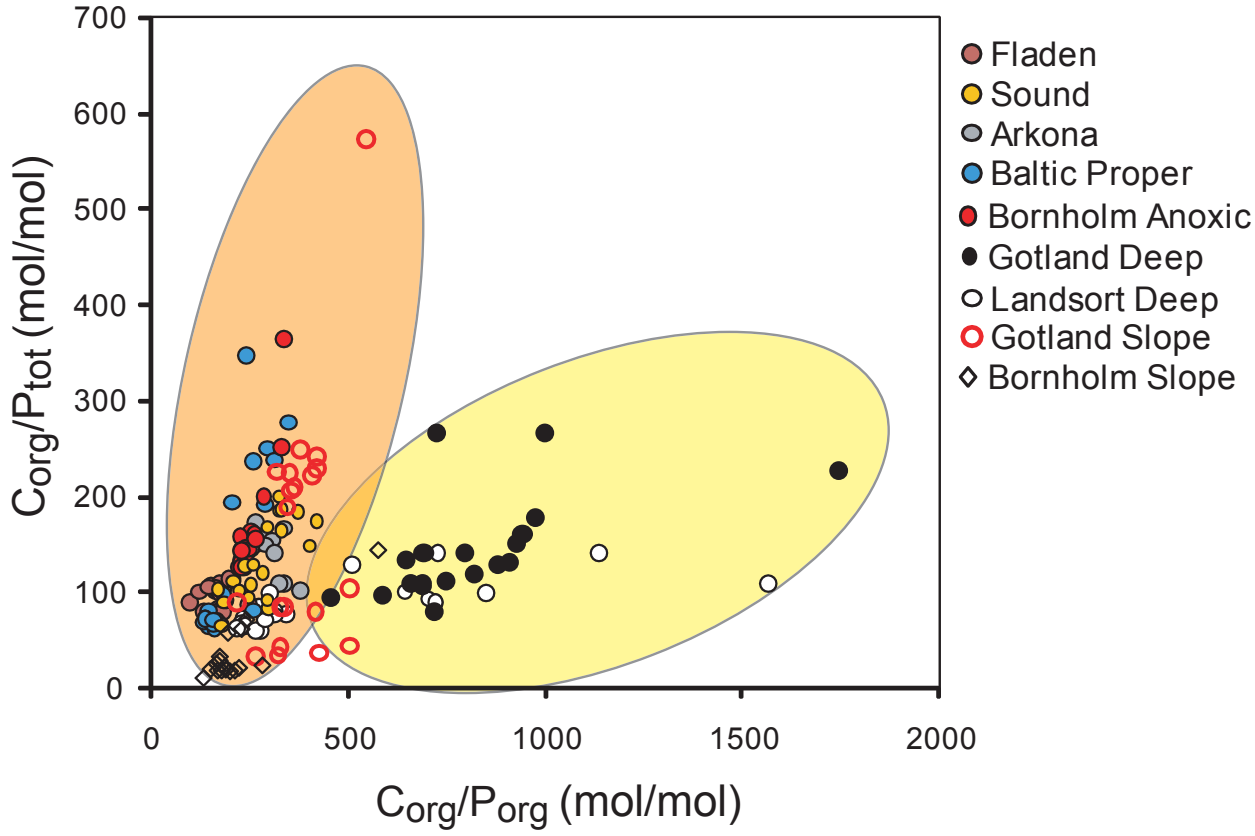


Figure 13. C_{org}/P_{org} versus C_{org}/Pt_{ot} for all 9 sites.

7. Conclusions

Porewater and sediment data indicate that sediment Fe-bound P acts as a temporary sink and source for P in oxic/seasonally hypoxic areas of the Baltic. Sediment-water exchange rates obtained from this study compare well to estimates of changes in water column PO_4 upon changes in hypoxic area from the literature (Conley et al., 2002). High ratios of Fe-oxide Fe/P compared to other marine and brackish environments suggest that the Fe-oxides in the surface enrichments of the sediment have a relatively low affinity for P.

Organic P is the major burial sink for reactive P in oxic/seasonally hypoxic sediments (group 1). There is no evidence for sink-switching of P from Fe-bound P or organic P to authigenic Ca-P in the oxic/seasonally hypoxic sediments in the Kattegat, Sound and Baltic proper. Sediment P retention relative to organic C is reduced under increased hypoxia at these sites: i.e., the more anoxic the sediment becomes, the more release of P from organic matter and the less net P burial.

Besides organic P, Fe-bound P and authigenic Ca-P phases are important at the anoxic sites (group 2) in the Gotland Deep and Landsort Deep. Enhanced regeneration of P from organic matter is compensated by "sink switching" of P to these inorganic P mineral phases. As a consequence, a similar average retention of P relative to organic C is observed compared to oxic sites.

Detrital P is a relatively minor phase, on average accounting for only 15% of total P. Total P burial concentrations average ~22 μmol/g in the studied regions. Apart from the surface enrichments in Fe-bound P at oxic/seasonally hypoxic sites and the P peaks in the Landsort Deep, sediment P concentrations are generally relatively constant at greater depth. This confirms earlier work (Jonsson et al., 1990) that P burial in the Baltic Proper is significant.

8. Implications

Long-term increased oxygenation of the deep basins of the Baltic (e.g. Stigebrandt and

Gustafsson, 2007) is expected to lead to major changes in sediment P dynamics in the Baltic. Our results confirm earlier work that there is a large reservoir of FeS and FeS_2 in the sediment. Oxygenation of the sediments and oxidation of this reduced iron may lead to oxidation of this reduced Fe and the formation of a larger pool of Fe-oxide bound P in the sediment and thus temporary increased P retention. Note, however, that this will increase the P store that can be released during hypoxic periods. The acidity generated during FeS_2 oxidation with oxygen might further enhance sediment P availability, potentially mobilizing Ca-P forms or P from less easily reducible Fe-oxides. New formation of inorganic P minerals in these basins may be reduced. However, increased burial of organic P, may partly compensate these changes. Low Corg/Ptot values reported for the Gotland Deep before 1960 by Emeis et al. (2000) suggest that the long-term retention of P in these basins will indeed be enhanced upon re-oxygenation.

Increased hypoxia of the oxic/seasonally hypoxic areas will lead to a further reduction of the burial of organic P and, due to the lack of sink-switching to other phases, an initial reduction of total P burial. Further insight in the formation conditions of the inorganic mineral forms in the deep basins is needed to assess whether these ultimately could form in the shallower regions also and whether "sink-switching" could become important. Increased oxygenation of the seasonal hypoxic areas will directly increase the retention of P in these areas.

9. Future work

The qualitative and quantitative connections between the diagenetic processes and the sedimentary P cycle in the sediments of this study can only be adequately resolved with multi-component reactive transport modeling. We will pursue this in a project which starts August 1, 2008 (Baltic Sea 2020 project 2917 "Benthic Pelagic Coupling in the Baltic Sea: the effect of redox changes on sediment P release and implications for water quality"). We will concentrate on modeling diagenetic processes including P cycling for key sites in the Baltic along a redox gradient (including Fladen, Arkona, Bornholm). We specifically aim at assessing the effects of changes in redox conditions and organic matter loading on P release and burial.

Given the fact that our site in the Gotland Deep was experiencing erosion, we are seeking opportunities and funding to obtain a new core from this region for full analysis. We also aim at performing a detailed (spectroscopic) study to elucidate the chemical and mineralogical composition of the P mineral phases in the Gotland basin and Landsort Deep and the Fe-oxides in the surface sediments at Arkona. This will allow us to assess the controls on their formation and the associated P retention. ^{210}Pb and ^{137}Cs dating for 4 cores in this study (not a part of this proposal) are still pending.

We will perform a study on P burial in Bothnian Sea sediments to assess its role in P sequestration from the Baltic Proper including its expected response to continued P loading. (Baltic Sea 2020 project 2930 "Phosphorus dynamics in the Baltic Sea: quantifying the Bothnian Sea burial sink").

10. Acknowledgements

We thank the captain and crew of RV Skagerrak, Andreas Nygren and all participants in the cruise to the Baltic Sea in 2007 (see cruise report in Appendix I) for their assistance with the field work. Pieter Kleingeld is greatly acknowledged for technical assistance. Helen de Waard and Dineke van de Meent are thanked for their contribution to the cruise preparations and chemical analyses (IC, ICP-OES). C.P. Slomp was funded by a VIDI-Grant (Netherlands Organisation for Scientific Research; NWO). T.J. Andersen performed the ^{210}Pb and ^{137}Cs analyses used to date 3 cores. We thank Dan Conley for continued support and valuable discussion.

11. References

Anderson, L.D. Delaney, M.L. and Faul, K.L., 2001. Carbon to phosphorus ratios in sediments: Implications for nutrient cycling. Global Biogeochemical. Cycles 15, pp. 65–79.

Appleby, P.G., 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M. and Smol, J.P. (eds). Tracking environmental changes using lake sediments. Volume 1. Basin analysis, coring and chronological techniques. Kluwer Academic Publishers, p171-203.

Algeo and Ingall, 2007. Sedimentary C-org : P ratios, paleocean ventilation, and Phanerozoic atmospheric pO(2). Palaeogeography, Palaeoclimatology and Palaeoecology, 256(3)

Boesen, C. and D. Postma, 1988. Pyrite formation in anoxic environments of the Baltic. American Journal of Science 288: 575-603.

Canavan, R.W., C.P. Slomp, P. Jourabchi, P. Van Cappellen, A.M. Laverman. 2006a. Organic matter mineralization in sediment of a coastal freshwater lake and response to salinization. Geochimica Cosmochimica Acta 70: 2836-2855.

Canavan, R.W. and C.P. Slomp, 2006b. Phosphorus cycling in sediment of a coastal freshwater lake and response to salinization. Chapter 6. In: Biogeochemical cycling of nutrients and trace metals in the sediment of Haringvliet Lake: response to salinization. PhD thesis, Utrecht University. 159p.

Carman, R. and Rahm, L., 1997. Early diagenesis and chemical characteristics of interstitial water and sediments in the deep deposition bottoms of the Baltic Proper. J. Sea Res. 37: 25–47.

Conley, D.J., Humborg, C., Rahm, L., Savchuk, O.P., and Wulff, F., 2002, Hypoxia in the Baltic Sea and Basin-Scale Changes in Phosphorus Biogeochemistry: Environmental Science Technology, v. 36, p. 5315-5320.

Emeis, K.-C., Struck, U., Leipe, T., Pollehne, F., Kunzendorf, H., and Christiansen, C., 2000, Changes in the C, N, P burial rates in some Baltic Sea sediments over the last 150 years—relevance to P regeneration rates and the phosphorus cycle: Marine Geology, v. 167.

Fonselius, S.H., 1985. Oxygen and hydrogen sulphides conditions in the Baltic Sea: Marine Pollution Bulletin, 12(6), 187-194

Gunnars, A. and Blomqvist, S., 1997. Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions – an experimental comparison of freshwater and brackish-marine systems Biogeochemistry 37: 203-226.

HELCOM, 2003. The Baltic Marine Environment 1999-202. Baltic Sea Environment Proceedings 87.

Hille, S., 2005, New aspects of sediment accumulation and reflux of nutrients in the Eastern Gotland Basin (Baltic Sea) and its impact on nutrient cycling [Dissertation thesis]: Rostock, Universität Rostock.

Ingall, E. D., Bustin, R. M. and Vancappellen, P., 1993. Influence of Water Column Anoxia on the Burial and Preservation of Carbon and Phosphorus in Marine Shales: Geochimica Et Cosmochimica Acta 57: 303-316

Jakobsen, R. and D. Postma, 1989. Formation and behaviour of Ca-rhodochrosites in marine muds of the Baltic deeps. Geochimica Et Cosmochimica Acta 53: 2639-2648.

Karlsson, K., Rosenberg, R. and Bonsdorff, E. 2002., Temporal and spatial large-scale effects of eutrophication and oxygen deficiency on benthic fauna in Scandinavian and Baltic waters-a review. Oceanography and Marine Biology: An Annual Review, 40, 427-489.

Kraal, P., Slomp, C.P., Forster, A., Kuypers, M.M.M., Sluijs, A., submitted. Pyrite oxidation during sample storage determines phosphorus fractionation in carbonate-poor anoxic sedimentsGeochimica et Cosmochimica Acta.

Koop K., Boynton W.R., Wulff F. and Carman R., 1990. Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea. Mar. Ecol. Prog. Ser. 63: 65–77.

Kullenberg, 1981. Physical oceanography. In: The Baltic Sea (eds. Voipio, A). Elservier, New York.

Larsson, U., R. Elmgren, F. Wulff, 1985. Eutrophicatino and the Baltic Sea. Ambio 14: 9-14.

Lehtoranta, J. 2003. Dynamics of sediment phosphorus in the brackish Gulf of Finland. Monographs of the Boreal Environment Research. No. 24.

Lehtoranta, J. et al., In press. Eutrophication-driven

sediment microbial processes can explain the regional varition in phosphorus concentrations between Baltic Sea sub-basins. doi:10.1016/j.jmarsys.2008.04.001

Jonsson, P., Carman, R. Wulff, F., 1990. Laminated sediments in the Baltic – a tool for evaluating nutrient mass balances. Ambio 19: 152-158.

Jansson, M. 2001. Role of sediments in nutrient dynamics of the Baltic. In: (eds. Wulff, F and Rahm, L) A Systems Analysis of the Baltic Sea. Ecological Studies, 148.

Nriagu, J. O., and Moore, P. B., (Editors), 1984. Phosphate Minerals. Springer-Verlag. ISBN 3-540, pp 0-387, New York.

Piker, L., Schmaljohann, R. and Imhoff, J., 1998. Dissimilatory sulphate reduction and methane production in Gotland Deep sediments (Baltic Sea) during a transition period from oxic to anoxic bottom water. Aquatatic Microbial Ecology. 14: 183–193.

Ruttenberg, K.C. 1992. Development of a sequential extraction procedure for different forms of phosphorus in marine sediments. Limnology and Oceanography 37: 1460-1482.

Ruttenberg, K.C. and Berner, R.A., 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. Geochimica Cosmochimica Acta 57: 991–1007.

Ruttenberg, 2003. The Global Phosphorus Cycle. In: Treatise on Geochemistry, vol. 8, 585-643. ISBN 0-08-043751-6.

Rysgaard, S., Fossing, H. and Jensen, M.M., 2001. Organic matter degradation through oxygen respiration, denitrification, and manganese, iron, and sulphate reduction in marine sediments (the Kattegat and Skagerrak). Ophelia 55: 77–91.

Savchuk, O. 2005. Resolving the Baltic Sea in to seven subbasins: N and P budgets for 1991-1999. Journal of Marine Systems 56: 1-15.

Schenau, S. J. and De Lange, G. J., 2000. A novel chemical method to quantify fish debris in marine sediments. Limnology and Oceanography 45: 963-971

Seeberg et al., 2005. Rhizon sampling of of aquatic systems. Limnology and Oceanography Methods 3: 361-371.

Slomp, C.P., E.H.G. Epping, W. Helder, W. van Raaphorst. 1996a. A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments. Journal of Marine Research 54: 1179-1205.

Slomp, C.P., S.J. van der Gaast, W. van Raaphorst. 1996. Phosphorus binding by poorly crystalline iron oxides in North Sea sediments. Marine Chemistry 52: 55-73.

Slomp, C. P., Malschaert, J. F. P. and Van Raaphorst, W., 1998. The role of adsorption in sediment-water exchange of phosphate in North Sea continental margin sediments. Limnology and Oceanography 43: 832-846

Slomp, C.P., Thompson, J.A., and de Lange, G.J., 2002, Enhanced regeneration of phosphorus during formation of the most recent eastern Mediterranean sapropel (S1): Geochimica Et Cosmochimica Acta: 66: 1-20.

SMHI (Swedish Meterological and Hydrological Institute), 2008. Cruise Report RV Argos.

Stigebrandt and Gustafsson, 2007. Improvement of Baltic Proper water quality using large-scale ecological engineering. Ambio, 36(2-3), 280-286.

Sundby, B., Anderson, L.G., Hall, P.O.J., Iverfeldt, Å., Rutgers van der Loeff, M.M., Westerlund, S.F.G., 1986, The effect of oxygen on release and uptake of cobalt, manganese, iron and phosphate at the sediment-water interface: Geochimica et Cosmochimica Acta, 50, 1281-1288.

Tuominen L., Heinänen A., Kuparinen J. and Nielsen L.P., 1998. Spatial and temporal variability of denitrification in the sediments of the northern Baltic Proper. Mar. Ecol. Prog. Ser. 172: 13–24.

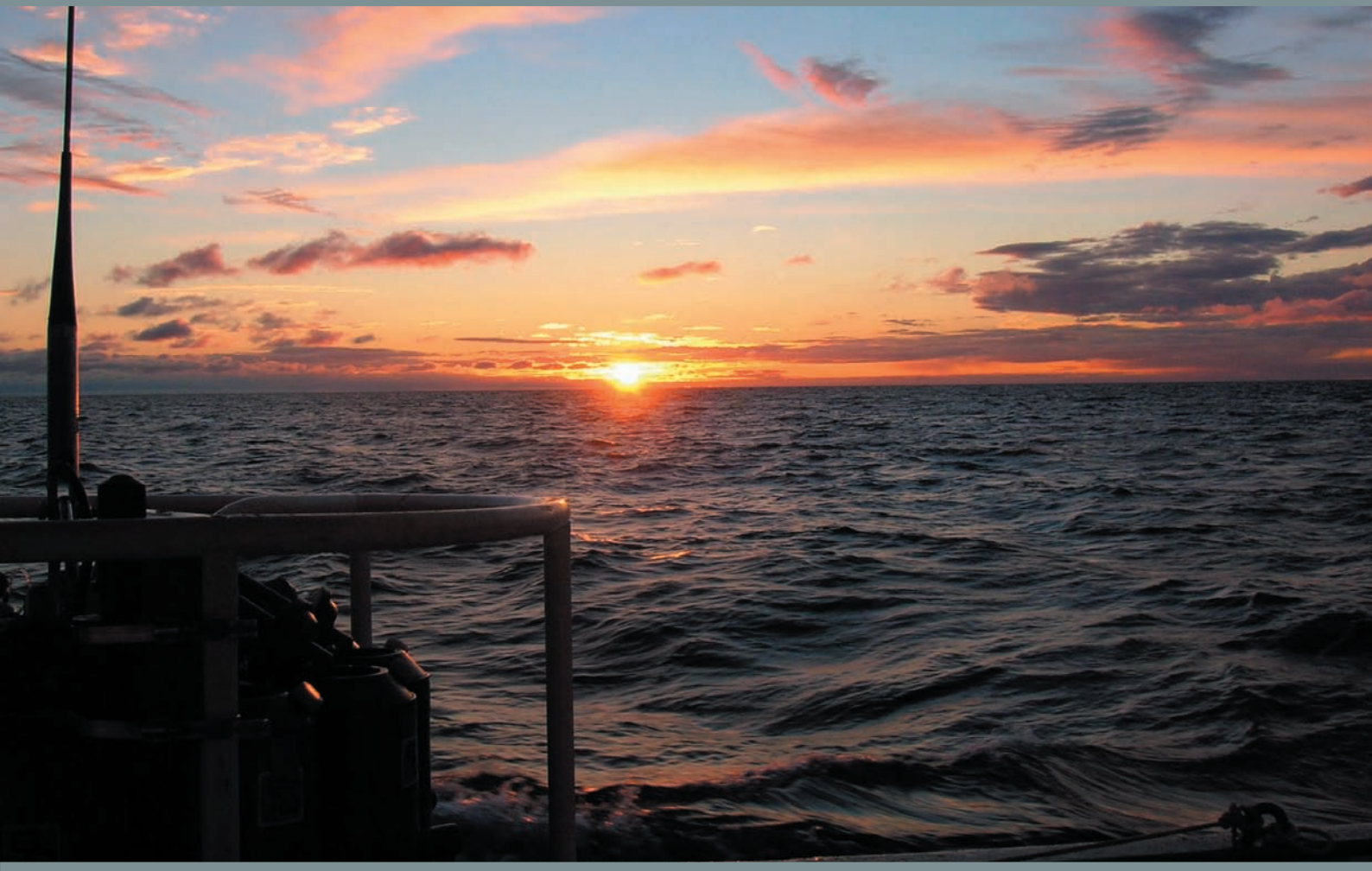
Westman, P., et al. 2003. Probable causes for cyanobacterial expansion in the Baltic Sea: Role of anoxia and phosphorus retention: Estuaries 26, 680-689.

Wijsman J, Herman, P. M. J., Middelburg, J. J. and Soetaert, K., A model for early diagenetic processes in sediments of the continental shelf of the Black Sea. Estuarine Coastal Shelf Science, 54(3): 403-421.

Wulff, F., Rahm, L.; Hallin, A.-K.; Sanberg, S. 2001. A nutrient budget model of the Baltic Sea. In: A Systems Analysis of the Baltic Sea; Wulff, F., Rahm, L., Larsson, P., Eds.; Springer- Verlag: Berlin; pp 353-372.

Appendix I

Shipboard summary



Funded by the Baltic Sea 2020

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SHIPBOARD REPORT

Cruise to the Baltic Sea with R.V. Skagerak

August 31 – September 7, 2007

Chief Scientist:
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CONTENTS

1. Abstract

The cruise to the Baltic Sea from August 31 to September 7, 2007, is part of a joint project of Goteborg University and Utrecht University on phosphorus (P) cycling in Baltic Sea sediments. This research runs from 2007-2008 and is funded by the Baltic Sea 2020 Foundation. The aim of the project is to improve our knowledge of the role of sediments as a permanent sink for P in the Baltic Sea and the processes that control this burial. During the cruise, water column, porewater and sediment samples for 10 sites with various redox conditions and salinities were collected. Preliminary results for alkalinity show high rates of organic matter degradation at most sites. The sediment samples will subsequently be analysed for concentrations of the various forms of P and other components (organic carbon and nitrogen, total element concentrations including trace metals) at Utrecht University. Additional cores were obtained for 6 sites to allow analysis of Hg and Hg isotopes by a researcher from the Univ. of Michigan..

Figure 1. View of the working deck of the Research Vessel RV Skagerak at Herrvik, Gotland on Sunday September 2.

Figure 2. The participants and crew. Note: no photographs were available for Andreas Nygren and the cook. (Photo's by Gretchen, Peter and Caroline)

2. Participants and their tasks

Table 1. Participants, contact information and tasks*

Name	Tasks
1. **Caroline Slomp** UU (slomp@geo.uu.nl)	Chief scientist, directing coring & sampling procedures, data management, porewater subsampling
2. **Haydon Mort** UU (h.mort@geo.uu.nl)	Anoxic core sectioning, subsampling, porewater centrifugation
3. **Peter Kraal** UU (p.kraal@geo.uu.nl)	O_2 microprofiles, bottom water samples, porewater subsampling, anoxic core sectioning
4. **Shauna Ni Fhlaithearta** UU (shauna@geo.uu.nl)	Anoxic core sectioning , porewater centrifugation, storage of cores, rhizons
5**. Iana Tsandev** UU (i.tsandev@geo.uu.nl)	Water sampling, O_2 titrations, alkalinity measurements
6. **Christian Nohr** GU (chno@oce.gu.se)	CTD-Rosette, water column samples, assisting the crew with coring
7. **Lena Victorsson** GU (lenav@gvc.gu.se)	Multicoring, CTD, titrations
8. **Madeleine Nilsson** GU (Madeleine.nilsson@gmail.com)	Multi- and boxcoring, titrations
9. **Gretchen Gehrke** Univ. of Michigan (gegehrke@umich.edu)	Sediment sampling for Hg & Hg-isotopes
10. **Per Hall**, GU	Multicoring, day 1
11. **Andreas Nygren**, GU	Multicoring, day 1

3. Acknowledgements

- We thank Andreas Nygren and the captain and crew of RV Skagerak for their excellent cooperation and assistance prior to and during the cruise.
- The Baltic Sea 2020 Foundation financed the use of the research vessel and the postdoc-position of Haydon Mort. Other funds were made available by Goteborg University and Utrecht University
- We thank Gert de Lange for making available various field materials for this cruise (including two gloveboxes and a centrifuge). We thank Per Hall for joining for one day to make the multicorer operational.

Coordinator at Goteborg University (GU)

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4. Introduction

This research cruise focused on collecting sediment cores to allow a quantification of sediment phosphorus burial in the Baltic Sea. The work was funded by the Baltic Sea 2020 Foundation (http://www.balticsea2020.com/).

Background: Increased human input of phosphorus (P) to the Baltic Sea since 1950 likely has led to enhanced primary production and the increased occurrence of hypoxia throughout the basin. Besides changes in P input, the P availability for primary producers in the water column of the Baltic is also determined by variations in the recycling efficiency within the system and the sinks for P, which are outflow to the North Sea and permanent burial in the sediments. Little is known, however, about the role of sediments as a permanent sink for P in the Baltic and the processes that control this burial.

Approach: We plan to perform detailed sediment core analyses to obtain quantitative insight into the factors controlling the burial of P in sediments of the various sub-basins in the Baltic Sea over the past century. Cores from selected anoxic and oxic sites will be analysed for organic C and N and total element concentrations (including trace metals) and will be subjected to a detailed P speciation. The latter will allow the determination of depth profiles of exchangeable P, Fe-bound P, authigenic Ca-P, biogenic Ca-P, detrital Ca-P and organic P. The sediment profiles will be interpreted quantitatively in a companion project. At a selected number of stations, porewater will be subjected to detailed chemical analysis. Since the water column of the Baltic Sea is well-monitored, we took only selected samples at each site to assess the oxygen, salinity and nutrient conditions at the time of sampling.

5. Time schedule of the fieldwork and map

Table 2. Time schedule of cruise

Day	Activity
Wednesday August 29	Flight to Goteborg of Peter, Caroline, Gretchen
Thursday August 30	Flight to Goteborg of Iana, Haydon, Shauna, Equipment placed on board, unpacking
Friday, August 31	Travel to harbour and boarding of ship, Departure from Hono at 12.30, Sampling at **Fladen (site 1)**, Andreas & Per from board at Varberg.
Saturday, September 1	Sampling of **Arkona basin (site 2; BY2)**
Sunday, September 2	Sampling of **Gotland deep (site 5; BY15)**
Monday, September 3	Sampling of **Gotland (not) oxic (site 4; BY15O)** Sampling of **Baltic Proper (site 6)**
Tuesday, September 4	Sampling of **Baltic Proper shallow (site 14; BY29O)** Sampling of **Landsort Deep oxic (site 8; BY31O)** Sampling of **Landsort Deep (site 9; BY31)**
Wednesday, September 5	Sampling of **Bornholm oxic (site 3; BY5O)** Sampling of **Bornholm basin (site 10; BY5)**
Thursday, September 6	Sampling of **Sound (site 11)**
Friday, September 7	Final site, including **Fladen (site 12 = site 1)**. Return to Goteborg, evening (18.00), packing
Saturday, September 8	Arrival of ship in Hono, return to Utrecht
Monday, September 10	Materials + Samples return to Utrecht

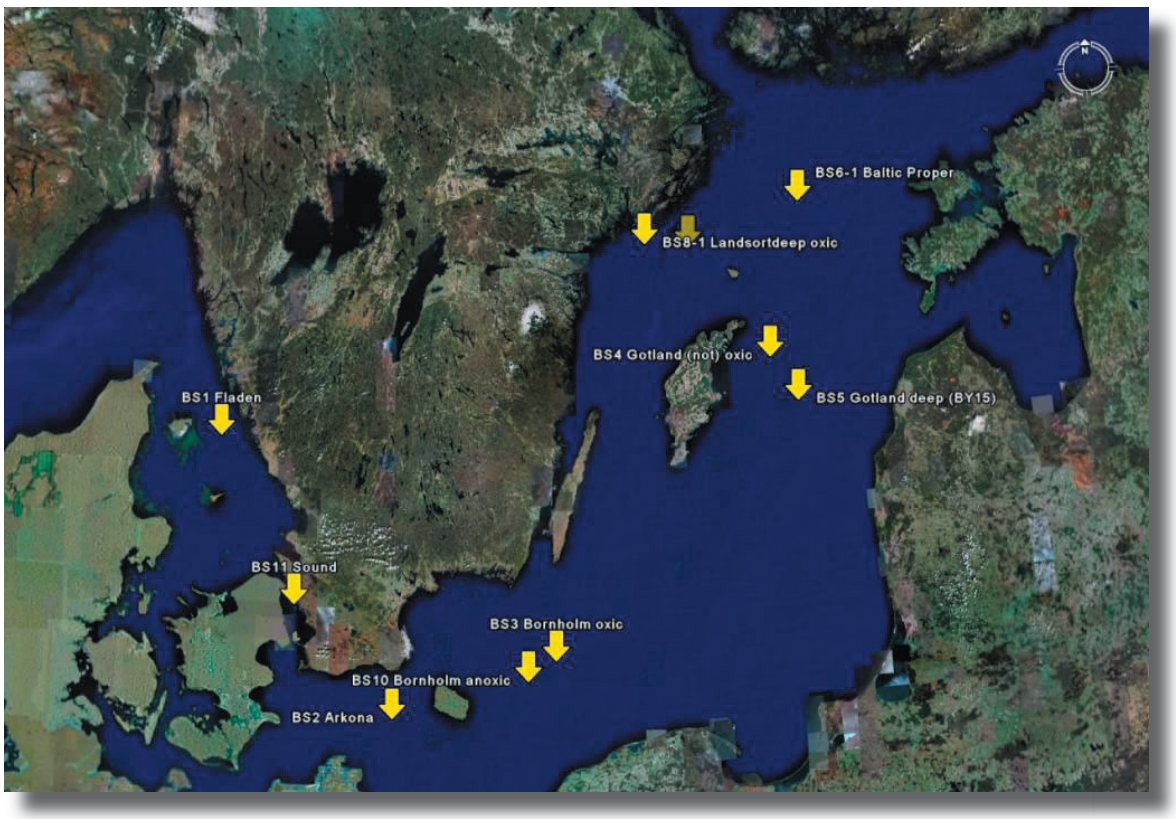


Figure 3. Map of the Baltic Sea. The arrows indicate the sampled sites.

6. Summary of CTD-casts and box- and multicores taken.

Table 3. Summary of CTD casts

Baltic Sea: August 31 - September 7, 2007

CTD - Stationfile

R/V Skagerak

STN	CAST	FILENAME	DATE	TIME	LON	LAT	CTD DEPTH	MAX DEPTH	COMMENTS	ADCP FILE
1	1	01FL_001	070831	15:50	011 39.402	57 11.382	80.0	82.6		BS07001_**
2	1	02BY2_001	070901	11:08	014 05.52	54 58.59	42.0	46.0		BS07003_**
2	2	02BY2_002	070901	11:15	014 05.52	54 58.59	25.0	46.0	Extra cast to get btl no 3	
3	1	03BY5O_001	070905	11:48	016 54.955	55 30.365	30.8	33.0	No sediments	BS07020_**
3	2	03BY5O_002	070905	13:06	016 37.165	55 29.906	41.9	46.9	No sediments	BS07020_**
3	3	03BY5O_003	070905	14:22	016 23.250	55 24.428	61.1	66.6		BS07020_**
4	1	04BY15O_001	070903	8:47	019 40.949	57 25.972	97.5	106.5		BS07011_**
5	1	05BY15_001	070902	11:29	020 02.064	57 19.734	225.0	231.0		BS07010_**
6	1	06BY29_001	070903	19:26	020 18.742	58 52.708	165.5	170.0		BS07013_**
7	1	07BY29O_001	070904	7:37	019 41.132	59 20.053	60.6	64.0		
8	1	08BY31O_001	070904	14:28	017 56.582	58 37.572	48.7	53.0		
9	1	09BY31_001	070904	16:12	018 13.816	58 35.394	443.4	447.4		BS07017_**
10	1	10BY5_001	070905	16:55	015 59.261	55 15.229	84.9	89.0		BS07021_**
11	1	11SO_001	070906	9:05	012 44.986	55 51.708	48.2	52.7	No sediments	BS07022_**
11	2	11SO_002	070906	9:49	012 44.448	55 52.556	42.0	46.5	Extra cast to get btl no 5	
12	1	12FL_001	070907	10:29	011 39.396	57 11.405	82.6	87.1		BS07025_**
12	2	12FL_002	070907	10:43	011 39.470	57 11.540	85.5	79.0	Ext to get btl no 2, 3 & 4	
13	1	13BY15O_001	070903	12:23	019 26.505	57 54.329	43.2	50.0	No sediments	BS07012_**

Table 4. Summary of box- and multicores taken (na = not available).

Baltic Sea Cruise 2007 - Summary of coring activities per station

na = not available

Site	Date	time	Latitude (N)	Longitude (W)	water depth	Measurements&subcores
1_Fladen			57°11.573	11°39.248	82 m	core disturbed, not used
1_Fladen			na	na	82 m	core disturbed, not used
1_Fladen			57°11.524	11°39.335	82 m	O2 (5 cm) and rhizons (10 cm)
1_Fladen		na	na	na	82 m	subcores for forams, not used
1_Fladen		na	na	na	82 m	3 subcores: forams Shauna
1_Fladen			57°11.476	11°39.393	82 m	4 subcores: 2 stored (-20C), 1 porewater, 1 forams
2_Arkona (near BY2)				14°05769	47 m	2 subcores: 1 rhizons, 1 stored (-20C)
2_Arkona (near BY2)				14°05.937	47 m	7 subcores: 1 porewater, 1 Hg (Gretchen), 1 stored (-20C)
5_Gotland Deep (BY 5)				20°01.928	240 m	3 subcores: 1 porewater, 1 rhizons, 1 storage (4C)
4_Gotland Deep (not oxic)		9:03		19°40.729	115 m	very little sediment, not used
4_Gotland Deep (not oxic)		9:11	57°25.711	19°40.709	115 m	very little sediment, not used
4_Gotland Deep (not oxic)		9:16		19°40.718	115 m	3 subcores: 1 porewater, 1 rhizons/Hg (Gretchen), 1 stored (-20C)
6_Baltic Proper				20°18.927	175 m	3 subcores: 1 rhizons, 1 stored (-20 C), 1 stored (4C)
6_Baltic Proper				20°18.569	175 m	6 subcores: 1 anoxic sampling, 1 Hg (Gretchen), 1 stored -20 C
14_Baltic Proper shallow		7:38		19°41.175	68 m	2 subcores: stored (-20C), stored (4C)
8_LandsortDeep oxic (BY31O)				17°56.662	54 m	not used -- boxcore empty
8_LandsortDeep oxic (BY31O)				17°56.695	54 m	1 O2 (5 cm)
8_LandsortDeep oxic (BY31O)				17°56.774	54 m	not used -- too rocky, too little sediment
8_LandsortDeep oxic (BY31O)				17°56.617	54 m	3 subcores: 1 rhizons, 1 Hg (Gretchen), 1 storage at 4C
8_LandsortDeep oxic (BY31O)				17°56.768	54 m	3 subcores: 1 O2, 1 porewater, 1 storage (-20 C)
9_LandsortDeep (BY31)				18°13.834	466 m	not used -- too full
9_LandsortDeep (BY31)				18°13.556	466 m	not used -- too full
9_LandsortDeep (BY31)				18°13.963	466 m	5 subcores: 1 porewater, 1 Hg (Gretchen), 2 storage (-20 C)
9_LandsortDeep (BY31)				18°14.047	466 m	1 subcore for rhizons

Table 4 (continued)

3_Bornholm oxic (near BY5O)		BC1	16°23.250	66 m	1 subcore: stored 4 C
3_Bornholm oxic (near BY5O)			16°23.114	66 m	not used -- too shallow
3_Bornholm oxic (near BY5O)			16°23.038	66 m	6 subcores: 1 O2 (5 cm), 1 storage (-20C), 1 porewater
3_Bornholm oxic (near BY5O)		BC2	16°22.923	66 m	not used -- too shallow
3_Bornholm oxic (near BY5O)		BC3	16°22.820	66 m	2 subcores: 1 rhizons, 1 storage (4C), 1 O2 core (5 cm)
10_Bornholm basin (BY5)		BC1	15°59.149	89 m	not used - too full
10_Bornholm basin (BY5)			15°59.160	89 m	6 subcores: 1 porewater, 1 Hg (Gretchen), 1 stored (-20 C),
10_Bornholm basin (BY5)		BC2	15°59.159	89 m	2 subcores: 1 rhizons, 1 storage (4C)
11_Sound	9:14	BC1	12°45.029	53 m	not used - too shallow
11_Sound	9:20	BC2	12°44.978	53 m	not used - too shallow
11_Sound	9:33	BC3	12°44.904	53 m	not used - too shallow
11_Sound	9:44	BC4	12°44 414	53 m	not used - too full
11_Sound	9:48	BC5	12°44 460	53 m	3 subcores: 1 oxygen, 1 rhizons, 1 porewater
11_Sound		BC6	12°44 410	53 m	1 subcore, stored at -20C
12_Fladen = 1_Fladen		BC1	11°39.248	82 m	1 O2 (5 cm)
12_Fladen = 1_Fladen			11°39.290	82 m	full cast for forams (Shauna)

Figure 3. The multicorer.

7. Shipboard procedures

A CTD profiling and water column sampling (CTD-Rosette)
Oxygen, temperature and salinity measurements were determined with water depth with the CTD-system.Water samples were taken at 6 water depths
For oxygen titrations: 3 samples were taken per CTD-bottle. O2-bottles were filled completely. A tygon tube was used while filling with the tube being at the bottom of the bottle. No air bubbles were present in the tube or bottle (done by spilling three times the volume of the bottle). The stop was placed on the bottle, secured with an elastic band and stored under seawater in a bucket.

For nutrients: a 50 ml syringe, closed with a 3-way stopcock, was used and connected with tubing to each CTD bottle. When oxic, the sample was directly filtered over 0.45 uM and subsampled for nutrient analyses (Si, NH_4, NO_3, PO_4). When anoxic, the subsampling and filtering was performed in the glovebox or in a glovebag.

B. Pore water (centrifugation; rhizons) and sediment collection & subsampling

Boxcores and/or Multicores were taken at each site during this cruise (except for Baltic proper shallow; site 14). Approximately 1 boxcore (BC) (31 cm i.d.) and 1 multicorer cast was needed at each location to carry out the full programme. Several cores were stored for each site (see Appendix IV). Six subcores from boxcores were carefully closed with two yellow caps, taped with yellow tape, coded and stored at 4 degrees C. Other subcores were frozen at -20 C for at least 8h, and then removed from the core liner through heating under a running tap, transferred to a plastic bag and sealed and stored at -20C.

Cutting the core: One sediment core per site was processed for sediment and porewater. Bottom water was removed with a syringe just before bringing the core into the glovebox (this water was discarded if a bottomwater sample had already been collected, see point 3). The sediment core was brought into the glovebox and was sliced under nitrogen with 20 depth intervals per core. Cores were sliced in the scheme presented at the end of this section unless otherwise determined on-board.

Ca. 10 ml of uncentrifuged material from each sediment layer was put into pre-weighed 15 ml glass vessels for the determination of the water content and for solid phase analyses. These vials were placed into gas-tight "weckflessen". The rest of the sediment in each section was placed in centrifuge tubes, which were sluiced out of the glove box and centrifuged at 3000 rpm for 10 minutes.

Table 5 General core sectioning scheme

Sample number	Depth range (cm)	Total thickness (cm)
1	0.0 - 0.5	0.5
2	0.5 -1.0	0.5
3	1.0 -1.5	0.5
4	1.5 - 2.0	0.5
5	2 – 3	1.0
6	3 – 4	1.0
7	4 – 5	1.0
8	5 – 6	1.0
9	6 – 7	1.0
10	7 – 8	1.0
11	8 – 9	1.0
12	9 – 10	1.0
13	10 – 12	2.0
14	12 – 14	2.0
15	14 – 16	2.0
16	16 – 18	2.0
17	18 – 20	2.0
18	20 – 24	4.0
19	24 – 28	4.0
20	28 – 32	4.0

Up to 10 additional samples possible, depending on the length of the core.

In addition to the centrifugation procedure, rhizons were used to collect porewater from selected cores (method description not included here).

Porewater subsampling: The centrifuge tubes were brought into the small glovebox where the supernatant was poured into a 25 ml syringe and filtered over 0.45 µm into a 30 ml Nalgene vial. The pH of a drop of pore water was measured in the glove box (using a Pasteur pipette). The remaining pore water was then subsampled in the glovebox following the scheme in Table 6. A small drop was kept for visual salinity analysis with a "Reichert" salinity meter outside the glovebox after the subsampling. The tubes with centrifuged sediment were sealed in a plastic bag and were stored in the freezer (-20 C).

Table 6 Subsampling scheme for porewater (9-15 ml expected)

Rank	Analysis	Vol.	Vial	Treatment	Code	Method	Storage
1	pH	0.5	Drop on electrode	-		on-board	
2	$PO_{4,}$ Si	2	AA-cup + cap	10 µl 1 M HCl per ml	**PO**	AA	4°C
3	NH_4	1.5	AA-cup + cap	-	**NH**	AA	-20°C
4	Trace metals + Major elements	2	Nalgene 8 ml	10 µl suprapur HNO_3 per ml	**ME**	ICP-MS + ICP-OES	4°C
5**	NO_3, NO_2	1.5	AA-cup + cap	-	**NO**	AA	-20°C
6	SO_4, Br, Cl	1	IC-vial, 2 ml	-	**IC**	IC	-20°C
7	Alk	2	Alkalinity tube	Titration	**ALK**	on-board	
8	HS^-	1	PE vial	20 µl 2 M Znac per ml	**HS**	Spectro-fotometer	4°C
	Total	11.5					

*When less than 11.5 ml was available, the sample volume of nutrients was reduced to 1 ml. This was indicated with a marker (a dot) on the vial. **Note that the nitrate analysis was omitted when the bottom waters were anoxic.

C Oxygen microprofiles and alkalinity & Winckler titrations

Oxygen micro-profiles at the sediment-water interface were determined directly after core collection at 4 sites with oxic bottom waters with a miniaturized Clark-type oxygen sensor (unisense) with an internal reference and a guard electrode attached to a micromanipulator. Alkalinity titrations were performed on porewater samples on board (procedure not included here). Winckler titrations were performed on most CTD-samples.

D Core storage

See appendix IV for overview of stored cores.

8. Preliminary results

A. CTD profiles

Oxygen, temperature and salinity profiles for each site are given in Appendix II and are in accordance with expections based on available monitoring data.

B. Sediments

The sediments at all sites are fine-grained. Sediment descriptions for the porewater core for sites are given in Appendix III.

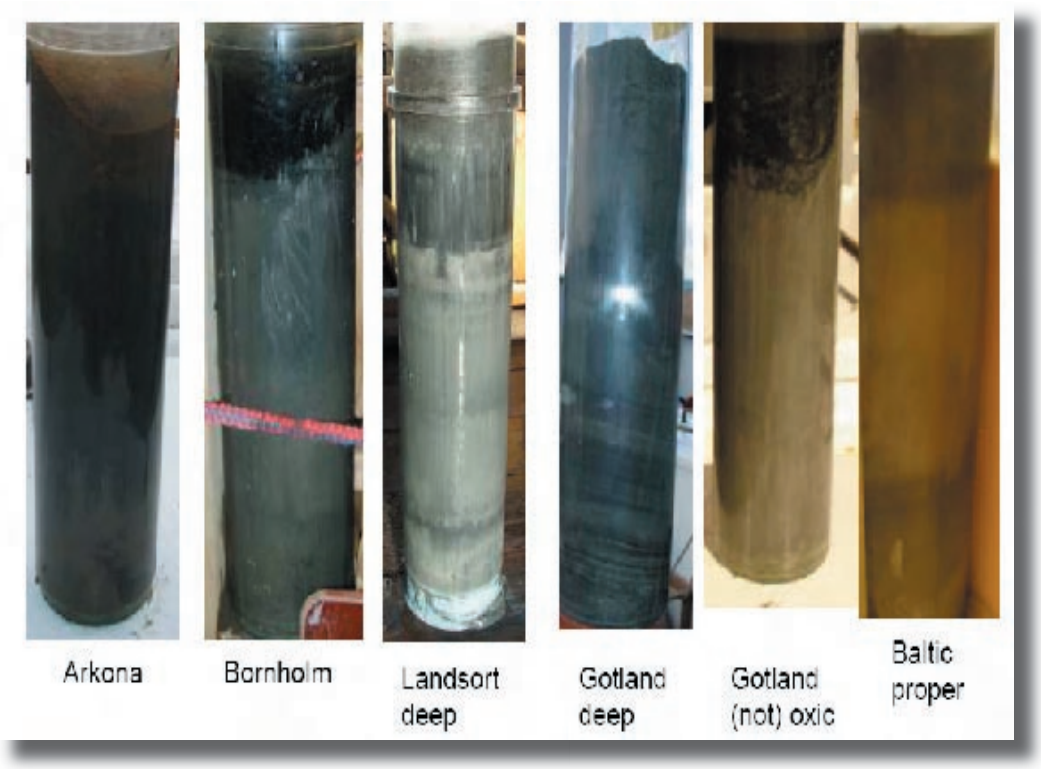


Figure 4. Subcores at five sites that were overlain by anoxic bottom waters during the time of sampling.

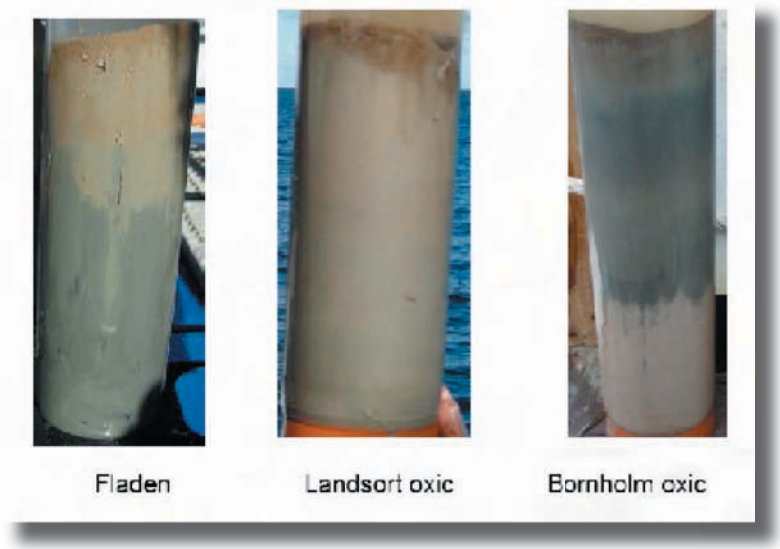


Figure 5. Subcores for three sites with oxic bottom waters.

B & C. Porewater At stations with oxic bottomwaters, oxygen concentrations in the surface sediment decrease rapidly with depth, as shown for4 sites in Figure 6. The maximum depth of oxygen penetration is highest at the Landsort oxic site (site 8) and lowest at the Sound (site 11).

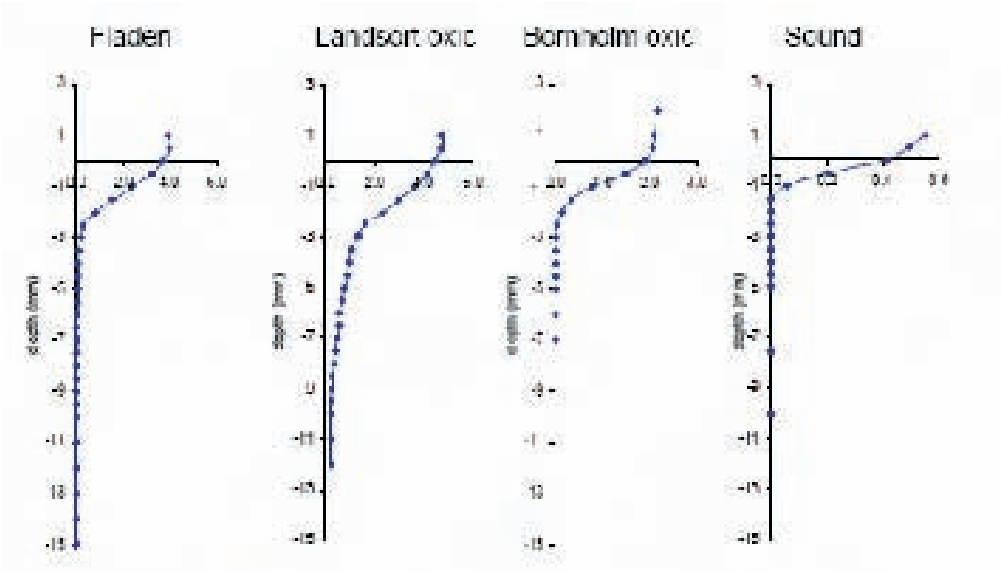


Figure 6. Oxygen profiles for 4 sites with oxic bottom waters (Fladen (site 1), Landsort Deep oxic (site 8), Bornholm oxic (site 3), Sound (site 11).

Alkality increased with depth at most sites. Only at the Landsort Deep oxic site a constant profile was observed, suggesting little active organic matter decomposition at the site. As an example, of a pH and alkalinity profile for an oxic site the profile for the Sound (site 11) is shown in Figure 7.

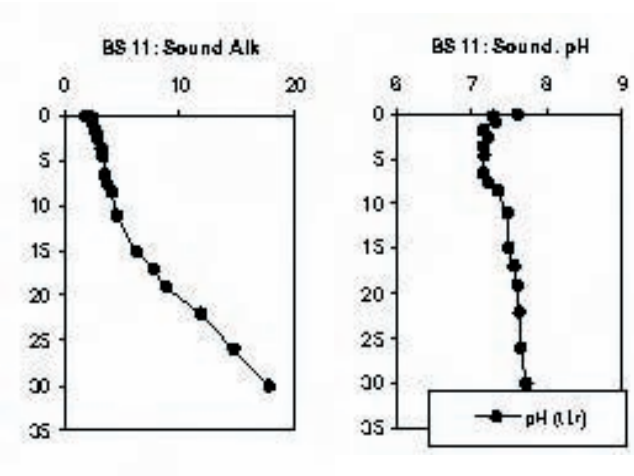


Fig 7. pH and alkalinity (in mM) profiles for the core from the Sound (site 11).

APPENDIX 1. Summary codes for cores and vials

Example: Code on core: BS-1-2 = Baltic Sea site 1 subcore 2

Box/Multi Core	# of subcore	Diameter	Core code*	Use
1	1	10 cm	BS1-1	Porewater and solid phase (anoxic) – processed on board – 1st core
1	2	10 cm	BS1-2	Porewater and solid phase (anoxic) – spare – 2nd core
1	3	10 cm	BS1-3	Solid phase (anoxic) for storage in plastic bag; frozen (-20 C)
1	4	10 cm	BS1-4	Solid phase core for Hg**
1	5	5 cm	BS1-5	O_2 microprofiles
1 BC	6	10 cm	BS1-6	Solid phase (anoxic) for storage, 4 degrees (subcore from boxcore)
1 BC	7	10 cm	BS1-7	Porewater core with holes for sampling with rhizons

There are lables available for all the PW and BW vials and CTD samples.

PW = porewater

BW = bottom water

Example:

Codes: BS-CTD1-2: Baltic Sea CTD sample site 1, depth 2 (total of 6 depths)
PW-PO-1-2: porewater PO4, site 1, sample 2 (total of 12 stations, max. 30 depths)

BW-PO-1: bottom water for PO4, site 1 (total of 12 stations, 1 per station)

Rank	Analysis	Vol.	Vial	Code	Treatment	Method	Storage
1	pH	0.5	Drop on electrode		-	On-board	
2	$PO_{4,}$ Si	2	AA-cup + cap	**PO**	10 µl 1 M HCl per ml	AA	4°C
3	NH_4	1.5	AA-cup + cap	**NH**	-	AA	-20°C
4	Trace metals + Major elements	2	Nalgene 8 ml	**ME**	10 µl suprapur HNO_3 per	ICP-MS + ICP-OES	4°C
5**	NO_3, NO_2	1.5	AA-cup + cap	**NO**	-	AA	-20°C
6	SO_4, Br, Cl	1	IC-vial, 2 ml	**IC**	-	IC	-20°C
7	Alk	2	Alkalinity tube	**ALK**	Titration	On-board	
8	HS^-	1	PE vial	**HS**	20 µl 2 M Znac per ml	Spectro-fotometer	4°C
	Total	11.5					

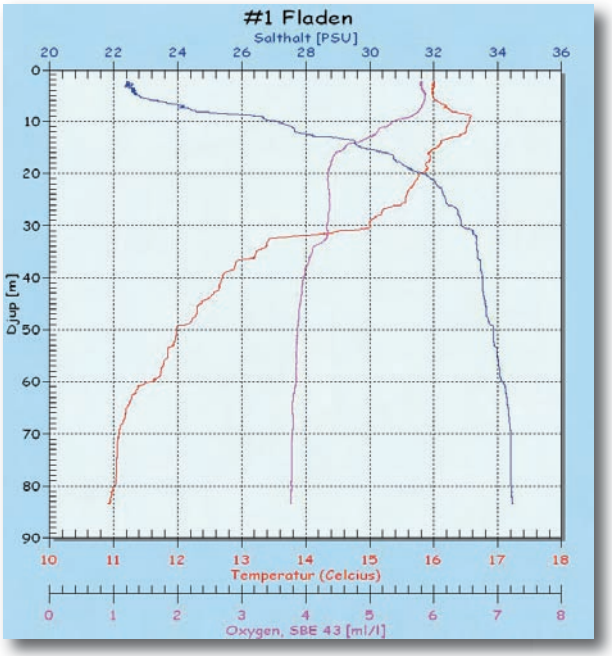
Summary of lables

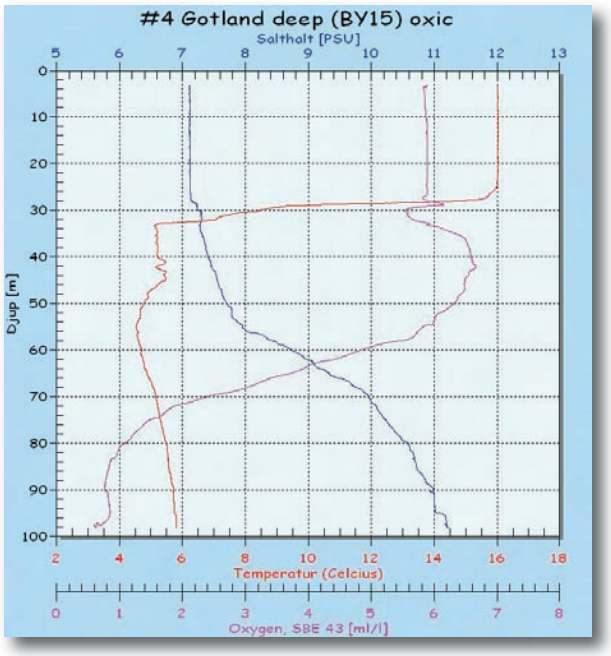
CTD: lables for 12 stations and 6 water depths, 4 types (BULK, PO, NH, NO) (72x4=288)

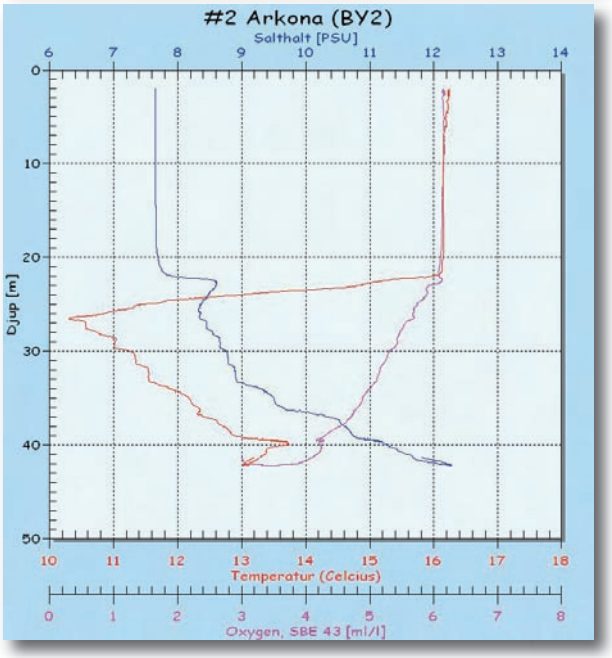
BW: lables for 12 stations, 8 types (PO, NH, ME, NO, IC, ALK, HS, BULK) (12 x 8= 96)

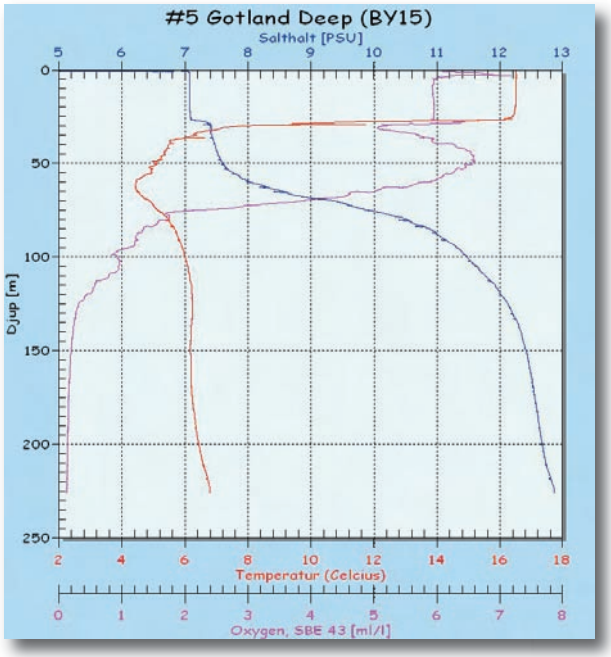
PW: lables for 12 stations, 30 depths, 8 types (PO, NH, ME, NO, IC, ALK, HS, BULK) (12 x 30 x 8 = 2880)

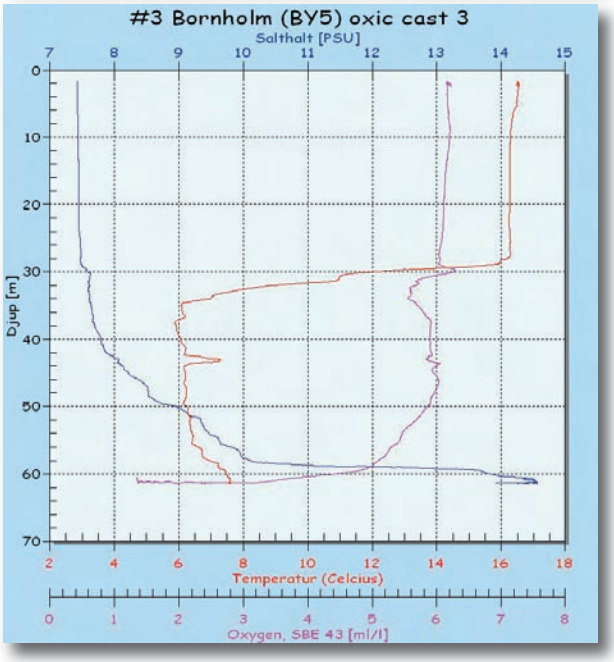
APPENDIX II CTD Profiles (temperature, salinity, oxygen)

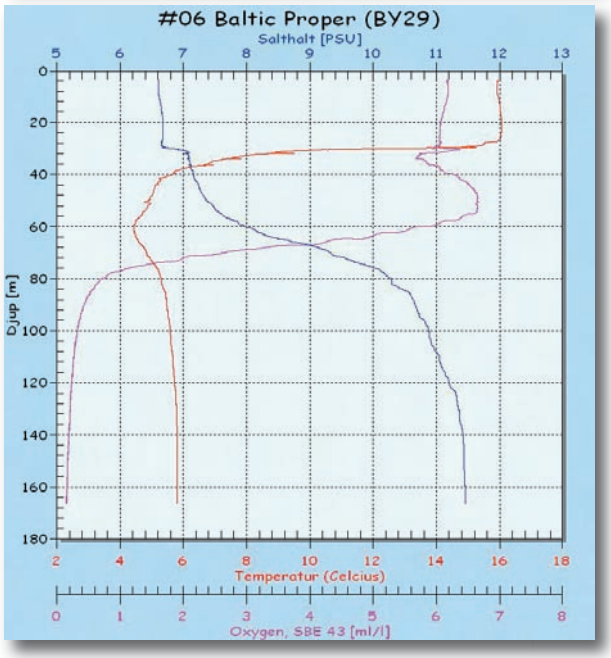


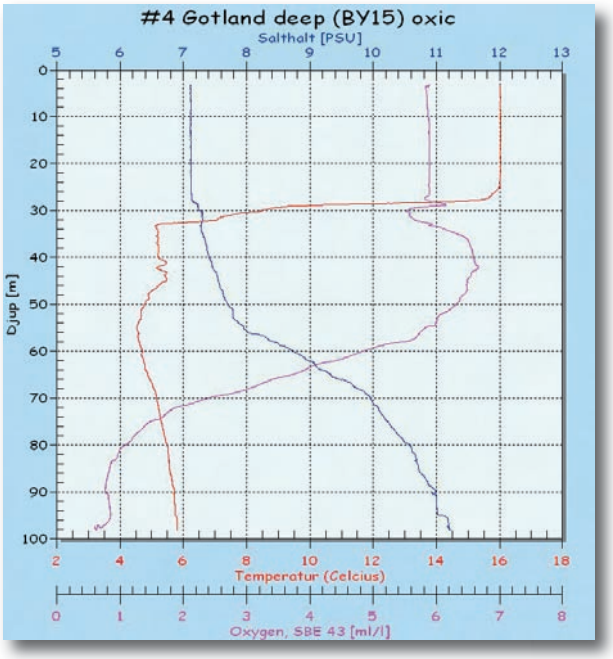


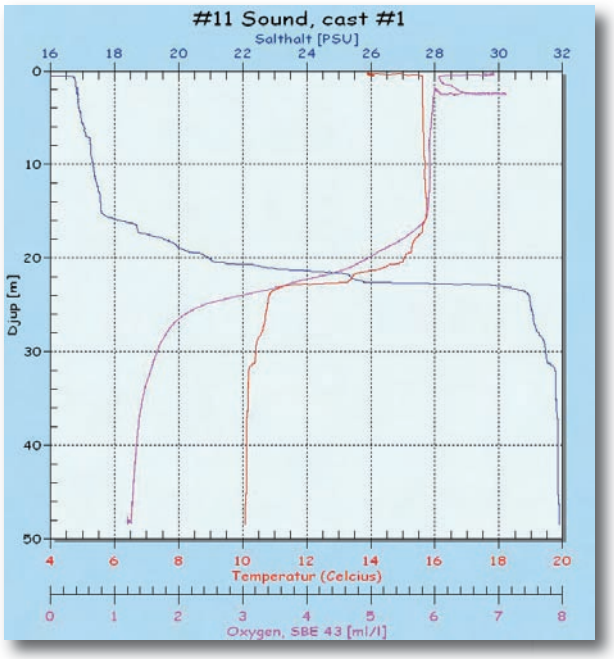


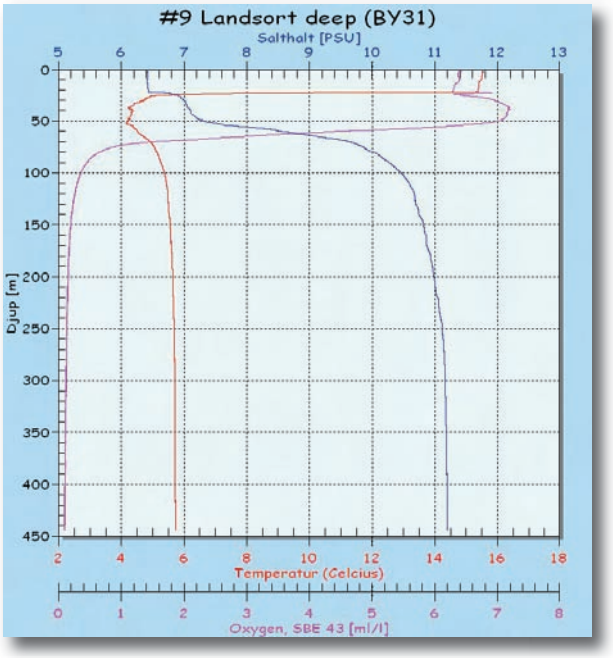


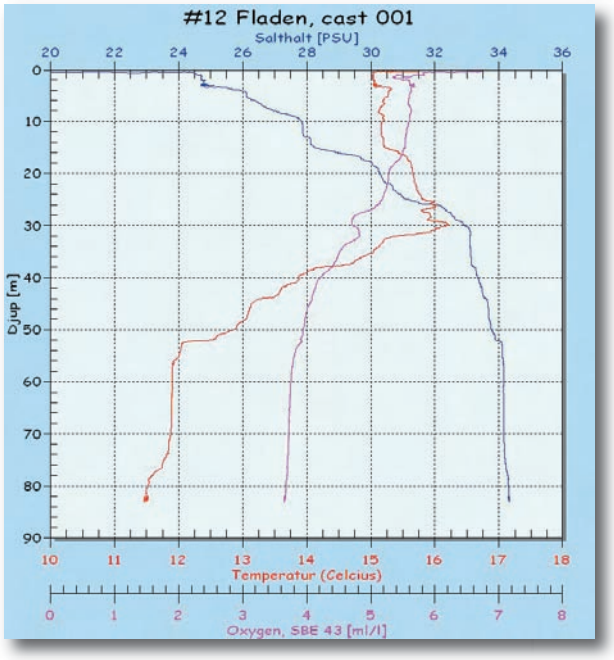


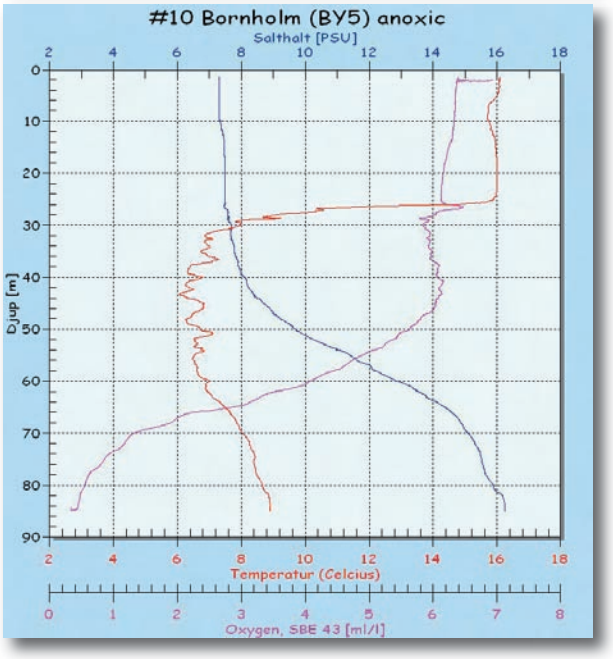


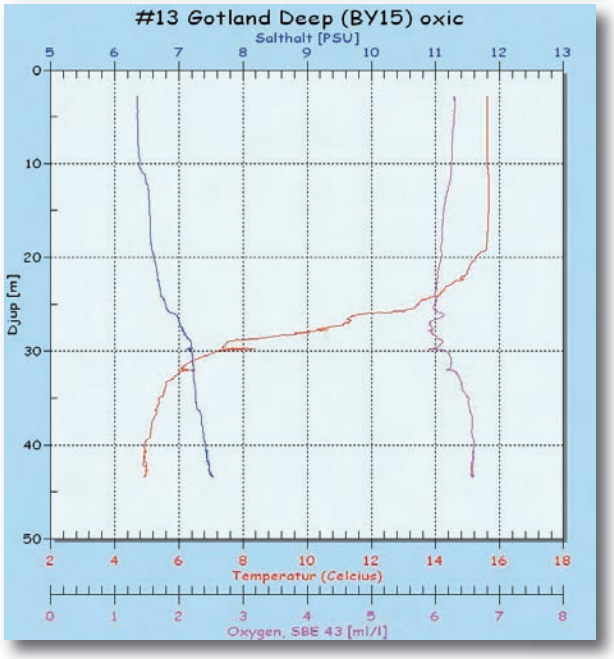

#4 Gotland deep (BY15) oxic
Salthalt [PSU]
Djup [m]
Temperatur (Celcius)
Oxygen, SBE 43 [ml/l]


#11 Sound, cast #1
Salthalt [PSU]
Djup [m]
Temperatur (Celcius)
Oxygen, SBE 43 [ml/l]


#9 Landsort deep (BY31)
Salthalt [PSU]
Djup [m]
Temperatur (Celcius)
Oxygen, SBE 43 [ml/l]


#12 Fladen, cast 001
Salthalt [PSU]
Djup [m]
Temperatur (Celcius)
Oxygen, SBE 43 [ml/l]


#10 Bornholm (BY5) anoxic
Salthalt [PSU]
Djup [m]
Temperatur (Celcius)
Oxygen, SBE 43 [ml/l]


#13 Gotland Deep (BY15) oxic
Salthalt [PSU]
Djup [m]
Temperatur (Celcius)
Oxygen, SBE 43 [ml/l]

APPENDIX III.

Sediment description site 1 (porewater core) - Fladen.

Cruise:	**Baltic Sea 2007**
Core:	**BS1 Fladen**
Length of core:	**36 cm**
Depth:	**82 m**
Latitude	**57 11.573 N**
Longitude	**11.39.248 E**
Description made by:	**Shauna**
Porewater on this core:	**yes (centrifugation)**
Date of subsampling:	**31 08 2007**

Sample no. tube/vial	PW-code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
1	BS1-1	0-0.5	0.25	soupy brownish sticky sediment, very fine grainedlumpy consistency
2	BS1-2	0.5-1.0	0.75	see above, with small particles
3	BS1-3	1.0-1.5	1.25	see above, with small particles
4	BS1-4	1.5-2.0	1.75	less soupy brownish
5	BS1-5	2.0-3.0	2.5	see above
6	BS1-6	3.0-4.0	3.5	greenish, brown soft lumpy consistency
7	BS-1-7	4.0-5.0	4.5	see above with shell fragments
8	BS-1-8	5.0-6.0	5.5	soft greenish brown, more consistent, worm, several shell fragments
9	BS-1-9	6.0-7.0	6.5	brownish green soft mud, worms
10	BS-1-10	7.0-8.0	7.5	as above, evidence of bioturbation
11	BS-1-11	8.0-9.0	8.5	as above
12	BS-1-12	9.0-10.0	9.5	as above
13	BS-1-13	10.0-12.0	11.0	medium soft stiff, greenish grey
14	BS-1-14	12.0-14.0	13.0	as above, with stiff lumps
15	BS-1-15	14.0-16.0	15.0	stiff, wetspots, bioturbation, greenish grey, dark patch
16	BS-1-16	16.0-18.0	17.0	grey stiff, wetspots, bioturbation
17	BS-1-17	18.0-20.0	19.0	as above
18	BS-1-18	20.0-24.0	22.0	darkgrey brownish, wet patches
19	BS-1-19	24.0-28.0	26.0	darkgrey stiff, evidence of bioturbation (tubes, other colour)
20	BS-1-20	28.0-32.0	30.0	as above

Sediment description site 2 (porewater core) - Arkona

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS2 Arkona (near BY2)**
Length of core:	**39 cm**
Depth:	**47 m**
Latitude	**54°58.504 N**
Longitude	**14°05.937 E**
Description made by:	**Shauna**
Porewater on this core:	**yes (centrifugation)**
Date of subsampling:	**1 09 2007**

Note: light brown particles+filaments may be Beggiatoa see paper Emeis et al. 2000

Sample no. tube/vial	PW-code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
21	BS2-1	0-1	0.50	soupy greensih brown + light brown particles
22	BS2-2	1-2	1.50	as above
23	BS2-3	2-3	2.50	dark greenish brown, more consistant
24	BS2-4	3-4	3.50	dark grey green, 2 mm long organic threads, soft more consistent
25	BS2-5	4-5	4.50	dark grey green, sticky mud, filaments of degraded organic matter
26	BS2-6	5-6	5.50	darker grey green, stickly mud shell, stored in greiner tube
27	BS-2-7	6-7	6.50	dark grey-green, sticky mud, less filaments
28	BS-2-8	7-8	7.50	as above shell remains, silicified?
29	BS-2-9	8-9	8.50	as above, less shell fragments
30	BS-2-10	9-10	9.50	as above
31	BS-2-11	10-12	11.00	stiff very dark grey green, shell
32	BS-2-12	12-14	13.00	dark grey-black, stiff
33	BS-2-13	14-16	15.00	grey black, stiff
34	BS-2-14	16-18	17.00	as above
35	BS-2-15	18-20	19.00	as above
36	BS-2-16	20-24	22.00	as above
37	BS-2-17	24-28	26.00	as above

Sediment description site 3 (porewater core) – Bornholm oxic

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS3 Bornholm oxic**
Length of core:	**ca. 30 cm**
Depth:	**66 m**
Latitude	**55°24.459 N**
Longitude	**16°22.820 E**
Description made by:	**Haydon**
Porewater on this core:	**yes**
Date of subsampling:	**05 09 2007**

Sample no. tube/vial	Sed code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
133	BS3-1	0-1	0.5	surface tilted, light brown, dark grey speckles, soft mud
134	BS3-2	1-2	1.5	same light brown mud, slightly stiffer
135	BS3-3	2-3	2.5	dark brown mud, few sandy particles, more clay like
136	BS3-4	3-4	3.5	same as before but more consistent
137	BS3-5	4-5	4.5	dark brown, more consistent, light brown patches some organic filaments (reconstituted
138	BS3-6	5-6	5.5	darker brown, more solid, few rounded granite particles (ca. 3 mm)
140	BS3-7	6-7	6.5	dark brown muddy sand (coarse), intermixed with light brown clay mud
141	BS3-8	7-8	7.5	less sand, more clay, with shell fragments (abundant)
142	BS3-9	8-9	8.5	light brown clay, 1 cm sized with lump: smectite?
143	BS3-10	9-10	9.5	same as before, with darker brown jelly-like mud (coring artefact?)
144	BS3-11	10-12	11.0	sand or shells
145	BS3-12	12-14	13.0	as sample 11
146	BS3-13	14-16	15.0	harder light brown clay mud, from this sample onwards, increasing hardness and finer
147	BS3-14	16-18	17.0	same as 13
148	BS3-15	18-20	19.0	same as 13
149	BS3-16	20-24	22.0	same as 13
150	BS3-17	24-28	26.0	same as 13 with fine red sand (rare) in patches.

Sediment description site 4 (porewater core) – Gotland (not) oxic (Gotland Slope)

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS4 Gotland (not) oxic**
Length of core:	**29.7 cm**
Depth:	**115 m**
Latitude	**19°40.718 N**
Longitude	**19°40.718 E**
Description made by:	**Shauna & Peter (slicing)**
Porewater on this core:	**yes (centrifugation)**
Date of subsampling:	**3 09 2007**

Sample no. tube/vial	PW-code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
59	BS4-1	0-0.5	0.25	soupy, dark grey mud with medium grey lumps
60	BS4-2	0.5-1.0	0.75	as above
61	BS4-3	1.0-1.5	1.25	soupy, dark grey mud with some lumps
62	BS4-4	1.5-2.0	1.75	as above
63	BS4-5	2.0-3.0	2.50	dark grey, some med. grey spots, more consistent
64	BS4-6	3.0-4.0	3.50	as above
65	BS4-7	4.0-5.0	4.50	dark slightly brownish grey mud
66	BS4-8	5.0-6.0	5.50	as above
67	BS4-9	6.0-7.0	6.50	dark slightly brownish grey, more consistent, light grey layer at base
68	BS4-10	7.0-8.0	7.50	grey mud
69	BS4-11	8.0-9.0	8.50	brownish grey mud, stiffer
70	BS4-12	9.0-10.0	9.50	stiff mud, brownish grey with stiffer patches
71	BS4-13	10.0-12.0	11.00	light greyish brown sandy clay
72	BS4-14	12.0-14.0	13.00	clayey sand, light greyish brown
73	BS4-15	14.0-16.0	15.00	as above with brownish grey clayey sand
74	BS4-16	16.0-18.0	17.00	as above with rock fragments (ca. 2 mm)
75	BS4-17	18.0-20.0	19.00	half same as above, other half more clay, greyer brown patch from
				underlying laminated interval
76	BS4-18	20.0-23.0	21.50	inclined laminated interval, dark grey and brownish grey bands, clayey
77	BS4-19	23.0-26.0	24.50	laminated section, same as above.

Sediment description site 5 (porewater core) – Gotland deep

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS5 Gotland deep (BY15)**
Length of core:	**36 cm**
Depth:	**240 m**
Latitude	**57°19.413 N**
Longitude	**20°01.928 E**
Description made by:	**Haydon & Shauna (slicing)**
Porewater on this core:	**yes (centrifugation)**
Date of subsampling:	**2 09 2007**

Sample no. tube/vial	PW-code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
38	BS5-1	0-1	0.50	medium grey, sticky and crumbly, mousse like, dark grey just below first mm's
39	BS5-2	1-1.5	1.25	mottled dark brownish grey, same texture
40	BS5-3	1.5-2	1.75	as above
41	BS5-4	2-3	2.5	as above
42	BS5-5	3-4	3.5	a bit darker, slightly stiffer
43	BS5-6	4-5	4.5	a little bit more lumpy, stickier, brownish sediment, has small black patches
44	BS5-7	5-6	5.5	as above
45	BS5-8	6-7	6.5	darker stiffer more jelly like
46	BS5-9	7-8	7.5	as above
47	BS5-10	8-9	8.5	as above
48	BS5-11	9-10	9.5	as above+some lighter patches
49	BS5-12	10-12	11.0	as above
50	BS5-13	12-14	13.0	as above
51	BS5-14	14-16	15.0	cutting through inclined layer, dark grey on top, brownish grey below
52	BS5-15	16-18	17.0	as above, dark grey (top, stiff jelly like) selectively sampled 15 ml vial (solid sample)
53	BS5-16	18-20	19.0	brownish layer sampled for 15 ml
54	BS5-17	20-24	22.0	dark grey & grey brown with light brown spots (top ice)
				jelly like, thin dark band ~3 mm, not individually sampled
55	BS5-18	24-28	26.0	brownish dark grey, jelly like
56	BS5-19	28-30	29.0	laminated section, 1-2 mm thick laminae (brown and grey layers, inclined)
57	BS5-20	30-32	31.0	dark gre and brownish grey laminae with 2 light brown layers

Sediment description site 6 (sediment core) – Baltic Proper

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS6-1 Baltic Proper**
Length of core:	**ca. 33 cm**
Depth:	**175 m**
Latitude	**58°52.759 N**
Longitude	**20°18.569 E**
Description made by:	**Shauna & Peter**
Porewater on this core:	**no**
Date of subsampling:	**03 09 2007**

Sample no. tube/vial	Sed code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
78	BS6-1	0-0.5	0.25	black fluff suspended in water
79	BS6-2	0.5-1	0.75	suspended black fluff, gelatinous black, light grey spots
80	BS6-3	1-1.5	1.25	as sample 2
81	BS6-4	1.5-2	1.8	as sample 2
82	BS6-5	2-3	2.5	as sample 2, but more jelly like
83	BS6-6	3-4	3.5	as sample 5 with mix of black and medium grey
84	BS6-7	4-5	4.5	as sample 6
85	BS6-8	5-6	5.5	as sample 7, but more solid and more material is grey, half grey, half black, lumpy
86	BS6-9	6-7	6.5	half black lumps, half soft grey mud
87	BS6-10	7-8	75.0	same as sample 9, but with two+thirds soft grey mud
88	BS6-11	8-9	8.5	brownish grey mud streaked with black
89	BS6-12	9-10	9.5	as sample 11
90	BS6-13	10-11	10.5	brownish grey mud streaked with black and brown
91	BS6-14	11-13	12.0	same as 13, but with voids
92	BS6-15	13-15	14.0	same as 14
93	BS6-16	15-17	16.0	brownish grey mud with black streaks
94	BS6-17	17-20	18.5	as sample 16 but stiff with sparse 3-5 mm voids
95	BS6-18	20-24	22.0	as sample 17
96	BS6-19	24-28	26.0	as sample 18 (black streaks seem reduction spots)
97	BS6-20	28-30	29.0	

Sediment description site 9 (porewater core) – Landsort deep anoxic

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS9-1 Landsortdeep anoxic**
Length of core:	**36 cm**
Depth:	**466 m**
Latitude	**58°35.314 N**
Longitude	**18°35.556 E**
Description made by:	**Haydon**
Porewater on this core:	**yes**
Date of subsampling:	**05 08 2007**

Sample no. tube/vial	Sed code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
112	BS9-1	0-0.5	0.25	Organic fluffy brown mat, suspended in bottom water. 'glompy' black mud. Red rounded clast, white particles
113	BS9-2	0.5-1.0	0.75	particles.
114	BS9-3	1.0-1.5	1.25	Dark grey to black mud, white particles. Patches of sandy particles.
115	BS9-4	1.5-2.0	1.75	Slightly stiffer, more sand patches. Becoming even more sandier at base.
116	BS9-5	2.0-3.0	2.50	Sandy mud becoming brownish clay
117	BS9-6	3.0-4.0	3.50	Sandy mud followed by a thin layer (approx 25 mm) of jet black jelly. Underneath jelly jelly is light grey watry
118	BS9-7	4.0-5.0	4.50	consistent
119	BS9-8	5.0-6.0	5.50	as sample 7
120	BS9-9	6.0-7.0	6.50	bits of grey
121	BS9-10	7.0-8.0	7.50	upper portion consists of light grey sediments. Lower portion is black jelly like mud (as in BS9-6)
122	BS9-11	8.0-9.0	8.5	black jelly, soupy.
123	BS9-12	9.0-10.0	9.5	top portion: dark grey jelly-like seds. Underlain by very light brownish grey mud.
124	BS9-13	10.0-12.0	11.0	light brown mud grading into light brown mud (over an interval of approx 50 mm).
125	BS9-14	12.0-14.0	13.0	light brownish grey mud (more consistent)
126	BS9-15	14.0-16.0	15.0	as sample 14
127	BS9-16	16.0-18.0	17.0	Light brownish grey mud gradting to medium grey mud
128	BS9-17	18.0-20.0	19.0	lighter grey brownish mud
129	BS9-18	20.0-24.0	22.0	sample as sample 17 but more clay like
130	BS9-19	24.0-28.0	26.0	more clay like
131	BS9-20	28.0-32.0	30.0	as above
132	BS9-21	32.0-36.0	34.0	as above

Sediment description site 8 (porewater core) – Landsort deep oxic

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS8-1 Landsortdeep oxic**
Length of core:	**28 cm**
Depth:	**54 m**
Latitude	**58°37.578 N**
Longitude	**17°56.768 E**
Description made by:	**Haydon**
Porewater on this core:	**yes**
Date of subsampling:	**04 08 2007**

Sample no. tube/vial	Sed code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
98	BS8-1	0-2	1.00	surrface: subangular clasts (0.5-2 cm) embedded in clayey mud, light brown
99	BS8-2	2-3	2.50	same as 1, fewer clasts, articulated bivalve shell, slightly harder clay
100	BS8-3	3-4	3.50	same as 2, but darker brown, no clasts, stiff texture
101	BS8-4	4-5	4.5	light brown clayey mud, stiff
102	BS8-5	5-6	5.5	as sample 4
103	BS8-6	6-7	6.5	as sample 5
104	BS8-7	7-8	7.5	as sample 6
105	BS8-8	8-9	8.5	as sample 6
106	BS8-9	9-11	10.0	as sample 6
107	BS8-10	11-13	12.0	dark light brown clayey mud, stiff
108	BS8-11	13-15	14.0	same as 10, less stiff towards bottom of interval, may be coring artefact?
109	BS8-12	15-17	16.0	same as 11, less stiff and more sticky, with a few mm gravel
110	BS8-13	17-19	18.0	same as 12
111	BS8-14	19-23	21.0	same as 12 with 0.5 mm dark grey particles (common)

Sediment description site 10 (porewater core) – Bornholm anoxic

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS10 Bornholm anoxic**
Length of core:	**37 cm**
Depth:	**89 m**
Latitude	**55°15.160 N**
Longitude	**15°59.160 E**
Description made by:	**Peter and Haydon**
Porewater on this core:	**yes**
Date of subsampling:	**06 08 2007**

Sample no. tube/vial	Sed code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
151	BS10-1	0-1	0.50	Black and grey fluffy material. Millimetric lamination. Abundant white specks.
152	BS10-2	1.0-2.0	1.50	As above but more jelly-like
153	BS10-3	2.0-2.5	2.25	Slightly less black material. Brown mud. Very wet
154	BS10-4	2.5-3.0	2.75	As above but with more brown and grey mud.
155	BS10-5	3.0-3.5	3.25	No more black white specks or black fluff. Brown grey mud. Still jelly-like.
156	BS10-6	3.5-4.0	3.75	More consistent. Black specks are back…numerous! Brown mud. Pale grey areas. Fluffy material
157	BS10-7	4.0-5.0	4.50	Dark grey and light grown grey mud. Black streeks. Jelly-like but even more consistent. Shell fragments.
158	BS10-8	5.0-6.0	5.50	Same but lighter brown grey mud towards base
159	BS10-9	6.0-7.0	6.50	black streeks.
160	BS10-10	7.0-8.0	7.50	base.
161	BS10-11	8.0-9.0	8.50	Little more sticky jelly like mud
162	BS10-12	9.0-10.0	9.50	As above plus a small black patch.
163	BS10-13	10.0-12.0	11.0	Same but stiffer. More light brownish grey. Still specks. Mud is more coarse.
164	BS10-14	12.0-14.0	13.0	towards the lower portion of the inteval. Even more coarse material.
165	BS10-15	14.0-16.0	15.0	Brownish greenish grey again but darker. Some streaks. Sandy texture becoming apparent.
166	BS10-16	16.0-18.0	17.0	Sandier. Black streeks. Stiffer, more clay-like.
167	BS10-17	18.0-20.0	19.0	streeks.
168	BS10-18	20-24	22.0	Sandy jelly-like. Dark brownish grey. Relatively dry. Light brown areas with black specks.
169	BS10-19	24-28	26.0	Same but a bit lighter.
				disturbance

Sediment description site 11 (porewater core) – Sound

Station information:	
Cruise:	**Baltic Sea 2007**
Core:	**BS11 Sound**
Length of core:	**ca. 36 cm**
Depth:	**53 m**
Latitude	**55°52.538 N**
Longitude	**12°44 460 E**
Description made by:	**Haydon**
Porewater on this core:	**yes (centrifugation)**
Date of subsampling:	**06 09 2007**

Sample no. tube/vial	Sed code	Depth interval (cm)	Average depth (cm)	Remarks (grain size, macrofossils, color etc.)
170	BS-11-1	0-0-5	0.25	soupy medium brown mud, starfish found on boxcore, tube worm (2 cm)
171	BS-11-2	0.5-1	0.75	as above, a little more consistent
172	BS-11-3	1-1.5	1.25	more consistent with a few black streaks
173	BS-11-4	1.5-2	1.75	same as above, more black streaks, one tube worm
174	BS-11-5	2-3	2.50	more black patches, black towards base, soupy
175	BS-11-6	3-4	3.50	black, more consistent, brownish grey patches
176	BS-11-7	4-5	4.50	top is same as previous, lower portion light brown mud with sandlike particles
177	BS-11-8	5-6	5.50	light brown mu, tube fragment, shells, tubes
178	BS-11-9	6-7	6.50	thick dark grey to black mud, becoming coarser
179	BS-11-10	7-8	7.50	as above
180	BS-11-11	8-9	8.50	more consistent, no more shells or organic fragments, darker
181	BS-11-12	9-10	9.50	as 11 but stiffer
182	BS-11-13	10-12	11.0	gastropod.
183	BS-11-14	12-14	13.0	as 13. but darker and wetter, still shell fragments
184	BS-11-15	14-16	15.0	same as previous, stiff dark grey mud + lots of woody fragments
185	BS-11-16	16-18	17.0	as above
186	BS-11-17	18-20	19.0	mud is stickier, fewer woody fragments, more consistent
187	BS-11-18	20-24	22.0	same as above except harder and stickier
188	BS-11-19	24-28	26.0	dark brownish grey stiff mud
189	BS-11-20	28-32	30.0	silty mud, plant (?) fragments molluscs, coarsening down and drier.

APPENDIX IV

Whole Cores stored Baltic Sea cruise

	Code	Site			Remark
1	BS1-3	1_Fladen	MC	-20	transferred to plastic bag
2	BS1-3EXTRA	1_Fladen	MC	-20	transferred to plastic bag
3	BS2-3	2_Arkona	MC	-20	transferred to plastic bag
4	BS2-3EXTRA	2_Arkona	BC	-20	transferred to plastic bag
5	BS5-3	5_Gotland	BC	***4C***	still in cold room (laminations)
6	BS4-3	4_Gotland_ notoxic	BC	-20	transferred to plastic bag
7	BS6-3	6_Baltic proper	MC	-20	transferred to plastic bag
8	BS6-3extra	6_Baltic proper	BC	-20	transferred to plastic bag
9	BS6-6	6_Baltic proper	BC	***4C***	still in cold room
	BS14-1	14_Baltic_shallow	BC	-20	transferred to plastic bag
	BS14-2	14_Baltic_shallow	BC	***4C***	still in cold room
	BS8-1	8_Landsort oxic	BC	-20	transferred to plastic bag
	BS8-2	8_Landsort oxic	BC	***4C***	still in cold room
	BS9-1	9_Landsort deep	MC	-20	transferred to plastic bag
	BS9-2	9_Landsort deep	MC	-20	transferred to plastic bag
	BS3-3	3_Bornholm oxic	MC	-20	transferred to plastic bag
	BS3	3_Bornholm oxic	BC	-20	transferred to plastic bag
	BS3	3_Bornholm oxic	BC	***4C***	still in core liner
	BS10	10_Bornholm	MC	*-20*	transferred to plastic bag
	BS10-3	10_Bornholm	MC	*-20*	transferred to plastic bag
	BS10-6	10_Bornholm	BC	***4C***	still in cold room
	BS11	11_Sound	BC	*-20*	transferred to plastic bag

Appendix II

Sequential extraction procedure for phosphorus

Funded by the Baltic Sea 2020

Funded by the Baltic Sea 2020

Aim

Fractionation of sediment P into Fe-bound P, authigenic P (this includes CFA, biogenic P, $CaCO_3$-bound P and possibly smectite-bound P), detrital Ca-P and organic P using a sequential extraction procedure modified from the method of Ruttenberg (1992).

Principle

Fe-bound P is determined as citrate-dithionite bicarbonate extractable P (CDB, pH = 7.3, 8 h, 20°C). Dithionite is a strong reductant and will reduce all iron oxides (e.g. ferrihydrite, akageneite, goethite) present in a sediment sample. Citrate acts as a chelating agent and the bicarbonate acts as a buffer to hold the pH at an optimum level (at lower pH's FeS and elemental sulfur may precipitate, at higher pH's iron oxide dissolution decreases). The sediment residue is subsequently washed with 1 M MgCl2, extracted with 1 M Na-acetate buffer (pH = 4, 6h, 20°C) and treated with a 1 M MgCl2 (pH = 8, 0.5 h, 20°C) wash solution. The acetate buffer has been shown to dissolve CFA, biogenic P and CaCO3-bound P and to leave detrital Ca-P largely intact. The MgCl2 rinse is necessary to reverse secondary adsorption. Authigenic P is calculated as the sum of the P extracted in these last two steps. The sediment residue is then treated with 1 M HCl (24 h, 20°C), which dissolves all remaining inorganic P, and the amount of extracted P is used as a measure of detrital Ca-P.

Materials

- centrifuge tubes 30-50 ml
- clean polyethylene vials for samples, 15-50 ml
- filters 0.45 µm
- syringes 25 ml
- dispensers 20 (1) or 25 ml (3)
- large plastic vessels for extraction solutions
- plastic spatula
- siphon with MQ
- pipette: 2.5 ml & tips
- container for MQ water
- 1 litre & 500 ml volumetric flasks
- 1 litre glass beakers

Chemicals

- 0.3 M sodium citrate ($Na_3C_6H_5O_7.2H_2O$ = 294.10): dissolve 88 g in MQ (1l tot. vol.)
- 1 M sodium bicarbonate ($NaHCO_3$, M = 84.01): dissolve 42 g in 500 ml MQ
- 0.5 g of solid sodium dithionite ($Na_2S_2O_4$) per sample
- 1 M Na-acetate (CH_3COONa): dissolve 82.03 g in MQ (1 l tot.vol.)
- 1 M Acetic acid (CH_3COOH): 60 ml conc. ac. acid in MQ (1 l tot. vol.)
- 1 M Acetate buffer pH = 4 (check the pH): 150 ml 1 M Na-ac., 850 ml 1 M Ac. acid
- 1 M $MgCl_2$ pH = 8dissolve 203.3 g in MQ (1 l tot. vol.)
- 1 M HCl (83,3 ml concentrated HCl (37%, 1.9 kg/l; ie 12 M) in 1 l)
- 1 M HCl for rinsing of vials etc.
- Standard reference sample: MM91

Equipment
- analytical balance
- shaker table
- centrifuge
- pH meter + buffer solutions
- freezer (-20°C

Procedure

Step 1 – Exchangable-P

Anoxically weigh ca. 100 mg of sediment into a 50 ml polyethylene tube. To the sediment, add 10 ml 1 M MgCl2 (oxygen-free) adjusted to pH 8 with NaOH. Shake at room temperature for 2 hours. Subsequently, centrifuge at ~2000 g or higher for 10 minutes, transfer to a glovebox (under Ar or N2) and anoxically remove the supernatant with a syringe (be careful not to disturb the sediment surface) and filter it (0.45 µm) into a polyethylene vial. Store the solution samples in the freezer (-20°C) until analysis.

Step 2 – Iron and Manganese oxyhydroxide-P

Transfer the samples to the glovebox. Add 9 ml of Na-citrate solution and 2.5 ml of NaHCO3 solution (oxygen-free). Add 0.5 g of Na2S2O4 (make sure before hand that the pH of the resulting solution is ~ 7.3). Shake at room temperature for 8 hours. Centrifuge, filter and store in a polyethylene vial at -20°C. sediment can now be exposed to oxygen.

Step 2A - Wash

Add 10 ml of 1 M MgCl2 (pH = 8) to the sediment residue in the centrifuge tube. Shake at room temperature for 30 minutes. Centrifuge, filter and store in a polyethylene vial at -20°C. Step 3: Add 10 ml of acetate buffer (pH = 4) to the sediment residue in the centrifuge tube. Shake at room temperature for 6 hours. Centrifuge, filter and store in a polyethylene vial at -20°C.

Step 3 – Authigenic Ca-P

Add 10 ml of acetate buffer (pH = 4) to the sediment residue in the centrifuge tube. Shake at room temperature for 6 hours. Centrifuge, filter and store in a polyethylene vial at -20°C.

Step 3A - Wash

Add 10 ml of 1 M MgCl2 (pH = 8) to the sediment residue in the centrifuge tube. Shake at room temperature for 30 minutes. Centrifuge, filter and store in a polyethylene vial at -20°C.

Step 4 – Detrital-P

Add 10 ml of 1 M HCl to the sediment residue in the centrifuge tube. Shake at room temperature for 24 hours. Centrifuge, filter and store in a polyethylene vial at 4°C.

Step 5 – Organic-P

Transfer the sediment to ceramic cruicibles, weigh, then ash at 550 deg C. Weight again, and then transfer back to the tubes. Add 10 ml of 1 M HCl and shake for 24 hours. Centrifuge, filter and store in a polyethylene vial at 4°C.

Chemical analyses of supernatants

The CDB solutions are analysed on an ICP-AES. Elements should at least include: Fe, Mn, P. Note that the samples should be diluted by a factor 10 and that the detection limit of the ICP is ca. 0.5 to 0.6 µmol/l). The acetate buffer, $MgCl_2$ and HCl solutions are analysed spectrophotometrically. Before analysis, the HCl solutions should be neutralized with NaOH (for procedure, see description of Aspila method). The phosphomolybdate blue complex formed in acetate buffer and $MgCl_2$ tends to be unstable when PO_4 concentrations exceed 5-10 µM. To solve this problem dilute samples to lower concentrations when necessary and keep the analysis time brief. Furthermore, it is recommended to analyze standards immediately before and after a series of samples.

Analysis: 2-3 sample duplicates, 2 internal standards and 2 blanks were included in each series. With the exception of solutions from step 2, all samples were analyzed on a Unicam UV1 Spectrophotometer. Step 2's solution were diluted 5x and analyzed via ICP-OES.

Modification of the procedure when additionally extracting fish-debris:

Extract the sediment 8 times (shake 4 h each time) with 25 ml of 2 M NH4Cl (106.96 g/l, brought to pH 7 with NH4OH) prior to the CDB extraction. Centrifuge, filter and store in a polyethylene vial at -20°C. Combine equal amounts of all 8 extraction solutions for one sediment sample and analyse (either on the ICP-AES or spectrophotometrically, depending on the P-concentration).

Further reading

Ruttenberg, K.C. 1992. Development of a sequential extraction procedure for different forms of phosphorus in marine sediments. Limnology and Oceanography 37: 1460-1482.

Slomp, C.P., S.J. van der Gaast, W. van Raaphorst. 1996. Phosphorus binding by poorly crystalline iron oxides in North Sea sediments. Marine Chemistry 52: 55-73.

Appendix III

Additional data

CDB phosphorus, iron and manganese data
Other porewater profiles

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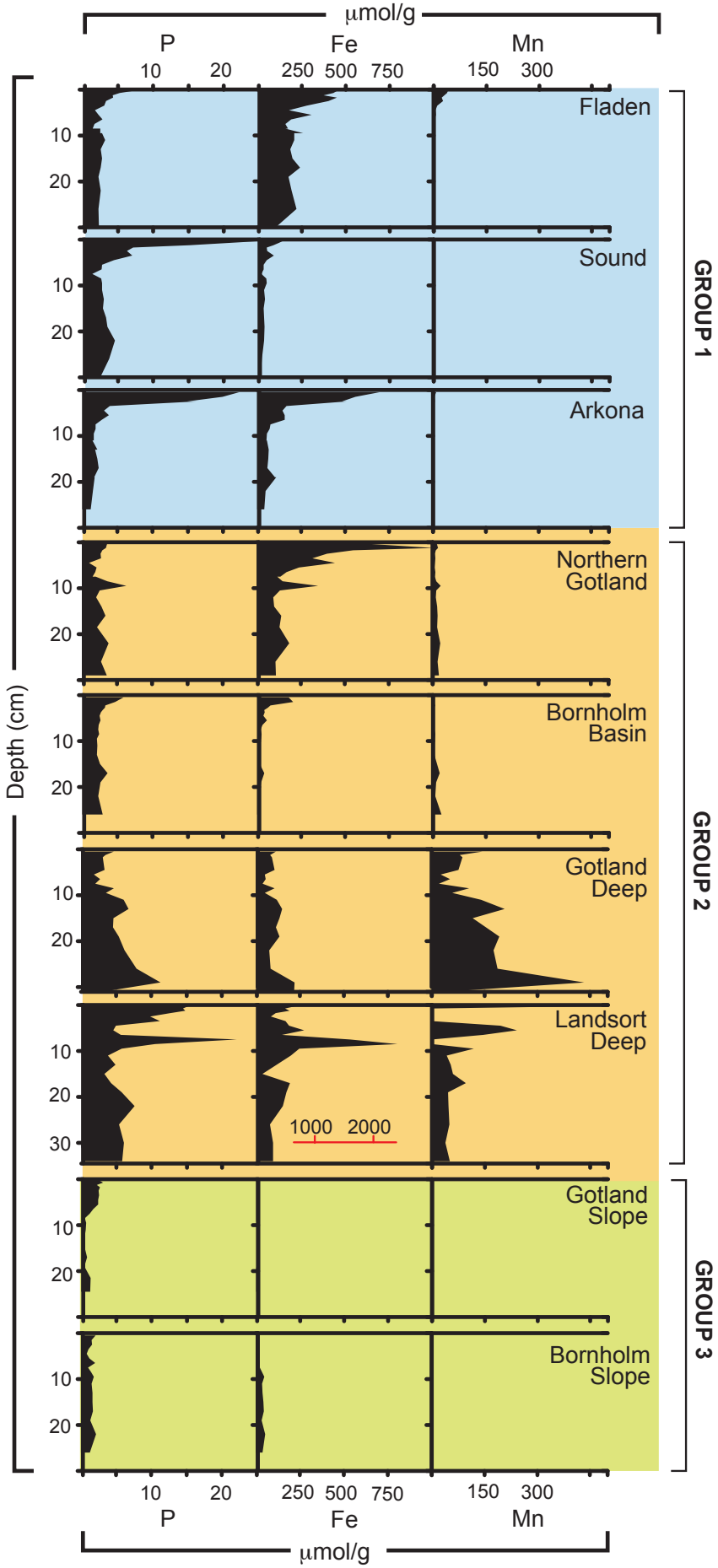
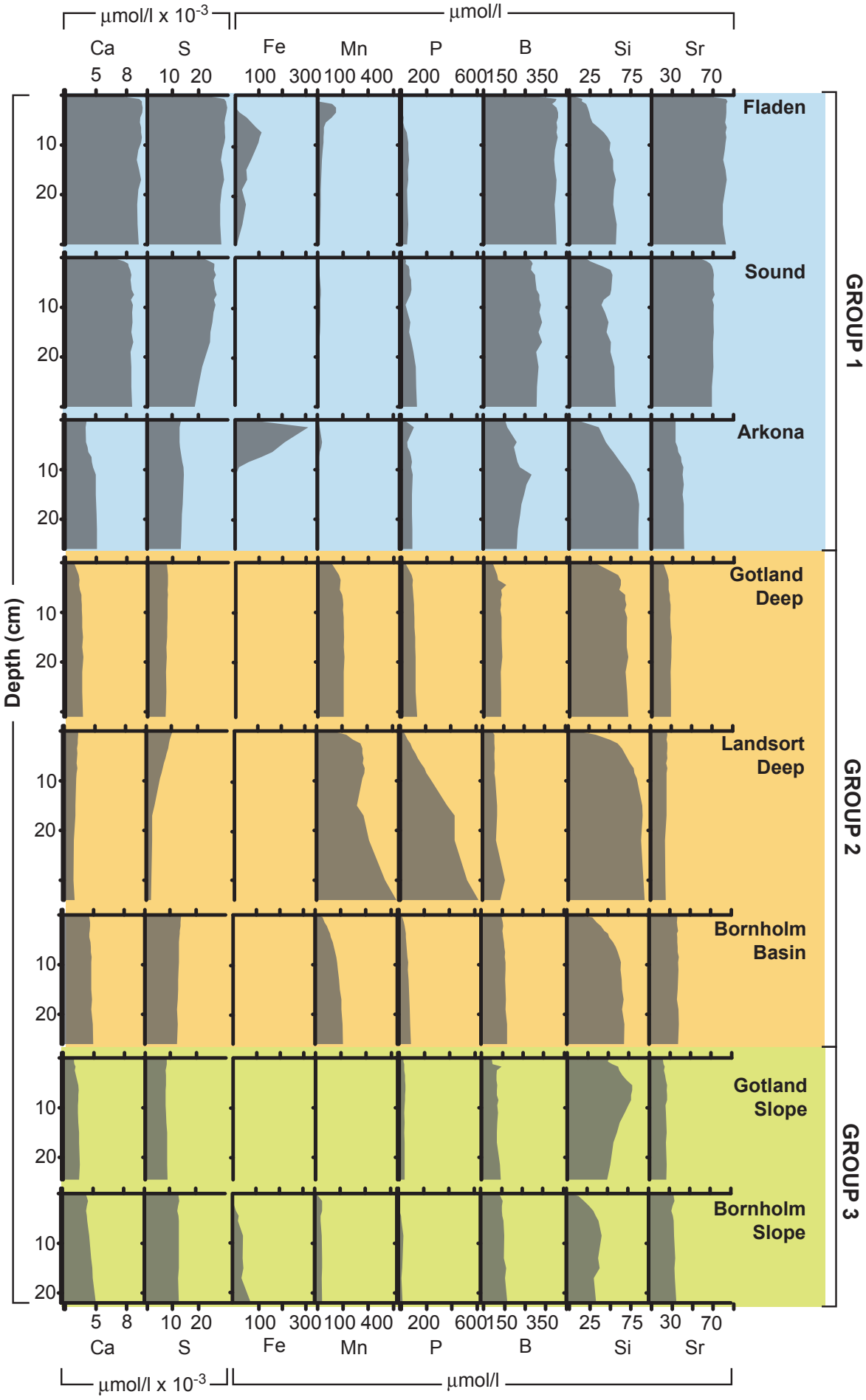
Fe bound-P and Fe and Mn-oxide concentrations



Other porewater elemental concentrations



Appendix IV

List of presentations and meetings

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List of Presentations

Title: Phosphorus burial in Baltic Sea sediments

Presenters: Caroline P. Slomp, Haydon Mort & Bo Gustafsson
Type: Oral
Location: Baltic 2020 meeting, Lund University, Sweden, 27-29 November 2007

Title: What controls Phosphorus burial in the Baltic Sea? (see Poster page 64)

Presenters: Haydon P. Mort, Caroline P. Slomp & Bo Gustafsson
Type: Poster
Location: Dutch Earth Sciences Day, Amsterdam, The Netherlands, 6 December 2007

Title: Phosphorus burial in Baltic Sea sediments

Presenters: Haydon Mort, Caroline P. Slomp & Bo Gustafsson
Type: Oral
Location: 8th Nederlands Aardwetenschappelijk Congres, Eindhoven, The Netherlands, 18-19 March 2008

Abstract
Increased human input of phosphorus (P) to the Baltic Sea likely has led to enhanced primary production and the increased occurrence of hypoxic bottom waters (O_2 < mg/l) throughout the various basins. As yet, the role of the sediments as a temporary and permanent sink for P is not well-quantified. Here we present detailed porewater and sediment data for three sites with contrasting bottom water oxygen regimes, that range from temporarily hypoxic (Arkona basin), predominantly hypoxic (Bornholm basin) to almost exclusively anoxic (Gotland deep). At Arkona, a large pool of Fe-oxide bound P was observed in the surface sediment. Porewater Fe^{2+} and PO_4 profiles indicate mobilization of this Fe-bound P near the sediment surface when bottom waters become hypoxic. This confirms earlier suggestions based on water column data that sediments in the Baltic can act as a major internal source of PO_4. The P speciation data for the Bornholm basin and Gotland deep suggest that these accumulation basins may an important burial sink for reactive P. At the Gotland deep site, reactive P burial appears to be inversely correlated to terrigenous input and authigenic Ca-P, organic P and Fe-bound P act as the major sinks of P.

Title: Phosphorus burial in Baltic Sea sediments with contrasting redox conditions.

Presenters: Haydon P. Mort, Caroline P. Slomp & Bo Gustafsson
Type: Oral
Location: 18th Annual V.M. Goldschmidt Conference, Vancouver, Canada, 13-18 July 2008.

Abstract
Increased human input of phosphorus (P) to the Baltic Sea from agricultural practices and sewage has led to enhanced primary production and the increased occurrence of hypoxic bottom waters (O_2 < 2 mg/l) throughout the various submarine basins. As yet, the role of the sediments as a temporary and permanent sink for P is not well-quantified. Here we present detailed porewater and sediment data for three sites with contrasting bottom water oxygen regimes. These range from temporarily hypoxic (Arkona basin), predominantly hypoxic (Bornholm basin) to almost exclusively anoxic (Gotland deep). At Arkona, a large pool of Fe-oxide bound P was observed in the surface sediment. Porewater Fe^{2+} and PO_4 profiles indicate mobilization of the Fe-bound P pool near the sediment surface when bottom waters become hypoxic. This confirms earlier suggestions based on water column data that sediments in the Baltic can act as a major internal source of PO_4 [1]. Phosphorus speciation data for the Bornholm basin and Gotland deep suggest that these accumulation basins may be an important burial sink for reactive P. At the Gotland deep site, reactive P burial appears to be inversely correlated to terrigenous input and authigenic Ca-P, organic P and Fe-bound P act as the major sinks of P.

[1] Conley *et al*. (2002) *Environ. Sci. Technol.* **36**, 5315-5320.

Appendix V

Poster of preliminary results

Funded by the Baltic Sea 2020

What Controls Phosphorus Burial in the Baltic Sea?

Universiteit Utrecht

Haydon Mort[1], Caroline P. Slomp[1], Bo Gustafsson[2]

GÖTEBORG UNIVERSITY

[1] Utrecht University, Department of Earth Sciences, The Netherlands [2] Göteborg University, Earth Sciences Centre, Sweden

Introduction

Increased human input of phosphorus (P) to the Baltic Sea since 1950 likely has led to enhanced primary production and blooms of cyanobacteria and the increased occurrence of hypoxic bottom waters (< 2 mg/l O_2) throughout the basin. Besides changes in P input, the P availability for primary producers in the water column of the Baltic is also determined by variations in internal recycling of P within the system and the sinks for P, which are outflow to the North Sea and permanent burial in the sediments. In this study, we focus on quantifying the role of sediments with contrasting bottom water oxygen regimes as a temporary and permanent sink for P in the Baltic and the processes that control this burial.

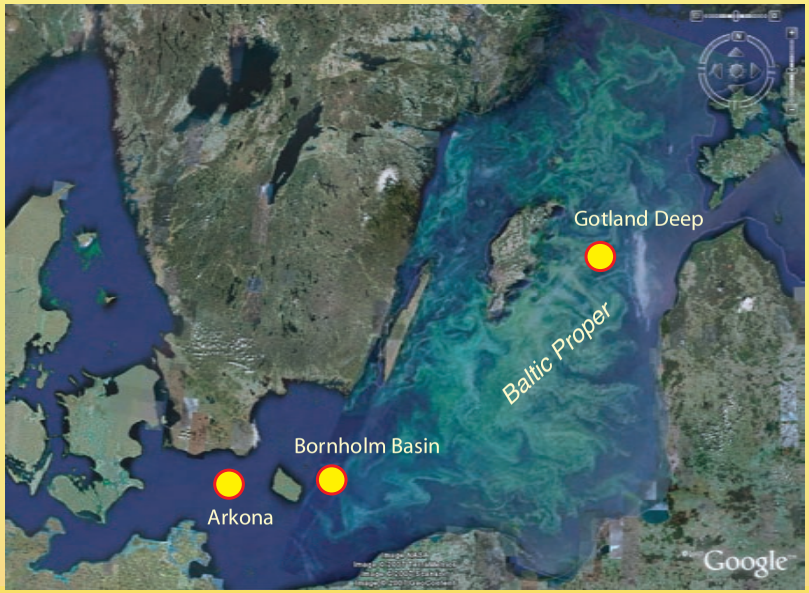


Figure 1. Study sites

Sediment cores were taken from 3 depositional areas in the Baltic Sea in September 2007 with RV Skagerak: Arkona Basin (47 m), Bornholm Basin (89 m) and Gotland Deep (240 m). All cores are being analyzed for porewater and sediment composition (total elemental concentrations and detailed P speciation).

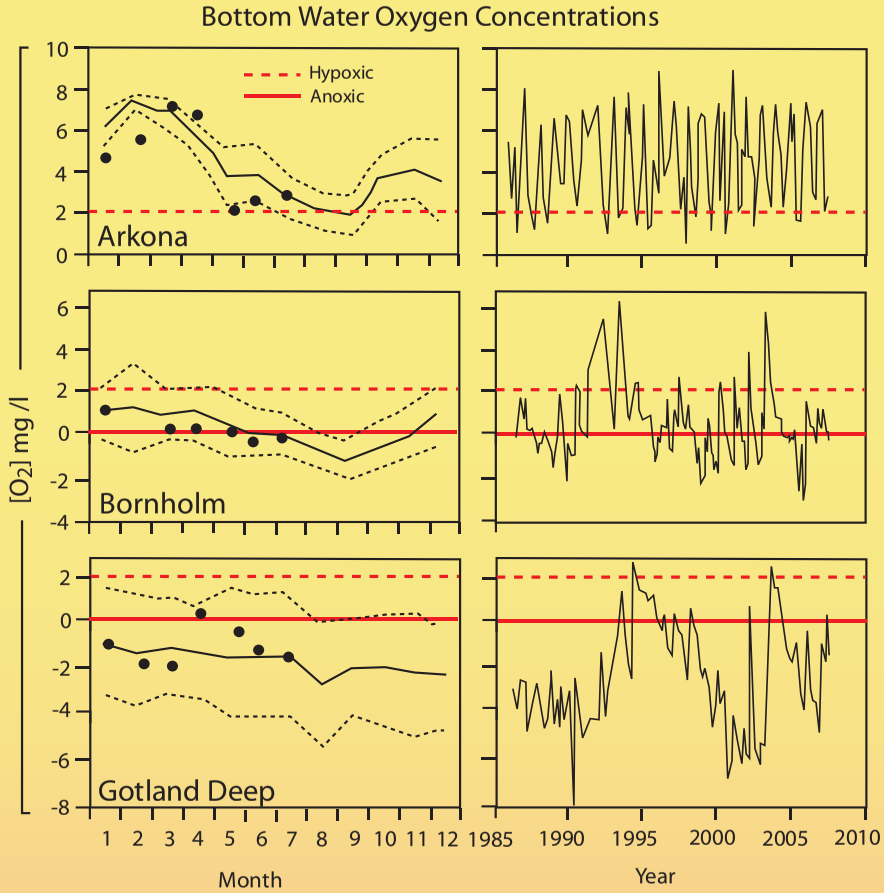


Figure 2.

Bottom water oxygen concentrations at all three sites (SMHI, 2007) show a seasonal (2007) and longer term variability (1985-2007). Arkona, Bornholm and the Gotland Deep (top, middle, bottom) clearly show a progression from an environmental regime which is only temporarily hypoxic (O_2 mostly > 2 mg/l) to predominantly hypoxic (average 1 mg/l) to almost exclusively anoxic (average < 0 mg/l)

RESULTS

Pore Water Data

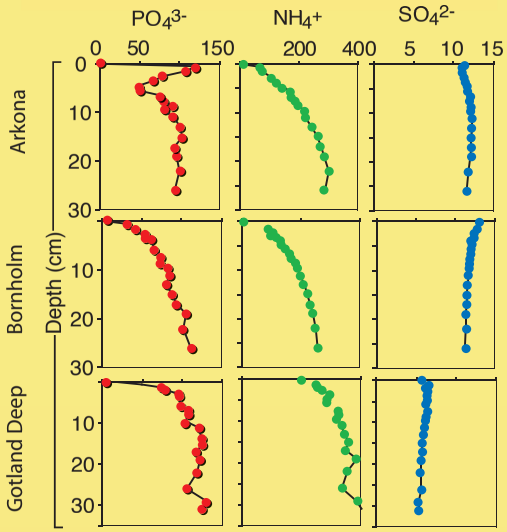
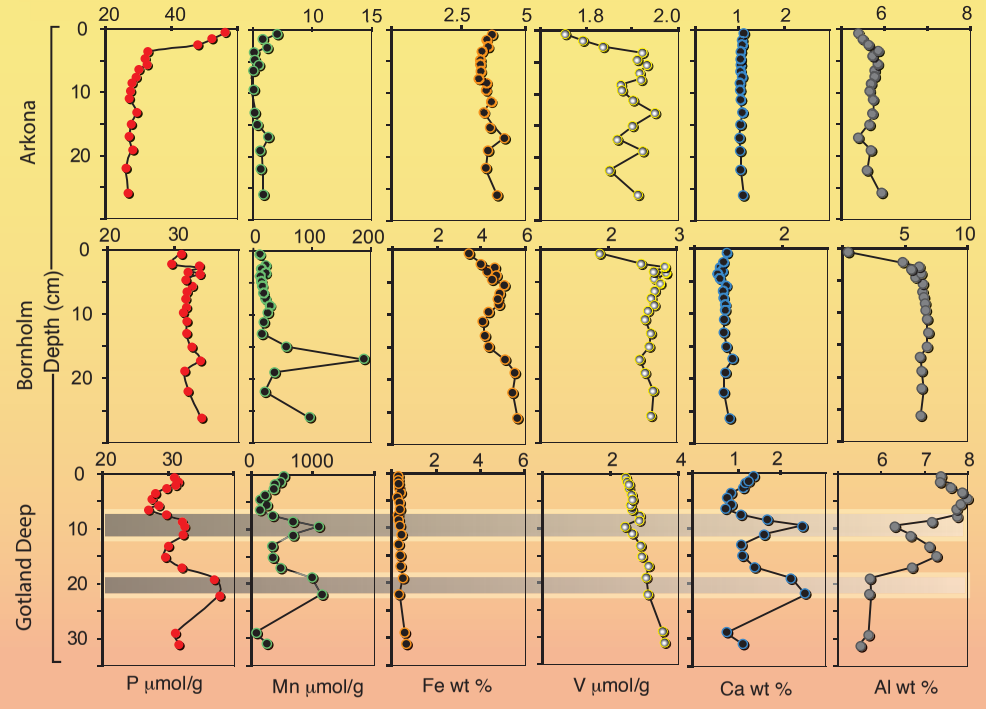


Figure 3 (left): Porewater PO_4 and NH_4 concentrations increase with depth at all sites due to regeneration of these nutrients from organic matter. For PO_4, release from Fe and possibly Mn oxides upon their reduction is an additional source (e.g., see spike in dissolved PO_4 near the sediment-water interface at Arkona). Porewater SO_4 concentrations depend on the interplay of temporally varying bottom water salinities and removal through sulphate reduction and show only a limited change with sediment depth

Figure 4 (below): At the Arkona site, total P and Fe profiles suggest an enrichment in Fe-oxide bound P near the sediment-water interface, which is in accordance with the oxic conditions that often prevail at the site. At the Bornholm and Gotland deep sites such an enrichment is absent. There is a close correlation between P, Mn and Ca concentrations at the latter site.These elements are inversely correlated with Al.

Total Destruction: Elemental Data



Phosphorus Speciation for the Gotland Deep

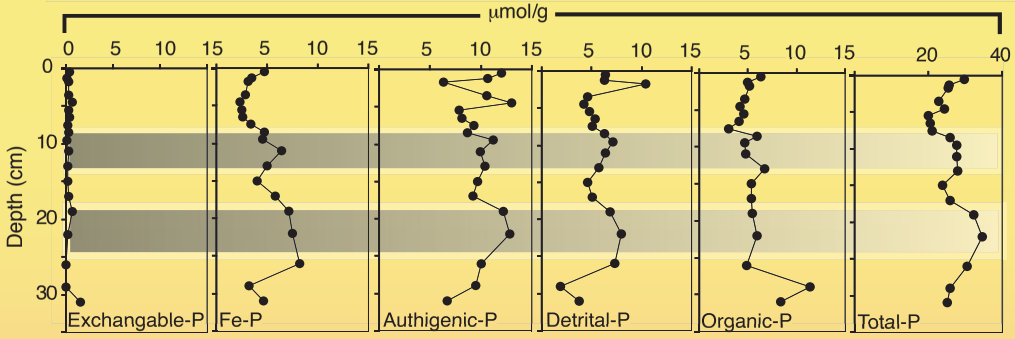


Figure 5 (above): Authigenic P is the most important form of P in the Gotland Deep. All inorganic phosphorus fractions (Fe-P, Authigenic and Detrital) share a similar profile to that identified in the shaded bars in the total destruction data (also highlighted above). Only the organic-P does not follow this pattern.

CONCLUSIONS

The pore-water and sediment data for Arkona basin suggest

(1) a large pool of Fe-oxide bound P in the surface sediment and
(2) the release of PO_4 from these Fe-oxides near the sediment-water interface when bottom waters become hypoxic. These result confirm earlier suggestions that sediments in the Baltic can act as a major internal source of PO_4.

The data for the Bornholm and Gotland Deep suggest that these accumulation basins may be an important burial sink for reactive P. At the Gotland Deep site, the correlation between P, Mn and Ca suggests a common source for these elements, which is likely authigenic.

REFERENCES

Swedish Meteorological and Hydrological Institute Marine Monitoring Data, 2007; http://www.smhi.se/oceanografi/oce_info_data/reports/)

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What controls phosphorus burial in the Baltic Sea?

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