The effect of redox conditions on early diagenesis in Baltic Sea sediments: a field and modelling investigation

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Introduction

The Baltic Sea is a semi-enclosed basin (Fig . 1) which is permanenly stratified. The upper layer consists of brackish water (salinity 7-8psu) and the deeper waters are more saline (11-12psu). A strong halocline is formed where the two layers meet, which restricts vertical mixing of the water column and transport of oxygen to the bottom waters (Zillen et al., 2008). When the oxygen supplied by physical processes cannot meet the demand of biological processes consuming it, the bottom waters become hypoxic (O_2 < 2ml L^{-1}). Although hypoxia is mainly induced by the restricted bathymetry of the basin, the areas of hypoxia have spread substantially over the last century. This increase is unlikely to be natural but rather induced by antropogenic inputs of phosphorus (P), causing severe eutrophication. This has increased the oxygen demand, magnifying the intensity, duration and spatial extent of hypoxia (Conley et al., 2009). In this study, the goechemistry of oxic (LF 1), seasonally hypoxic (LF 1.5) and permanetly hypoxic/anoxic (LF 3) sediments is investigated, with emphasis on the effect of redox conditions on P cycling. Solid phase P speciations, bulk sediment and porewater geochemical analyses were performed on cores from these sites, and reactive transport modelling was used to mechanistically investigate the influence of oxygen on early diagenetic processes in the sediment.

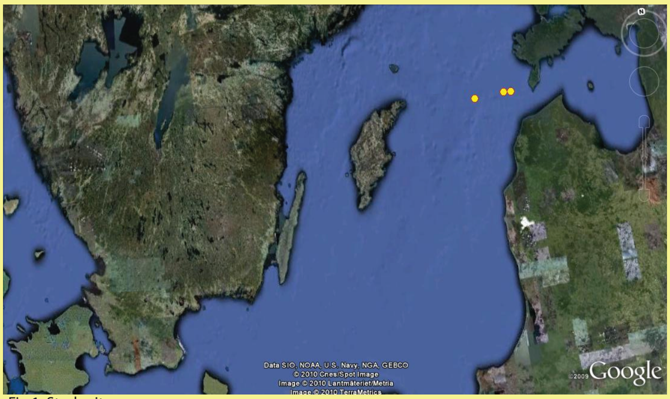


Fig 1. Study sites
Core samples were taken from 3 depositional sites in the Gotland basin. The yellow dots represent the sampling locations (from east to west, LF 1; LF 1.5; LF 3 , the sites become progressively more hypoxic).

Approach of the modelling study

- Reactive transport modelling was performed using the software package "R". A comprehensive network of primary and secondary redox reactions is included.
- The model parameters were adjusted to fit the data for the oxic site LF 1 (the so-called groundtruthing process).
- By changing only bottom water oxygen concentration and porosity to values realistic for LF 1.5 and LF 3, we attempted to model these sites, to establish whether contrasting oxygen conditions can explain the observed differences.

Discussion

- LF1 could only be properly groundtruthed by assuming an increasing organic carbon flux over the 80 years of the model simulation. Specifically, the gradient in organic carbon concentration towards the sediment-water interface could not be reproduced with a constant carbon flux.
- Assuming this increase, the groundtruthing of LF1 is reasonable. Organic carbon remineralisation occurs principally via aerobic respiration in the uppermost milimetres, with an important secondary role for Fe-oxide reduction in the top 5 cm. The latter generates a subsurface peak in porewater Fe. Phosphorus released during organic matter degradation is bound to Fe-oxides where these are present. The poor quantification of porewater P deeper in the core may represent a lack of knowledge of the reactivity of the carbon flux to the sediment.
- LF 1.5 and LF 3 could not be accurately modelled by simply switching off or reducing the oxygen concentration, suggesting that these sites also contrast with respect to other parameters. This will be the focus of ongoing work.

Results

Pore water data

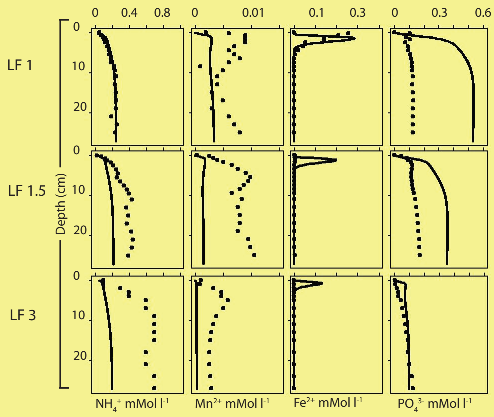
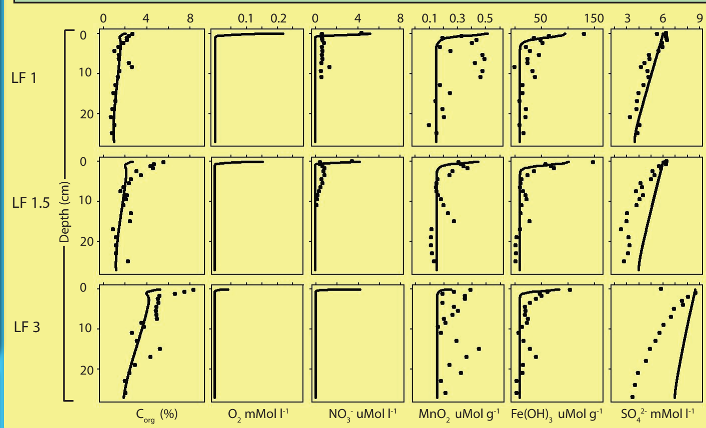


Fig 2 (left): Pore water profiles. The dots represent the field data and the lines represent the modelled constituents. NH_4^+ and PO_4^{3-} increase with depth due to organic matter remineralisation. The subsurface Fe^{2+} and Mn^{3+} peaks are due to metal oxide reduction.

Fig 3 (below): Organic carbon and oxidants as a function of depth. The dots represent field data, the lines are the modelled profiles. Organic carbon decreases with depth due to organic matter remineralisation. Simultaneously, oxidants are reduced. Oxygen, nitrate and metal oxides are reduced in the shallow subsurface zone. At depth, when these species are exhausted, sulphate reduction begins.

Organic Carbon & oxidants



Phosphorus speciation

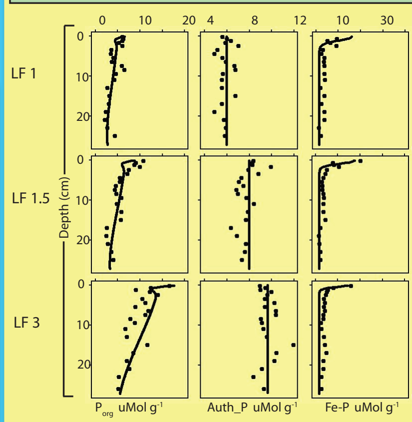


Fig 4: Phosphorus species over 30 cm depth. The dots represent field data, the lines are the modelled profiles. Organic phosphorus and iron bound phosphorus are modelled according to a fixed ratio with their host phases, so the distributions of these species are mainly controlled by iron oxides and organic carbon. According to the field data, authigenic P stays constant over depth, indicating no formation of authigenic P in the sediments.

Site	O	Nitrate	MnO	Fe(OH)	Sulphate	Methanogenesis
LF1	66,09	11,29	0,61	23,96	2,24	0,72

Table 1: Depth integrated reaction rates of organic matter remineralisation per electron acceptor (uMol C_{org} cm^{-2} y^{-1} in the month of May after a period of 80 years).

Conclusions & Future work

- The gradient of increasing organic matter concentration towards the sediment-water-interface at LF1 can only be obtained by assuming an increasing organic matter flux over the last 80 years. This supports the hypothesis that primary productivity has increased in the Baltic Sea during the last century. Such a gradient is also observed at LF 1.5 and LF 3,
- At LF 1, organic carbon remineralisation is dominated by oxygen reduction, with Fe-oxide reduction the second most important pathway.
- The difference in early diagenetic processes at the three sites are not only controlled by bottom water oxygen concentration, as evidenced by the poor fits achieved for LF 1.5 and LF 3 after adjustment of oxygen concentration in the model. Thus, other contributing factors must be investigated. Ongoing work will focus on:
  - Sensitivity analysis to investigate the influence of variable reactivities of the organic matter influx on degradation rates and porewater profiles
  - Sensitivity analysis to investigate the influence of bioturbation and mixing depth (oxygen sensitive parameters).
  - Tuning the model to fit LF 1.5 and LF 3, to investigate the changes neccessary to recreate these sites.

References

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