Popular report for three BS2020 projects on
“Phosphorus dynamics in Baltic Sea sediments” 2007-2009

Introduction

Human activities over the past century have greatly increased inputs of nitrogen and phosphorus to the Baltic Sea. Because these elements act as limiting nutrients for algae, this has greatly increased the abundance of algae in Baltic Sea surface waters. When the algae die, they sink down and decompose at or near the seafloor. This leads to an increased oxygen demand in the bottom water. Since large portions of the deep waters in the Baltic Sea are poorly ventilated, the increased demand for oxygen can easily lead to the development of low oxygen conditions (“hypoxia”) and the death of organisms living on the seafloor. This “eutrophication-induced hypoxia”, where eutrophication indicates that the system is nutrient-rich or “well-fed”, is the main cause of the large expansion observed in the hypoxic area in the Baltic over the past decades. Similar problems with expanding hypoxia have been reported for many coastal regions worldwide.

The role of phosphorus

Bottom water hypoxia and anoxia in aquatic systems are known to enhance the release of phosphorus from sediments. This “internal cycling” of phosphorus likely plays a key role in maintaining low oxygen conditions in anoxic marine systems by fueling algal growth and organic matter supply to bottom waters. For the Baltic Proper, annual changes in dissolved phosphate pools on a basin scale have been shown to be positively correlated to the sediment area covered by hypoxic water and not to changes in phosphorus inputs from rivers. This phosphorus likely fuels the cyanobacterial blooms in the Baltic that are considered to be harmful.

The big unknown: what is happening in the sediment?

Little is known about the processes in the sediments during the transition from oxic to hypoxic conditions in the Baltic Proper. From water column studies and incubations of whole sediment cores in the laboratory, it has been inferred that release of phosphorus from sediment Fe-oxides is responsible for the internal recycling in the Baltic Proper. However, this has not been proven. In addition, various budgets for nutrients suggest that the sediments in the various sub-basins of the Baltic Sea act as a permanent burial sink for phosphorus but it is not clear in what form this phosphorus is buried. The Bothnian Sea is of specific interest in this respect because earlier studies suggest that a lot of the phosphorus from the Baltic Proper may in fact be transported northwards and may be sequestered in the well-oxygenated and iron-rich sediments of the much more oligotrophic Bothnian Sea.

Aims of this work

The aims of our work in the three 1-year postdoc projects funded by the BS2020 were to obtain quantitative insight in the role of the sediments as
(1) a temporary sink and source for phosphorus in the Baltic Proper
(2) a permanent sink for phosphorus in the various subbasins of the Baltic Sea (Danish Straits, Baltic Proper and Bothnian Sea)

Our ultimate aim was to provide information that would allow improvement of the biogeochemical models that are used to take management decisions for the Baltic Sea.

Field studies
In these projects, we collected samples from the seafloor and the water column during 2 research cruises to the Baltic Sea using the Swedish research vessel RV Skagerrak. Our cruise to the Baltic proper took place in early fall of 2008, when the hypoxic area was extensive. We visited the Bothnian Sea in the fall of 2009. During both cruises, we analyzed the solid phase and interstitial waters (“pore waters’) of the sediment cores in detail for a wide range of chemical constituents.

Biogeochemical modeling
We developed a detailed mathematical model to describe the reactions and transport of the chemical components in the sediment and the interactions with the overlying waters. The model was used to describe the dynamics of phosphorus and 22 other key biogeochemical elements at a seasonally hypoxic site in the southern Baltic Sea (Arkona). We also assessed how the coupled sediment-water system at Arkona would respond to increased stagnation and decreased deposition rates of material to mimic the processes that occur in the almost permanently anoxic deep basins of the Baltic Proper. Our work provides relationships between redox conditions and phosphorus cycling for use in biogeochemical models for the Baltic Sea (e.g. Baltsem).

Seasonally hypoxic sediments: a source and sink for phosphorus
Our work indicates the presence of strong surface enrichments of Fe-oxide bound phosphorus at oxic and seasonally hypoxic sites at intermediate water depths in the Baltic Proper. At the seasonally hypoxic sites, a part of the Fe-oxides are reduced upon the onset of the hypoxia in late summer and the associated phosphorus is released to the water column. Upon the recovery of oxic conditions in fall, net accumulation of Fe-oxides and associated phosphorus occurs again. Extended hypoxia and anoxia leads to depletion of the sediment Fe-bound phosphorus pool and an associated flux of dissolved phosphorus to the water column. In the anoxic deep basins, the Fe-bound phosphorus pool is totally depleted and the associated source of dissolved phosphorus ceases. Future work should concentrate on obtaining more detailed insight in the lateral extent of the Fe-oxide bound phosphorus layer in the sediments of the Baltic Proper.

Permanent burial of phosphorus in the Baltic Proper
Most permanent burial of phosphorus in the sediments of the Baltic Proper takes place in the form of organic phosphorus. We find no evidence for significant in-situ formation of inorganic calcium phosphorus minerals. This is important because this means that the Baltic Sea is very sensitive for the feedback loop between increased hypoxia, increased release of phosphorus from the sediment and increased algal growth since any phosphorus released from Fe-oxides will return to the water column where it can fuel algal growth or is exported to adjacent basins. Our preliminary burial calculations indicate that burial of organic phosphorus in hypoxic and anoxic areas in the Baltic is significant and should be accounted for in budgets and models for the Baltic Sea.

Sediments as a recorder of water column conditions
Various sediment components are known to reflect bottom water redox conditions and have been coined as “redox proxies” (i.e. redox indicators) based on work in other marine systems. These include elements such as sulphur and molybdenum and ratios of organic carbon to phosphorus. For a site in the Northern Gotland basin, we demonstrate that trends in these “redox proxies” are consistent with historical records of bottom water oxygen. These redox proxies can thus be used to map lateral changes in redox conditions and phosphorus cycling in the Baltic, also for sites for which we do not have historical oxygen records. Although not a primary objective of this study, this result is important since it will greatly facilitate interpretation in future sediment core studies in the Baltic Sea.

The role of the Bothnian Sea as a sink for phosphorus
Our work demonstrates that poorly crystalline Fe-oxides are the major sink for phosphorus in Bothnian Sea sediments. This is an easily mobilizable phophorus form, which can be released upon a decline in bottom water oxygen or a rise in salinity. At a value of 7, the current Fe/P ratio of Fe-oxides in the surface sediment is relatively high for a brackish environment, suggesting a further capacity to sequester additional phosphorus. Further work is needed, however, to determine at what point the Fe-oxides become saturated with phosphorus and will start to release phosphorus to the overlying water. At one deep basin location, some phosphorus at depth in the sediment is bound in the form of a reduced Fe-P mineral: vivianite. This phase acts as a permanent sink for phosphorus. Further work on longer sediment cores is needed to assess the importance of this burial phase for phosphorus in the deep basin of the Bothnian Sea. Our work indicates that the Bothnian Sea acts as a major sink for phosphorus from the Baltic Proper. Our estimate of 13,000 tons of phosphorus per year lies within the range of 9,600-18,600 tons of phosphorus per year obtained from mass balance studies.

Major conclusions:
Our work demonstrates that

- There is a pool of Fe-bound phosphorus in the surface sediments of the Baltic Proper in seasonally hypoxic areas along the rim of the deep basins that acts as a major temporary source/sink for phosphorus in the water column.
- Sediments in the deep basins of the Baltic Proper and in the Bothnian Sea are important sinks for phosphorus in the Baltic Sea system. While the magnitude of these sinks are similar, the controlling processes are very different: in the Baltic Proper burial mainly takes place in organic form, whereas in the Bothnian Sea Fe-oxide bound phosphorus is most important.
- The Baltic Proper is prone to the development of hypoxia because it is very sensitive to the feedback loop between increased hypoxia, enhanced release of phosphorus from the sediment and increased algal production.

Further work is needed to quantify the pool of Fe-oxide bound phosphorus in the sediments of the Baltic Proper and the role of vivianite formation in the Bothnian Sea. Our work will be used to improve the sediment module in biogeochemical models of the Baltic Sea (e.g. Baltsem).