

# Phosphorus regeneration in the Baltic Sea: Spatial and temporal variability

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Introduction

The Baltic Sea is a restricted brackish basin with a catchment population of over 85 million people. Although biogeochemical cycles within the Baltic are directly sensitive to changes in anthropogenic nutrient inputs, variable rates of internal regeneration of nutrients from the sediments are the principal driver of interannual changes in the total dissolved nutrient pools of the basin and therefore the severity of eutrophication phenomena. The density contrast between the deep saline inflows spilling through the Danish straits, and the freshwater outflow at the surface, creates a semi-permanent stratification throughout the Baltic. The intermittent (decadal) nature of the major inflow events results in stagnation of the deep basins, triggering widespread hypoxia (dissolved O<sub>2</sub> <2ml/L) and complete oxygen starvation below ~80m in the water column. Superimposed on this background state, the high-latitude seasonal cycle induces strong variability in organic matter production and decay rates, causing vertical migration of the redox zonation in the water column and underlying sediments. This study investigates the effect of spatial and temporal redox gradients on regeneration of the key nutrient phosphorus (P) from the sediments to the water column, as a basis for establishing the role of the P in sustaining hypoxia in the Baltic.

### The Baltic Sea

Multicoring during the HYPER cruise (June 2009)

Gulf of Finland transect

Gotland Basin transect

Arkona Basin seasonal monitoring station

Bornholm Basin transect

100km

Depth (m)

0

600

### The sedimentary P cycle

Water column

Oxidized sediment

Reduced sediment

Org. P

HPO<sub>4</sub><sup>2-</sup>

Fe-P

Detr. Ca-P

Auth. Ca-P

Phosphorus is delivered to the sediment in decaying organic matter, where it is remineralized to HPO<sub>4</sub><sup>2-</sup>. In oxidized sediment, HPO<sub>4</sub><sup>2-</sup> can bind to Fe-oxides, but is released again as the Fe-oxides dissolve upon burial into the reduced sediment zone. If this occurs close to the sediment surface, HPO<sub>4</sub><sup>2-</sup> is ‘regenerated’ into the water column due to the strong concentration gradient across the sediment-water interface. Because the depth of the redoxcline in Baltic sediments is highly variable through space and time, fluxes of HPO<sub>4</sub><sup>2-</sup> from the sediments are as yet poorly quantified.

### Seasonality of redox conditions

O<sub>2</sub> in bottom water (ml/L)

Fe<sup>2+</sup><sub>(aq)</sub> (μmol/L)

Fe-P (μmol/g)

Sediment Depth (cm)

June

Sept

In Arkona Basin, spring and summer productivity blooms lead to a steady decrease in bottom water O<sub>2</sub> throughout the middle of the year. Sediment and porewater data from June and September show how the pool of Fe-oxide bound phosphorus (Fe-P) is depleted during this period, as the dissolution depth of Fe-oxides (tracked by Fe<sup>2+</sup><sub>(aq)</sub>) rises in the sediment column. By this mechanism, phosphorus is released back to the water column as HPO<sub>4</sub><sup>2-</sup>.

Depth dependence of phosphorus regeneration

Gotland Basin transect (June 2009)

Arkona Basin (June 2009)

Salinity (psu)

O<sub>2</sub> (ml/L)

Water Depth (m)

Diffusive HPO<sub>4</sub><sup>2-</sup> flux (μmol/m<sup>2</sup>/d)

HPO<sub>4</sub><sup>2-</sup> (μmol/L)

Fe<sup>2+</sup><sub>(aq)</sub> (μmol/L)

Sediment Depth (cm)

194m

95m

72m

67m

48m

Water column salinity and oxygen data along a depth transect into the Gotland basin highlight the stratification of the Baltic Sea. Oxygen is depleted in the stagnating deeper waters, with major impacts on the processes controlling nutrient regeneration from the underlying sediments.

Phosphorus transported to the sediment as organic matter is released into the porewater as HPO<sub>4</sub><sup>2-</sup> during remineralization. At shallow sites where oxygen is plentiful (eg. Arkona Basin in June, shown here), Fe-oxides can persist in the upper sediment, trapping HPO<sub>4</sub><sup>2-</sup>. As water depth increases and oxygen becomes scarcer, Fe-oxides are utilized progressively more rapidly to degrade organic matter and by reaction with free sulfide. This results in an unstable zone at intermediate water depths, where a thin and intermittent surface layer of Fe-oxides expels seasonal pulses of HPO<sub>4</sub><sup>2-</sup> back into the upper porewaters upon reductive dissolution to Fe<sup>2+</sup><sub>(aq)</sub>. In the deepest waters, no Fe-oxides persist in the sediment and the porewater HPO<sub>4</sub><sup>2-</sup> profile reflects the rate of organic matter degradation by sulfate reduction.

Diffusive HPO<sub>4</sub><sup>2-</sup> fluxes from the sediment to the water column are calculated using Fick’s first law. Along the depth transect, two maxima are observed; one in the intermediate-depth zone where Fe-oxide dissolution takes place close to the sediment surface, and one in the deepest basins where anoxic conditions accelerate the relative rate of P release during organic matter breakdown.

Summary

Internal regeneration of phosphorus from the sediments is the dominant source of this key nutrient element for productivity in the Baltic Sea. The rate of P regeneration is controlled by redox conditions, which vary seasonally and with water depth. Since low-oxygen conditions favor P release, both by reduction of Fe-oxides and preferential remineralization from organic matter, the P dynamics of the Baltic are highly sensitive to the distribution of physically and anthropogenically induced hypoxia.

Funding sources

BONUS

Baltic Organisations Network for Funding Science EEC

Universiteit Utrecht

Baltic Sea 2020

Stockholm University

Baltic Nest Institute

NWO

Netherlands Organisation for Scientific Research