

Phosphorus cycling in Gulf of Finland sediments

Eefje van Zadelhoff, MSc candidate, University of Utrecht-Geochemistry
supervisors: Tom Jilbert and Caroline Slomp

Introduction

The Gulf of Finland (GoF) is vulnerable to hypoxia due to permanent salinity stratification and high anthropogenic nutrient input. Although the potential effects of bottom water hypoxia on phosphorus regeneration and burial are known in principle, the GoF presents an unusual combination of geochemical conditions which may influence the importance of these processes relative to the rest of the Baltic. Specifically, GoF sediments are characterized by hypoxic, low salinity porewaters, and a high organic carbon flux. This study aims to establish the effects of these conditions on phosphorus cycling, especially with regards to the severity of hypoxia.

Material and methods

GOF 5 and GOF 6 are located at 64m and 70m, respectively, on the northern slope of the Gulf of Finland (Fig. 1). These depths lie within the halocline, and the deeper site GOF 6 experiences more severe and frequent hypoxia. We performed sequential phosphorus extractions on cores from the two sites using the scheme of Ruttenberg (1992, see table below) and a complete solid-phase and porewater geochemical characterization.

step	extractant	extracted
1	MgCl ₂ (pH8)	Exchangeable P
2	CDB (pH~7,5)	Fe-bound P
3	Acetate buffer (pH4)	Authigenic P
4	HCl (1M)	Detrital P
5	Ashing (550°C) + HCl (1M)	Organic P

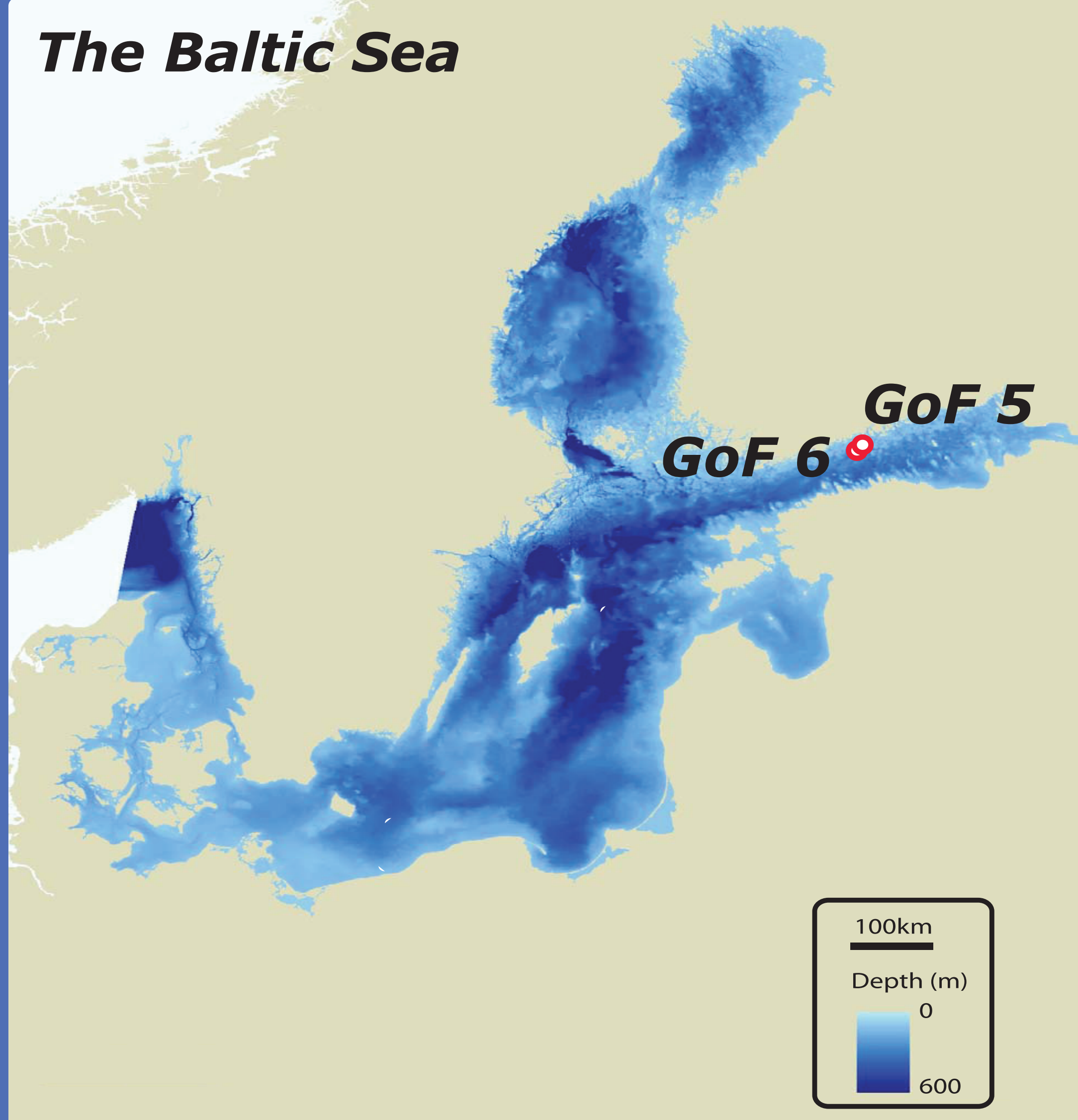


Figure 1. Bathymetric map of the Baltic Sea, showing the deep inlet to the GoF. This connectivity allows the halocline and hypoxia of the Baltic proper to penetrate into the GoF.

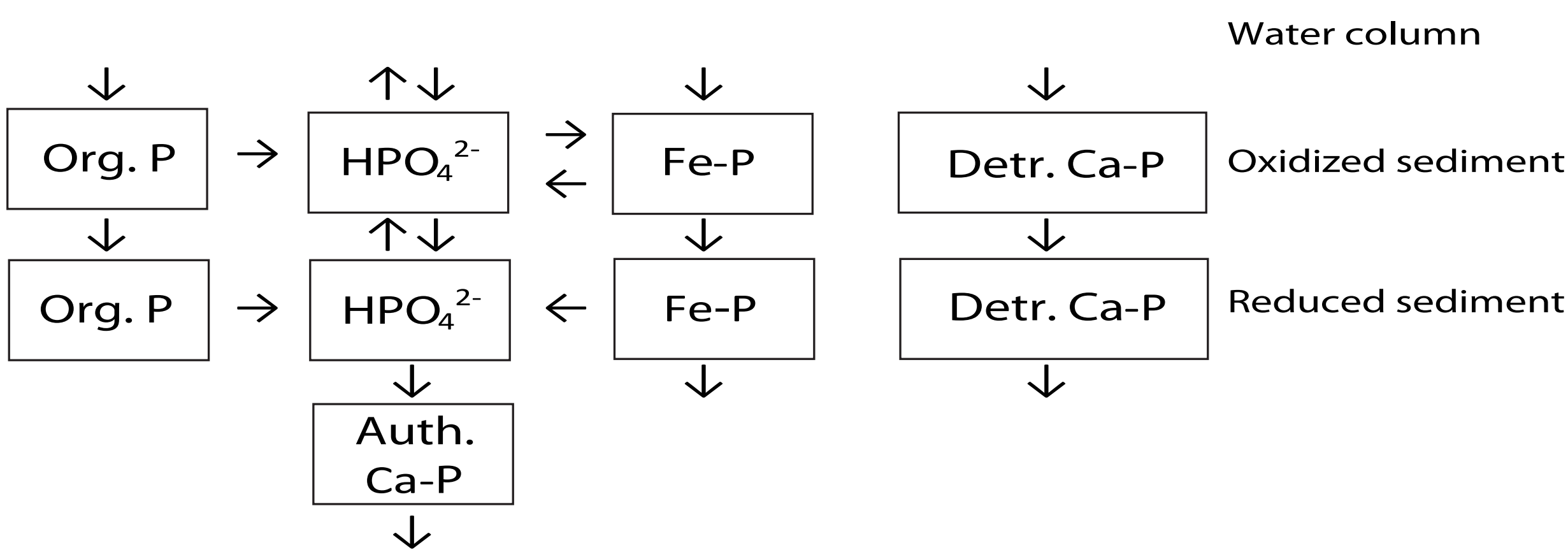
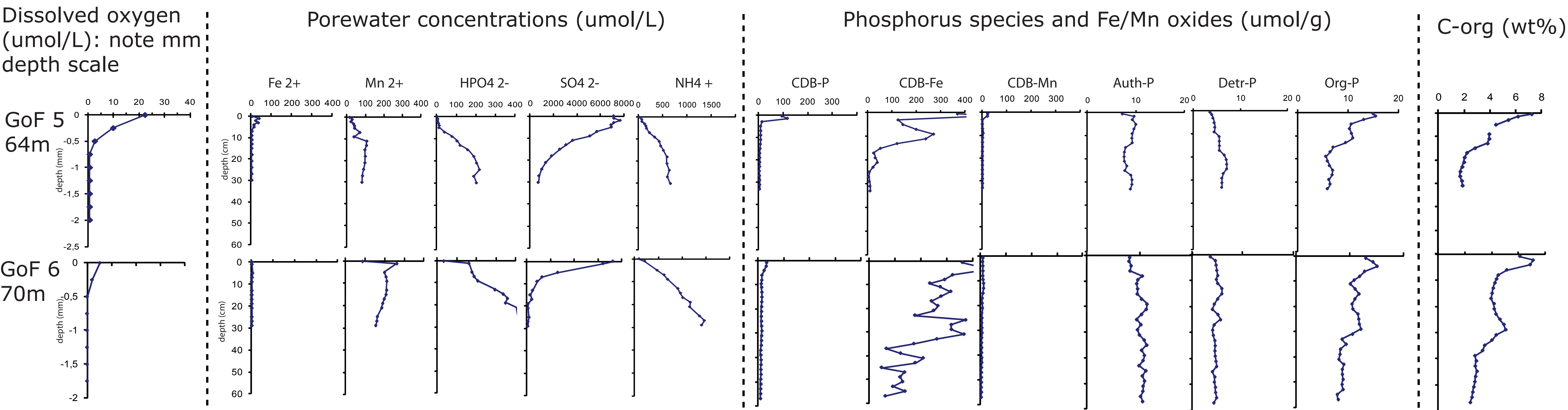


Figure 2. Schematic overview of phosphorus forms in oxidized and reduced sediments.

Phosphorus (P) reaches the sediment in two principal forms: as organic material and as detrital apatite. While the detrital apatite is unreactive, a fraction of the organic phosphorus is remineralized to HPO₄ 2- in the sediment. Under oxic conditions, this HPO₄ 2- binds to Fe-oxides. Under reducing conditions, the Fe-oxides dissolve, releasing HPO₄ 2-. At depth, when HPO₄ 2- concentrations are high enough, authigenic apatite may precipitate, forming a permanent P sink. A shift towards hypoxia in the water column should increase the regeneration of P by dissolving the shallow-sediment Fe-oxides and potentially increasing the relative remineralization of P from organic matter. These processes establish a positive feedback in which the P supply for primary productivity is sustained.



Results and Interpretations

The onboard oxygen penetration measurements confirm that GoF 5 is more oxic than GoF 6. Accordingly, the concentration of Fe-P at the core-top is higher at GoF 5 than GoF 6, indicating greater shallow-sediment P retention at GoF 5. Fe-P is also by far the dominant P fraction in the surface sediments at GoF 5. This retention is confirmed by the HPO₄ 2- profiles, which show far higher core-top concentrations at GoF 6, thus higher diffusive efflux from the sediments.

The vertical profiles of 'authigenic' P suggest that no in-situ precipitation of apatite minerals is taking place; rather, that this fraction is in fact detrital in origin. Although the low salinity of the system results in rapid removal of SO₄ 2- at both sites, there is also no apparent evidence for precipitation of vivianite (Fe-phosphate) as may occur in association with sulfate depletion elsewhere in the Baltic.

In the absence of authigenic P mineral formation, the dominant burial phase of non-detrital P at both sites is organic-P. The rate of organic P burial is strongly coupled to the rate of C-org burial, and shows an increasing trend towards the present day. Thus, the expansion of hypoxia in the GoF over the 20th century has increased the rate of P burial as well as P regeneration.