

COMPARING THE PHOSPHORUS REGIMES IN SOFT SEDIMENTS FROM TWO SUB-SYSTEMS OF THE BALTIC SEA WITH DIFFERENT REDOX CONDITIONS

En jämförelse mellan fosforbindningen i sediment från Bottenhavet och Egentliga Östersjön och syrehaltens betydelse

by J. MIKAEL MALMAEUS* and O. MAGNUS KARLSSON
IVL Svenska Miljöinstitutet; Box 21060; SE-10031 Stockholm

* Corresponding author: mikael.malmaeus@ivl.se



Abstract

The role of sediments in the phosphorus (P) dynamics of the Baltic Sea is often highlighted. The impact of the sediments on the water column is strictly limited by the amount of potentially mobile P available in the sediments. We present total P measurements for ten sediment cores from the Bothnian Sea and the Baltic Proper and detailed measurements of different P forms with different mobility in two cores. The Baltic Proper is characterized by anoxic conditions in the bottom waters overlying the accumulation sediments, whereas the bottom waters of the Bothnian Sea are generally oxidized which is also reflected in the sediments. Integrating the sediment concentrations over the depth profiles, amounts of mobile phosphorus were estimated in each sediment core. Average mobile P content in the sediments of the Bothnian Sea was found to be an order of magnitude higher than in the Baltic Proper. By contrast, the bottom waters of the Baltic Proper contained dramatically higher P concentrations indicating that the available mobile P was largely present above the sediments. An indicative distribution of P between deep water and sediment in the Bothnian Sea is 1:16, while the corresponding ratio in the Baltic Proper is 3:1.

Key words – Baltic Sea, Bothnian Sea, eutrophication, hypoxia, phosphorus

Sammanfattning

Ofta framhålls sedimentens betydelse för fosfordynamiken i Östersjön. Sedimentens inverkan på vattenmassan är dock strikt begränsad av den tillgängliga mängden mobil fosfor i sedimenten. Här redovisar vi analyser av totalfosforinnehållet i tio sedimentkärnor från Bottenhavet och Egentliga Östersjön, samt detaljerade analyser av olika fosforformer med olika tillgänglighet i två av dessa kärnor. Egentliga Östersjön utmärks av syrefria förhållanden i bottenvattnet ovanför ackumulationsbottnarna, medan djupvattnet i Bottenhavet i allmänhet är oxiderat vilket också återspeglas i sedimenten. Genom att integrera koncentrationer i sedimentprofilerna har vi uppskattat den totala mängden mobil fosfor i varje sedimentkärna. Den genomsnittliga mängden mobil fosfor i Bottenhavets sediment visade sig vara en storleksordning högre än i Egentliga Östersjön. Däremot innehöll bottenvattnet i Egentliga Östersjön dramatiskt högre fosforkoncentrationer vilket tyder på att den tillgängliga mängden mobil fosfor där till största delen återfinns ovanför sedimenten. En indikativ fördelning av fosfor mellan djupvatten och sediment i Bottenhavet är 1:16, medan motsvarande fördelning i Egentliga Östersjön är 3:1.

1 Introduction

Eutrophication in the Baltic Sea is pronounced in the Baltic Proper, the Gulf of Finland, the Gulf of Riga and in the Kattegat, whereas the Bothnian Sea and the Bothnian Bay are less affected (HELCOM, 2009). Hence the

Baltic Sea Action Plan (BSAP) stipulates drastic reductions of phosphorus (P) emissions to the Baltic Proper, the Gulf of Finland and the Gulf of Riga. In these basins and in the Kattegat, nitrogen reductions are required as well (HELCOM 2007).

According to the latest assessment from the Helsinki

Commission (HELCOM, 2011) the annual external P load to the Baltic Proper amounts to some 13 000 tonnes ($0.08 \text{ tonnes km}^{-2}$), while the corresponding P loads to the Bothnian Sea and the Bothnian Bay sum up to 2 800 tonnes and 3 500 tonnes, respectively ($0.05 \text{ tonnes km}^{-2}$). The Baltic Proper also receives a substantially larger reflux of P from the sediments compared to the Bothnian Sea and the Bothnian Bay. Although numbers are uncertain, the fluxes estimated from simple budget calculations indicate that the sediments of the Baltic Proper release some 20 000 tonnes of P annually, while in the Bothnian Sea an equivalent amount of P is permanently buried on an annual basis (Savchuk, 2005). Fluxes derived from core data indicate that the annual P release from the sediments in the Baltic Proper is between 2 000 and 20 000 tonnes (Emeis et al., 2000; Hille et al., 2005; Ahlgren et al., 2006). To our knowledge, very few empirical studies address the P dynamics of the Bothnian Sea and the Bothnian Bay (Niemistö et al., 1978; Slomp et al., 2013).

Sediments appear to play a pivotal role in the P dynamics of the Baltic Proper and most likely explain temporal differences in the amount of P contained in the water column (HELCOM, 2009; Eilola et al., 2009). During the 1990s the amount of P present in the water column of the Baltic Proper increased from around 360 000 tonnes to 490 000 tonnes (Conley et al. 2002). The dominant explanation for this is the reduced ability of the sediments to contain redox sensitive P forms, especially P associated with iron hydroxides (Mort et al., 2010). This explanation is supported by numerous studies on the role of bottom water oxygen in controlling the P content in sediments both in lakes (Mortimer, 1941; 1942; Boström et al., 1982) and marine areas (Sundby et al., 1986; McManus et al., 1997). The oxygen content of the deep waters of the Baltic Proper has shown a clearly negative trend since the 1950s (Gustafsson et al., 2012). Since a minimum in 1993 until the year 2006, the bottom area covered by hypoxia (less than 2 mL L^{-1} dissolved oxygen) increased from $11\,050 \text{ km}^2$ to $67\,700 \text{ km}^2$ (Conley et al., 2009), the latter figure making up around one third of the total bottom area, clearly reducing the capacity of the sediments to retain P. In the Bothnian Sea on the other hand, most of the bottom area, including the deeper locations, remain oxic on the long term (Raateoja, 2013).

Although the external P load to the Baltic Sea has decreased from more than $50\,000 \text{ tonnes yr}^{-1}$ in the 1980's to around $35\,000 \text{ tonnes yr}^{-1}$ in the 2000's the surface water P concentration remains high and relatively stable or even increasing (HELCOM, 2009; Hille et al., 2005; Stigebrandt et al., 2014). Therefore, artificially improving the ability of the sediments to retain P by oxygena-

tion or by chemical treatment has been suggested as a means to improve the nutrient status (Stigebrandt and Gustafsson, 2007; Blomqvist and Rydin, 2009). There have also been a number of objections raised against such measures. Some argue that in situ measures are less efficient than external load reductions, and that the ecological effects of such geo-engineering are not well known (Granéli, 2006; Conley, 2012). To this one might add that ecological effects of natural processes are also less than well understood. One concern is that oxygenation – natural or artificially induced – may not facilitate long-term removal of P from the water column due to iron limitation (Blomqvist et al., 2004). It has also been argued (Reed et al., 2011) that re-oxygenation of anoxic sediments may mobilize organically bound P to the water column and thus further exhaust the sedimentary P sink.

P release from the sediments appear to be of less importance in the Bothnian Sea, as indicated by mass balance calculations (Savchuk, 2005) and by deep water P concentrations. Slomp et al. (2013) find that pore water phosphate concentrations in the surface layer of Bothnian Sea sediments were extremely low and close to the values in the bottom water implying a low flux of phosphate to the water column. In terms of ecological status the Bothnian Sea is closer to target levels and may thus indicate how the P regime in the Baltic Proper might appear in a less eutrophic condition. Although there are differences between the two sub-systems in terms of external P load, bathymetry and water circulation they are closely connected to each other and similar in terms of climate and biogeochemistry.

The impact of the sediments on the water column is strictly limited by the amount of potentially mobile P available in the sediments. A method to quantify the mobile P content in sediments from sediment profiles was suggested by Rydin et al. (2011) and has been applied in a number of studies in the Baltic Sea (Malmaeus and Karlsson, 2012; Malmaeus et al., 2012; Puttonen et al., 2013). The methodology assumes that the P content in a sediment profile reaches a stable level below a certain sediment depth where, in effect, all mobile P has been mobilized and released from the sediment. Although the stabilization depth may be difficult to locate precisely, the method is able to provide statistically robust estimates of mobile P content that may be used to study the temporal and spatial variation of this key parameter. We will address some critical aspects of this method later in the discussion.

In this study we compare the phosphorus content and long-term storage in sediments from ten stations (14 cores, 10 positions) from the Bothnian Sea and the Baltic Proper. As noted above, the sediments in the two

systems differ in terms of redox conditions and apparently also in their P retaining capacities. We also examine the composition of different forms of P in two of the sediment cores. The aim is to provide quantitative insights into the role of the sediments in the P dynamics of the two systems, with possible implications for strategies to control the eutrophication of the Baltic Sea.

2 Methods

Sampling in water and sediments were performed during a field expedition with R/V Sunbeam in July 2012. Sampling positions are shown in Figure 1.

2.1 Water sampling

Water samples were collected at 5 meters and 100 meters water depth (or at maximum depth when this was less than 100 meters) in each station with a Ruttner sampler and stored cold in plastic bottles. Profiles of water salinity, temperature and oxygen concentration were measured online in the field using a SEBA KLL-Q2 CTD device complemented with an optical oxygen sensor.

2.2 Sediment sampling

Sediment cores were collected using a Gemini corer (a twin-barrel Niemistö corer with inner diameter 80 mm and core length 1 m) (Niemistö, 1974). After visual in-

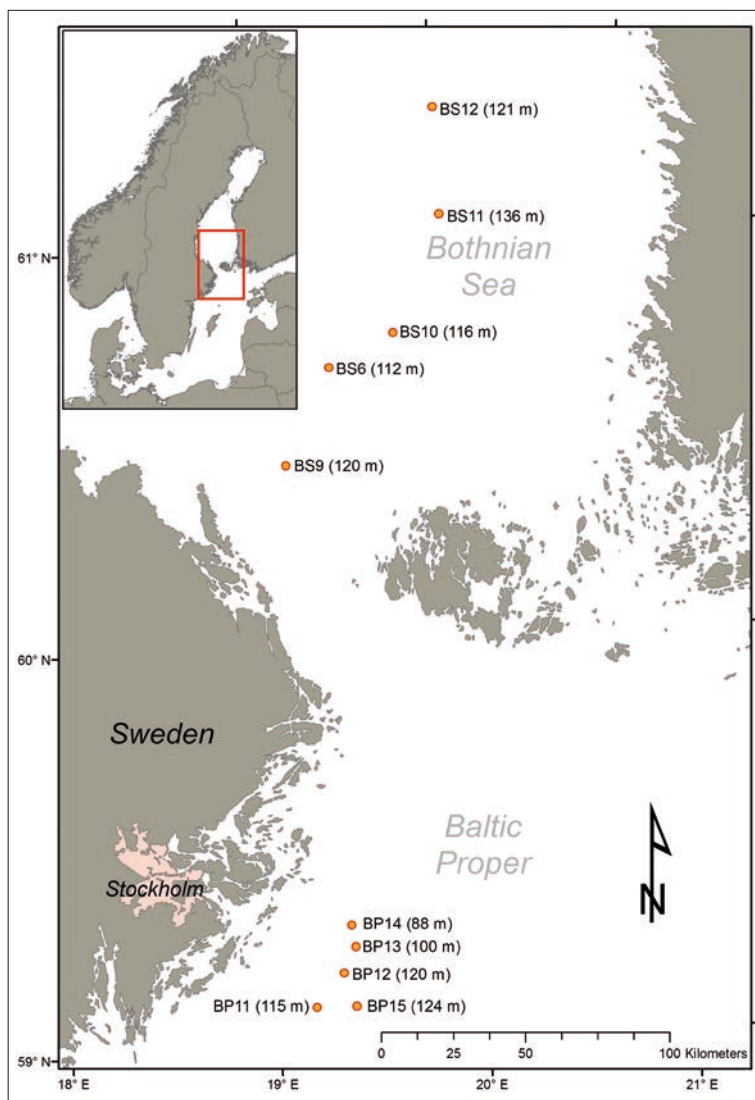


Figure 1. Positions of sampling stations.

spection, core samples were sliced in the field in 0.5 cm thick layers from the surface down to 5 cm sediment depth. From 5 to 15 cm depth the cores were sliced in 2 cm thick layers and below that level 2 cm slices were extracted every 10 cm down to the end of the cores (maximum 45 cm). The sliced sediment samples were stored in darkness at 4 °C until preparation in the laboratory.

2.3 Chemical analyses

Chemical analyses were performed at the Erken Laboratory at Uppsala University. For the water samples, standard methods were used for the analyses of dissolved inorganic phosphorus (DIP) and total phosphorus (Karlsson, 2010). Total phosphorus (TP) content in the sediments was determined by ashing (520 °C) followed by hot HCl extraction and measurement of dissolved inorganic phosphorus in the extract. Water content was determined after freeze-drying, and organic content after ignition at 550 °C for two hours (loss on ignition) following the Swedish standard method, SS-EN 15169:2007.

In two cores, phosphorus forms were also separated into $\text{NH}_4\text{Cl-rP}$, BD-P, NaOH-rP, NaOH-nrP, HCl-rP, and residual phosphorus following, in principle, the sequential extraction scheme suggested by Psenner et al. (1988), see Rydin et al. (2011) for further details. Generally, $\text{NH}_4\text{Cl-rP}$ is regarded as loosely bound phosphorus, BD-P as phosphorus associated with iron hydroxides, NaOH-rP as phosphorus bound to aluminum, NaOH-nrP as organic phosphorus forms, and HCl-rP as calcium bound phosphorus compounds. Residual phosphorus is computed by subtracting extracted and identified phosphorus from TP. Phosphorus fractionations were started within a week after sampling. In the following, we will refer to BD-P as iron bound phosphorus and NaOH-nrP as organic phosphorus.

2.4 Quantifying the pool of mobile phosphorus

We follow the approach suggested by Rydin et al. (2011) to compute the amount of mobile P per unit area from sediment core data. The P concentration in deep sediment where sediment diagenesis has ceased, i.e., the burial concentration, was subtracted from the higher concentrations in more shallow layers. The burial concentration was either taken as the site specific average concentration below 10 cm depth in each core, or as generic mean values for burial concentrations derived for the Bothnian Sea and the Baltic Proper, respectively. This resulted in two estimates of the mobile P amount for each position.

Concentrations were multiplied with dry matter con-

tent (adjusting for sediment water content) to get the amount of mobile P in each layer. The mobile P content was integrated over the depth profile to obtain the amount of mobile P per square meter.

3 Results

3.1 Water quality

In the Baltic Proper there was a clear halocline present at around 70 m water depth, while only a weak halocline was observed in the Bothnian Sea. Below the halocline the oxygen concentration dropped to near 0 mL L^{-1} in the Baltic Proper. In the Bothnian Sea the oxygen concentrations were above 6 mL L^{-1} at all water depths.

DIP was below the detection limit ($<0.1 \mu\text{mol L}^{-1}$) in all surface water samples. Average TP concentration in surface water was 0.45 $\mu\text{mol L}^{-1}$ in the Bothnian Sea and 0.58 $\mu\text{mol L}^{-1}$ in the Baltic Proper. Deep water concentrations of TP were on average 4 $\mu\text{mol L}^{-1}$ in the Baltic Proper and 1 $\mu\text{mol L}^{-1}$ in the Bothnian Sea. DIP constituted more than 90 percent of TP in the deep waters of the Baltic Proper and around 75 percent of TP in the deep waters of the Bothnian Sea.

3.2 Sediments

Water content, organic content and TP were analyzed along the profiles in all stations, and for two stations triplicate cores were analyzed. Coefficients of variation ($\text{CV} = \text{standard deviation}/\text{mean value}$) for these triplicates are shown in Table 1. Basic sediment characteristics are given in Table 2. Water content and organic content indicate that all bottoms were accumulation areas (areas where fine material, < medium silt, is continuously deposited) except BS9 which represented a transportation bottom (area where fine material is discontinuously deposited) (Håkanson, 1977). The triplicates indicate slightly higher CV's in BS9 compared to the BP12 samples (Tab. 1) although the internal variation was relatively small.

Profiles of TP content for all analyzed cores are shown in Figure 2. As noted in several cores there were clay

Table 1. Average CV value for three replicate samples. The BS9 core represents a T-bottom and the BP12 core represents an A-bottom, n = number of sliced samples, W = water content, LOI = loss on ignition, TP = total phosphorus.

	W	LOI	TP
Baltic Proper (BP12) $n=17$	0.02	0.13	0.06
Bothnian Sea (BS9) $n=12$	0.09	0.14	0.08
All	0.05	0.13	0.07

Table 2. Characteristics of surface sediment (0–0.5 cm) samples.

Station (position WGS-84)	Water depth (m)	Water content (%)	LOI (%)	TP ($\mu\text{g/g dw}$)	Comment
BP14 (59°08.70, 19°12.06)	88	98	24	2400	0–5 cm laminated, 2–3 mm clear laminae, <i>Beggiatoa</i> , overlying gray-black muddy clay and older clay
BP13 (59°04.60, 19°13.20)	100	93	17	1000	0–10 cm dark laminated, overlying clay
BP12 (58°59.90, 19°08.70)	120	94	22	1100	0–30 cm dark laminated overlying dark muddy clay
BP11 (58°53.60, 18°58.05)	115	95	22	1200	0–30 cm dark laminated overlying gray clay
BP15 (58°53.42, 19°12.67)	124	94	20	1100	0–5 cm dark laminated overlying dark muddy clay
BS9 (60°34.91, 18°56.00)	120	33	1.8	620	0–3 cm oxic recent material mixed with sand and gravel. Benthic fauna <i>Mysis</i> , <i>Saduria entomon</i> . Below old clay, T-bottom.
BS6 (60°52.80, 19°14.40)	112	87	11	1900	0–5 cm oxic, Benthic fauna <i>Mysis</i> , overlying gray-black muddy clay
BS10 (60°58.62, 19°39.71)	116	86	11	2100	0–5 cm oxic brown, overlying gray-black muddy clay
BS11 (61°20.00, 20°00.00)	136	87	10	2700	0–7 cm oxic brown, overlying gray-black muddy clay
BS12 (61°40.00, 20°00.00)	121	85	9.7	2200	0–3 cm brown oxic, Benthic fauna <i>Monoporeia</i> , <i>Mysis</i> . Below gray old clay, at 4–6 cm a band of brown silt.

minerals dominating the material below the top 5–10 cm, indicating that most organic materials had been mineralized at these depths. In general TP content was higher (both surface sediments and deep sediments) in the Bothnian Sea sediments than in the Baltic Proper, and this pattern is remarkably consistent in all samples except in the transportation bottom BS9. The results compare well with other data from the Bothnian Sea (Slomp et al., 2013) and the Baltic Proper (Malmaeus and Karlsson, 2012). After observing the unusually high TP values between 4 and 7 cm in BS12 these samples were re-analyzed, although without altering the result. The visual inspection (Tab. 2) indicated a band of brown silt coinciding with this apparent anomaly. The generally higher TP content in the surface sediments in the Bothnian Sea compared to the Baltic Proper is most likely explained by the fact that the sediment surfaces were oxidized in the Bothnian Sea as opposed to the anoxic sediments of the Baltic Proper.

The average burial concentration (including all samples below 10 cm sediment depth) in the Baltic Proper ($810 \mu\text{g g}^{-1} \text{ dw}$) was significantly lower (Mann-Whitney *U*-test, $p=0.016$) than in the Bothnian Sea ($1100 \mu\text{g g}^{-1} \text{ dw}$).

Results from P fractionation in the cores from BP11 and BS11 are shown in Figure 3. Loosely bound P represented around 1 per cent in both cores and residual P around 10 per cent of TP in the Baltic Proper and close to zero in the Bothnian Sea sediment. Since the residual P and the loosely bound P were small compared to the other fractions they are not shown in the graphs. The TP content was higher in the Bothnian Sea core which is largely explained by the iron bound fraction but also by the aluminum bound and organic fractions. Given the large difference in iron bound P between surface and deep sediment layers in BS11 it may be concluded that this fraction constitutes a large part of the mobile P.

Using two values for the burial concentration (see Methods section) mobile P was calculated in each sediment core (Table 3). In this calculation we excluded values from BS9 since this core did not represent an accumulation sediment. The amount of mobile P was significantly higher in the Bothnian Sea sediments than in the Baltic Proper sediments using both estimates (Mann-Whitney *U*-test, $p=0.016$). The two methods gave similar results on average, although in individual cores (notably BP12 and BS11) the difference was large.

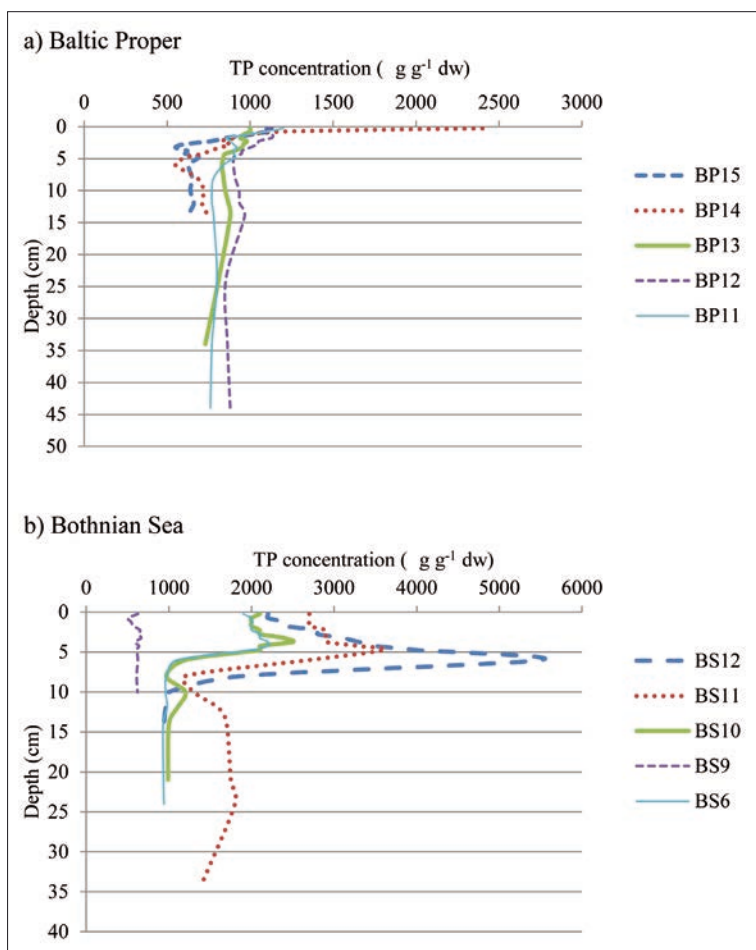


Figure 2. Depth profiles of TP in sediments in a) Baltic Proper and b) Bothnian Sea.

Table 3. Store of Mobile P as calculated with two methods (see text). Triplicates have been averaged.

Station	Water depth (m)	Mobile P – site specific calculation (g m^{-2})	Mobile P – generic calculation (g m^{-2})
BP14	88	1.4	0.8
BP13	100	1.8	2.3
BP12	120	1.4	8.2
BP11	115	2.3	0.8
BP15	124	1.4	0.4
BS9	120	1.4	0
BS6	112	12	9.0
BS10	116	16	13
BS11	136	26	67
BS12	121	69	64
Mean BP		1.6	2.5
Mean BS ^a		25	31
Mean all		13	17

^a Including the transport bottom BS9

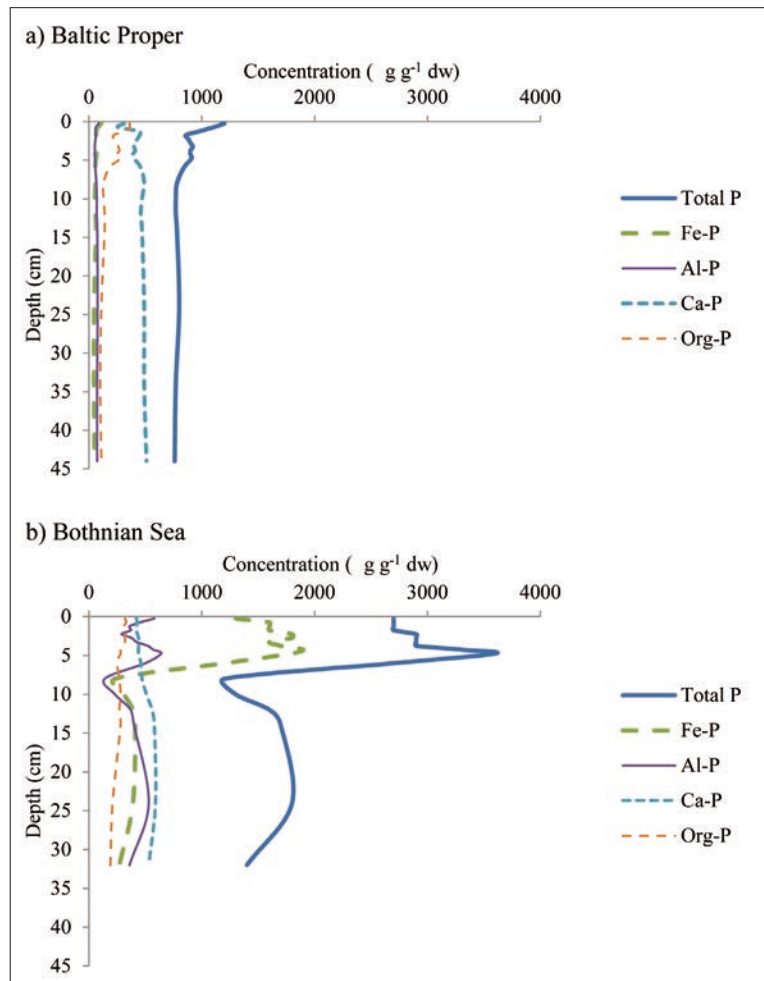


Figure 3. Depth profiles of total P, iron bound P (Fe-P), aluminum bound P (Al-P), calcium bound P (Ca-P) and organic P (Org-P) in a) Baltic Proper (BP11) and b) Bothnian Sea (BS11).

4 Discussion

A notable difference between the Baltic Proper and the Bothnian Sea is the different redox conditions in the deep waters and sediments. The former sub-system is characterized by anoxic conditions in the bottom waters overlying the accumulation sediments, whereas the bottom waters of the other sub-system are generally oxidized which is also reflected in the sediments. This is a likely explanation for the different distributions of P between water and sediments in the two sub-systems. If the measured TP concentration in the deep water at each station is multiplied by the depth between the halocline and the bottom the amount of TP in the deep water of the Bothnian Sea is on average 1.5 g m^{-2} , and the corresponding value for the Baltic Proper is 5.1 g m^{-2} . This means that an indicative distribution of P between deep water and sediment in the Bothnian Sea is 1:16 if

site specific burial concentrations are assumed, while the corresponding ratio in the Baltic Proper is 3:1. Hence the greater part of the available P is present in the water column in the Baltic Proper while the opposite is true for the Bothnian Sea.

The P fractionation in two of the sediment cores indicate that the greatest difference between the two subsystems is to be found in the iron bound fraction, which supports the explanation that the different redox conditions are responsible for the different P regimes. There are also differences in aluminum bound and organic P fractions between the cores but these differences are quantitatively less important in the top 10 cm of the sediments. The pattern was similar when oxic and anoxic sediments were compared in Baltic coastal areas (Rydin et al., 2011; Malmaeus et al., 2012) and a mobile P content below 2 g m^{-2} in offshore sediments of the Baltic Proper found by Malmaeus and Karlsson (2012)

is consistent with our results. Conley et al. (2002) found by regression that 2 tonnes of P were released per km² turning anoxic in the Baltic Proper during a study period between 1970 and 2000, but given the average amount of mobile P in our samples more P could be released per km² in the Bothnian Sea if bottom waters for some reason would become anoxic, with potentially drastic effects on the water column P concentration.

The calcium bound P appears to increase slightly with sediment depth in both cores, which was also the case in several cores presented by Malmaeus and Karlsson (2012) although this was not observed by the authors at the time. This might indicate that calcium bound P is formed inside the sediments over time, which has not been assumed by other authors (Boström et al., 1982; Reitzel et al., 2005; Rydin et al., 2011). Interestingly, Wilson et al. (2010) observed a similar trend for aluminum bound P in three oligotrophic North-American lake sediments. Formation of authigenic P in Baltic Sea sediments were extensively discussed by Jilbert and Slomp (2013). The burial concentration of iron bound P is notably higher in the Bothnian Sea than in the Baltic Proper, which is consistent with the results presented by Slomp et al. (2013).

In a quantitative sense, the organic and iron bound P fractions apparently make up the greater part of the mobile (and potentially bioavailable) P. This is due to the fact that only a minor part of the iron bound P remains in the sediment below the redoxcline, and that organic P is successively mineralized with time and released to the pore water. Hence it seems inevitable that these two fractions become mobilized with time and that, in effect, only inert P forms remain in the sediment below a certain sediment depth, including organic P which becomes increasingly refractory with depth. Our results together with other studies (Rydin et al., 2011; Lukkari et al., 2009a, b) indicate that the major part of the potentially mobile P is present above 7–8 cm sediment depth and that the P concentration asymptotically stabilizes below that level to reach a background or “burial” concentration. Even if variation in P content may occur below this stabilization depth we would argue that any P below around 10 cm is effectively immobile. Since the sedimentation rate in these areas is a few mm per year (Ignatius et al., 1981; Jonsson et al., 1990), this stabilization depth would correspond to a sediment age of several decades which may raise questions regarding the stability of the sedimentation regime. Although there may be temporal variability in the composition of the settling material due to eutrophication and other potential factors we would argue, however, that the burial concentration is relatively stable compared to the overall variability of P concentration along the depth profile. Firstly, this argument is supported by a large number of

sediment cores collected in coastal areas (Lukkari et al., 2009a; Malmaeus et al., 2012; Puttonen et al., 2013) as well as in lakes (Boström et al., 1982; Rydin, 2000) even during periods of ongoing eutrophication, e.g. in the Stockholm archipelago. Secondly, the depth variation is comparatively small below the stabilization depth also in the cores presented in this study. Thirdly, the increase in P concentration above the stabilization depth is largely explained by the iron bound and organic fractions which are affected by biogeochemical processes. Hence the increasing concentration towards the surface is better explained by dynamics within the sediment than by temporal dynamics in the water column. The increase towards the surface in the Bothnian Sea sediment does not correspond to any known increase in external P load, whereas the lack of P accumulation in the surface sediments from the Baltic Proper despite severe eutrophication in the water column indicates that external factors have little influence on burial concentrations. Further, the variability in burial P concentration in our data could not be statistically explained by the water depth or the investigated sediment characteristics including water content and organic content. In spite of these arguments there is little doubt that there is some variation in the burial P concentration which is also observed in our data. However, this variation does not seem to preclude a fairly robust estimation of the pool of mobile P in a comparative analysis, see Rydin et al. (2011) for further discussion on this issue.

The burial concentration reflects the efficiency of the sediments to act as a sink for P. It does appear that the burial concentration of P is higher in the Bothnian Sea than in the Baltic Proper. If this reflects the general situation it would be consistent with the findings of Carey and Rydin (2011) that oligotrophic systems exhibit higher burial P concentrations than more eutrophic systems. It would also be consistent with the view expressed by Blomqvist et al. (2004) that a higher Fe:P ratio in oligotrophic systems facilitate a more effective P removal in the water column. Mean values of mobile P pools calculated both using generic and site specific burial concentrations indicate that the difference in mobile P content between the two sub-systems is around an order of magnitude and this seems to be a robust result, although the numbers differ substantially for individual samples.

We also find in the analysis of different P fractions that the concentration of organic P in the oxic core was substantially higher than in the anoxic core, indicating that the burial of this P form is no less efficient in the oxic sediment. In fact, there is a much clearer pattern of declining organic P content with depth in the Baltic Proper relative to the Bothnian Sea, arguably due to more efficient mineralization of this P fraction. In BP11,

below the top layers organic P stabilizes at less than 150 $\mu\text{g g}^{-1}$ dw which is around 50 percent lower than the corresponding content in BS11 (280 $\mu\text{g g}^{-1}$ dw). The invariable content of organic P below this depth indicates that this fraction is refractory, which does not support the reasoning by Reed et al. (2011) that oxygenating anoxic sediments may mobilize organically bound P to the water column. Hence we do not find support for the existence of a latent “P-bomb” in anoxic sediments of the Baltic Sea (HYPER, 2011).

In terms of eutrophication, the Bothnian Sea is in a more desirable state than the Baltic Proper. Target levels specified in the BSAP are given as winter values of DIP: 0.20 $\mu\text{mol L}^{-1}$ in the Bothnian Sea and 0.25 $\mu\text{mol L}^{-1}$ in the Baltic Proper (HELCOM, 2007). These targets are nearly met in the Bothnian Sea but in the Baltic Proper the levels are nearly twice the target level (HELCOM, 2009). Our measurements were made in the summer but our TP values are close to the winter values of DIP reported in the literature for the Baltic Proper, but much higher than DIP in the Bothnian Sea. DIP therefore constitutes a much larger proportion of TP in the Baltic Proper during the winter period, and it is reasonable to at least partly explain this by the much higher DIP concentration in the deep water which we attribute to the low P binding capacity of the sediments. The high DIP concentrations in the Baltic Proper constitutes a real problem in terms of environmental quality, and target levels could possibly be met by reducing the ratio of P in the deep water to P in the sediments – hence to make the Baltic Proper to more resemble the Bothnian Sea in terms of P distribution.

5 Conclusion

We conclude that there seems to be a fundamental difference between the Baltic Proper and the Bothnian Sea in terms of P distribution between deep water and sediments. From an environmental quality point of view, there is little doubt that the Bothnian Sea is in a more desirable state. In the oxidized deep water environment of the Bothnian Sea an indicative distribution of mobile P between deep water and sediment in the Bothnian Sea is 1:16, while the corresponding ratio in the Baltic Proper is 3:1. This is also reflected in the surface water where winter concentrations of DIP are nearly twice the target concentration in the Baltic Proper while they are close to the target concentration in the Bothnian Sea.

We argue that there are mainly beneficial consequences to be expected if the deep waters of the Baltic Proper would become oxidized. In particular the organic P pool in the anoxic core was small and stable with depth, indicating that there is little reason to expect any substantial release of P even under aerobic mineraliza-

tion of organic material. Oxygenation would, however, not necessarily result in a permanently higher burial efficiency of P, but would generate an instant redistribution of the P reserve in the system.

Acknowledgements

We thank Professor Per Jonsson for sharing old sampling protocols and the crew of R/V Sunbeam for excellent field work.

References

- Ahlgren, J., Reitzel, K., Tranvik, L., Gogoll, A. and Rydin, E. (2006) Degradation of organic phosphorus compounds in anoxic Baltic Sea sediments: A ^{31}P -NMR study. *Limnol. Oceanogr.* 51: 2341–2348.
- Blomqvist, S. and Rydin, E. (2009) How to enhance long-term removal of phosphorus by bottom sediments in the Baltic Sea (In Swedish with English Summary). Swedish Environmental Protection Agency Report 5914.
- Blomqvist, S., Gunnars, A. and Elmgren, R. (2004) Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: A matter of salt. *Limnol. Oceanogr.* 49: 2236–2241.
- Boström, B., Jansson, M. and Forsberg, C. (1982) Phosphorus release from lake sediments. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 18: 5–59.
- Carey, C.C. and Rydin, E. (2011) Lake trophic status can be determined by the depth distribution of sediment phosphorus. *Limnol. Oceanogr.* 56(6): 2051–2063.
- Conley, D.J. (2012) Save the Baltic Sea. Geoengineering efforts to bring oxygen into the deep Baltic should be abandoned. *Nature* 486: 463–464.
- 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. *Environ. Sci. Technol.* 36: 5315–5320.
- Conley, D.J., Björck, S., Bonsdorff, E., Carstensen, J., Destouni, G., Gustafsson, B.G., Hietanen, S., Kortekaas, M., Kuosa, H., Meier, H.E.M., Müller-Karulis, B., Nordberg, K., Norkko, A., Nürnberg, G., Pitkänen, H., Rabalais, N.N., Rosenberg, R., Savchuk, O.P., Slomp, C.P., Voss, M., Wulff, F. and Zillén, L. (2009) Hypoxia-Related Processes in the Baltic Sea. *Env. Sci. Tech.* 43(10): 3412–3420.
- Eilola, K., Meier, H.E.M. and Almroth, E. (2009) On the dynamics of oxygen, phosphorus and cyanobacteria in the Baltic Sea; A model study. *Journal of Marine Systems* 75 (1–2), 163–184.
- Emeis, K.-C., Struck, U., Leipe, T., Pollehne, F., Kundendorf, 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* 167: 43–59.
- Granéli, W. (2006) In Swedish: Ekologisk ingenjörskonst för Östersjön – inget att rekommendera. In Johansson B, editor. Östersjön – Hot och Hopp. Forskningsrådet Formas, ISBN 91-540-5970-4, pp 91–100.
- Gustafsson, B.G., Schenk, F., Blenckner, T., Eilola, K., Meier, H.E.M., Müller-Karulis, B., Neumann, T., Ruoho-Airola,

- T., Savchuk, O.P. and Zorita, E. (2012) Reconstructing the Development of Baltic Sea Eutrophication 1850–2006. *Ambio* 41: 534–548.
- Håkanson, L. (1977) The influence of wind, fetch, and water depth on the distribution of sediments in Lake Vänern, Sweden. *Can J Earth Sci* 14: 397–412.
- HELCOM (2007) Towards a Baltic Sea unaffected by eutrophication. HELCOM Ministerial Meeting, Krakow, Poland 15 November 2007, 35 p.
- HELCOM (2009) Eutrophication in the Baltic Sea – An integrated thematic assessment of the effects of nutrient enrichment and eutrophication in the Baltic Sea region: Executive Summary. *Balt. Sea Environ. Proc. No. 115A*.
- HELCOM (2011) Fifth Baltic Sea Pollution Load Compilation (PLC-5). *Balt. Sea Environ. Proc. No. 128*.
- Hille, S., Nausch, G. and Leipe, T. (2005) Sedimentary deposition and reflux of phosphorus (P) in the eastern Gotland Basin and their coupling with P concentrations in the water column. *Oceanologica* 47: 663–679.
- HYPER (2011) Hypoxia in the Baltic Sea. BONUS briefing Number 11, October 2011.
- Ignatius, H., Axberg, S., Niemistö, L. and Winterhalter, B. (1981) Quaternary geology of the Baltic Sea. In: Voipio, A. (Ed), *The Baltic Sea*. Elsevier Oceanography Series, 30. Pp 54–104.
- Jonsson, P., Carman, R., and Wulff, F. (1990) Laminated sediments in the Baltic – a tool for evaluating nutrient mass balances. *Ambio* 19:152–158.
- Karlsson, O.M. (2010) Forms and variability of phosphorus in Baltic coastal waters – a challenge to ecosystem modelling. *Air, Soil and Water Research* 3:79–93.
- Lukkari, K., Leivuori, M., Vallius, H. and Kotilainen, A. (2009a) The chemical character and burial of phosphorus in shallow coastal sediments in the northeastern Baltic Sea. *Biogeochemistry* 94: 141–162.
- Lukkari, K., Leivuori, M. and Kotilainen, A. (2009b) The chemical character and behaviour of phosphorus in poorly oxygenated sediments from open sea to organic rich inner bay in the Baltic Sea. *Biogeochemistry* 96: 25–48.
- Malmaeus, J.M. and Karlsson, O.M. (2012) Estimating the pool of mobile phosphorus in offshore soft sediments of the Baltic Proper. *Air, Soil and Water Research* 5: 1–13.
- Malmaeus, J.M., Rydin, E., Jonsson, P., Lindgren, D. and Karlsson, O.M. (2012) Estimating the amount of mobile phosphorus in Baltic coastal soft sediments of central Sweden. *Boreal environmental research* 17: 425–436.
- McManus, J., Befelson, W.M., Coale, K.H., Johnson, K.S. and Kilgore, T.E. (1997) Phosphorus regeneration in continental margin sediments. *Geochimica et Cosmochimica Acta* 61: 2891–2907.
- Mort, H.P., Slomp, C.P., Gustafsson, B.G. and Andersen, T.J. (2010) Phosphorus recycling and burial in the Baltic Sea sediments with contrasting redox concentrations. *Geochimica et Cosmochimica Acta* 74: 1350–1362.
- Mortimer, C.H. (1941) The exchange of dissolved substances between mud and water in lakes. I. *J. Ecol.* 29: 280–329.
- Mortimer, C.H. (1942) The exchange of dissolved substances between mud and water in lakes. II. *J. Ecol.* 30: 147–201.
- Niemistö, L. (1974) A Gravity Corer for Studies of Soft Sediments. Merentutkimuslait. Julk/Havsforskningsinst. Skr. 238: 33–38.
- Niemistö, L., Tervo, V. and Voipio, A. (1978) Storage of iron and phosphorus in the sediments of the Bothnian Sea. *Finn. Mar. Res.* 244: 36–41.
- Psenner, R., Boström, B., Dinka, M., Pettersson, K. and Puckso, R. (1988) Fractionation of suspended matter and sediment. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 30: 98–103.
- Puttonen, I., Mattila, J., Jonsson, P., Karlsson, O.M., Kohonen, T., Kotilainen, A., Lukkari, K., Malmaeus, J.M. and Rydin, E. (2013) Distribution and estimated release of sediment phosphorus in the northern Baltic Sea archipelagos. In review, *Estuarine, Coastal and Shelf Science*.
- Raateoja, M. (2013) Deep-water oxygen conditions in the Bothnian Sea. *Bor. Env. Res.* 18: 235–249.
- Reed, D.C., Slomp, C.P. and Gustafsson, B.G. (2011) Sedimentary phosphorus dynamics and the evolution of bottom-water hypoxia: A coupled benthic–pelagic model of a coastal system. *Limnol. Oceanogr.* 56(3): 1075–1092.
- Reitzel, K., Hansen, J., Andersen, F.Ø., Hansen, K.S. and Jensen, H.S. (2005) Lake Restoration by Dosing Aluminum Relative to Mobile Phosphorus in the Sediment. *Environ. Sci. Technol.* 39(11): 4134–4140.
- Rydin, E. (2000) Potentially mobile phosphorus in Lake Erken sediment. *Water Res* 34:2037–2042.
- Rydin, E., Malmaeus, J.M., Karlsson, O.M. and Jonsson, P. (2011) Phosphorus release from coastal Baltic Sea sediments as estimated from sediment profiles. *Estuarine, Coastal and Shelf Science* 92: 111–117.
- Savchuk, O.P. (2005) Resolving the Baltic Sea into seven sub-basins: N and P budgets for 1991–1999. *Journal of Marine Systems* 56: 1–15.
- Slomp, C.P., Mort, H.P., Jilbert, T., Reed, D.C., Gustafsson, B.G. and Wolthers, M. (2013) Coupled dynamics of iron and phosphorus in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane. *PLoS ONE* 8(4): e62386. doi:10.1371/journal.pone.0062386
- Stigebrandt, A. and Gustafsson, B.G. (2007) Improvement of Baltic proper water quality using large-scale ecological engineering. *Ambio* 36: 280–286.
- Stigebrandt, A., Rahm, L., Viktorsson, L., Ödalen, M., Hall, P.O.J. and Liljebldh, B. (2014) A New Phosphorus Paradigm for the Baltic Proper. *Ambio* 43, 634–643.
- Sundby, B., Anderson, L.G., Hall, P.O.J., Iverfeldt, Å., Rutgers van der Loeff, M.M. and 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.
- Wilson, T.A., Amirbahman, A., Norton, S.A. and Voytek, M.A. (2010) A record of phosphorus dynamics in oligotrophic lake sediment. *J. Paleolimnol.* 44: 279–294.