

Estimating the Pool of Mobile Phosphorus in Offshore Soft Sediments of the Baltic Proper

Authors: Malmaeus, J. Mikael, and Karlsson, O. Magnus

Source: Air, Soil and Water Research, 5(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/ASWR.S8597

The BioOne Digital Library (<u>https://bioone.org/</u>) provides worldwide distribution for more than 580 journals and eBooks from BioOne's community of over 150 nonprofit societies, research institutions, and university presses in the biological, ecological, and environmental sciences. The BioOne Digital Library encompasses the flagship aggregation BioOne Complete (<u>https://bioone.org/subscribe</u>), the BioOne Complete Archive (<u>https://bioone.org/archive</u>), and the BioOne eBooks program offerings ESA eBook Collection (<u>https://bioone.org/esa-ebooks</u>) and CSIRO Publishing BioSelect Collection (<u>https://bioone.org/csiro-ebooks</u>).

Your use of this PDF, the BioOne Digital Library, and all posted and associated content indicates your acceptance of BioOne's Terms of Use, available at <u>www.bioone.org/terms-of-use</u>.

Usage of BioOne Digital Library content is strictly limited to personal, educational, and non-commercial use. Commercial inquiries or rights and permissions requests should be directed to the individual publisher as copyright holder.

BioOne is an innovative nonprofit that sees sustainable scholarly publishing as an inherently collaborative enterprise connecting authors, nonprofit publishers, academic institutions, research libraries, and research funders in the common goal of maximizing access to critical research.

Air, Soil and Water Research



ORIGINAL RESEARCH

OPEN ACCESS Full open access to this and thousands of other papers at http://www.la-press.com.

Estimating the Pool of Mobile Phosphorus in Offshore Soft Sediments of the Baltic Proper

J. Mikael Malmaeus and O. Magnus Karlsson

IVL Swedish Environmental Research Institute, Stockholm, Sweden. Corresponding author email: mikael.malmaeus@ivl.se

Abstract

Background: Eutrophication is a major threat to many coastal ecosystems worldwide. This paper deals with the sediment-water exchange of phosphorus, one of the elements that may stimulate primary production in the aquatic environment. The lack of phosphorus-binding capacity in sediments at low redox-potential is recognized as an important mechanism for eutrophication-related effects in some areas. **Methods:** Twelve sediment cores were collected in the Baltic Proper between 61 m and 175 m water depth and a number of phosphorus fractions were analyzed. Integrating the concentrations over the depth profiles, the amounts of mobile phosphorus were estimated in each core.

Results: It was found that sediments below the redox cline in the Baltic Proper contained small amounts of mobile phosphorus. The total amount of mobile phosphorus in the entire Baltic Proper sediments below 65 m water depth was estimated to between 55,000 tonnes and 156,000 tonnes or between less than 10% to around 25% of the phosphate in the system (water plus sediments). This represents the maximum amount of phosphorus that could possibly be released to the water column from these areas. We argue that the most reasonable estimate of the pool of mobile phosphorus in the sediments is the lower number.

Conclusion: The amounts of mobile phosphorus in sediment cores with oxidized surface layers were higher compared with sediment cores with reduced surfaces, indicating that there is a potential phosphorus-binding capacity in sediments below the redox cline if oxic conditions improved. Oxygenation of the Baltic Proper bottom water between 65 m and 100 m could probably remove around 100,000 tonnes of phosphorus from the water column and reduce phosphorus concentrations in the deep water by on average 30 mg/m³, which would possibly be felt also in the surface water.

Keywords: mobile phosphorus, phosphorus fractionation, sediments, oxygenation, Baltic Proper

Air, Soil and Water Research 2012:5 1-13

doi: 10.4137/ASWR.S8597

This article is available from http://www.la-press.com.

© the author(s), publisher and licensee Libertas Academica Ltd.

This is an open access article. Unrestricted non-commercial use is permitted provided the original work is properly cited.

Air, Soil and Water Research 2012:5

Introduction

Improving the ecological status of the Baltic Sea is largely associated with reducing concentrations of phosphorus and nitrogen in the system.^{1,2} Several studies indicate that the reflux of phosphorus from the sediments is similar in magnitude to the terrestrial load. According to the Helsinki Commission,³ the waterborne inputs of phosphorus to the entire Baltic Sea in 2000 were close to 35,000 tonnes. According to the Baltic Sea Action Plan, the annual phosphorus load should be reduced with around 15,000 tonnes, including 12,500 tonnes to the Baltic Proper.⁴ Budget calculations for the Baltic Proper indicate that the sediments annually release between 18,000 and 285,000 tonnes of phosphorus to the water column,^{5,6} the latter including resuspension of old clays due to land uplift. Savchuk⁷ found that a net flux of around 20,000 tonnes of phosphorus from the sediments of the Baltic Proper was required to sustain measured levels of phosphorus in the water column. According to Conley et al,⁸ the variation in the size of the phosphorus pool of the water column is largely explained by the flux of phosphate between the sediments and the bottom water rather than by variations in external load. The size and direction of this flux depends on redox conditions at the sediment surface. Between 1960 and 1990, the area of laminated sediments indicating permanent deep water anoxia increased around 50,000 km² in the Baltic Proper.⁹ Among measures suggested to address eutrophication, oxygenation of the deep waters to reduce diffusive phosphorus flux from the sediments has been suggested.¹⁰

Experimental data from the coastal Gulf of Finland showed that the phosphate flux from reduced sediments to water was 4.7 g/m²/year.¹¹ A corresponding value for the German Baltic Sea coast was 6.1 g/m²/year.¹² The annual phosphorus flux from soft sediments at various sites, mainly in the Gotland Basin (approximately 30,000 km²) of the central Baltic Proper, have been estimated between 0.1 and $3 \text{ g/m}^{2.13-16}$ Ahlgren et al¹⁷ found that the phosphorus release from a sediment in the Landsort deep was approximately 0.6 g/m²/year, and considered that if this value was relevant for the entire area of laminated sediments in the Baltic Proper (about 55,000 km² at the time), some 33,000 tonnes of phosphorus would be released from these sediments to the water column annually.

The diffusive flux of phosphate from accumulation bottoms is a reflux of phosphorus originating in settling material, mobilized in the sediments due to degradation of organic material, or anoxic release of phosphorus bound to iron and manganese.¹⁸ Hence, in the long run, the release rate of phosphorus cannot exceed the rate of phosphorus deposition. Ultimately, the maximum release is limited by the amount of potentially mobile phosphorus in the sediments. Estimating the pool of mobile phosphorus in accumulation sediments may hence provide information about potential release of phosphorus to the water column and implications for the ecological status of the Baltic Sea.

Carman and Jonsson¹⁹ attempted to calculate total amounts of phosphorus in Baltic Sea soft sediments and concluded that a major proportion (approximately 95%) of the potentially mobile phosphorus fractions is present in near-shore and archipelago areas. Carman and Cederwall²⁰ analyzed total phosphorus concentrations in surface sediments (0-1 cm) from different parts of the Baltic Sea and in different bottom types measuring concentrations between 700 µg/g and $2500 \,\mu g/g \,dry \,weight (median 1300 \,\mu g/g)$. The highest concentrations were found in accumulation areas and the lowest in erosion areas. Emelyanov²¹ compiled at least 386 samples of surface sediments (0–5 cm) from different parts of the Baltic Sea with average phosphorus concentrations in different bottom types ranging between 600 μ g/g and 1400 μ g/g dry weight.

Potentially mobile phosphorus mostly consists of organic phosphorus forms and phosphorus associated with iron and manganese.^{18,22,23} Mobile phosphorus pools in accumulation sediments have been estimated for the Gulf of Finland and the Archipelago Sea²³ and for the coastal sediments of central Sweden.²⁴ Average depth integrated amounts of mobile phosphorus in Swedish coastal sediments were estimated to 2.5 g/m².²⁴ Conley et al⁸ found a significant correlation between the annual change in the anoxic area and the change in the inorganic phosphorus pool in the Baltic Proper with a regression slope of around 2 tonnes of phosphorus per km², which would be consistent with a mobile phosphorus amount around 2 g/m² released when sediments turn anoxic. A shift in the redox conditions may influence the distribution of the mobile phosphorus between water and sediments while the total amount of phosphorus in the system remains essentially unchanged, as illustrated in Figure 1.

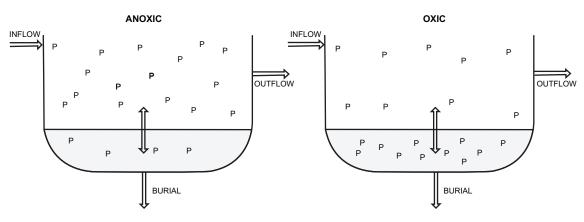


Figure 1. Principal illustration of a system redox change from anoxic sediments containing little mobile phosphorus (left) to oxic sediments containing more mobile phosphorus (right).

In the Baltic Sea, deep soft sediments below 75 m water depth are typically areas of accumulation^{9,25} where only diffusive processes operate to release phosphorus and other chemicals, but the actual boundary between accumulation and transportation areas may vary depending on, eg, slopes, topographical sheltering, and water currents. It is sometimes difficult to judge whether a sediment core represents strict accumulation conditions or where resuspension takes place as seldom as once a decade or century. Hence the term "long-term transportation bottoms" has been introduced.²⁶ Accumulation areas occupy around one third of the bottom area of the Baltic Proper.^{9,25,27–29}

In this paper, we analyze 12 sediment cores collected in the Baltic Proper between 61 m and 175 m water depth and calculate the amounts of mobile phosphorus. We assume that our sediment results can be representative of the order-of-magnitude estimate for the entire bottom area of the Baltic Proper. We also compare this amount with the phosphate pool in the water column estimated from monitoring data in the water column to compute the total amount of bioavailable phosphorus in the aquatic ecosystem.

Methods

Sediment sampling, water sampling, and oxygen measurements were performed during a field expedition with R/V Sunbeam in July 2010. Sampling stations are shown in Figure 2.

Water sampling

Water samples at two depth levels in seven stations were collected with a Ruttner sampler and stored cold in plastic bottles. The 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.

Sediment sampling

Twelve sediment cores were collected using a Gemini corer (a twin-barrel Niemistö corer with inner diameter 80 mm³⁰). After visual inspection, core samples were sliced in the field in 1 cm thick layers from the surface down to 5 cm sediment depth. In addition, one deeper level was sampled at each site (except in BP6 due limited length of core) to represent burial conditions after sediment diagenesis. All sliced sediment cores were stored in darkness at 4 °C until preparation in the laboratory.

Chemical analyses

Chemical analyses of phosphorus were performed at the Erken Laboratory at Uppsala University. In water samples, standard methods were used for the analyses of dissolved inorganic phosphorus and total phosphorus. Total phosphorus content in the sediments was determined by ashing (520 °C) followed by hot HCl extraction and measurement of dissolved inorganic phosphorus in the extract.³¹ 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.

Phosphorus forms were separated into NH₄Cl-rP, BD-P, NaOH-rP, NaOH-nrP, HCl-rP, and residual phosphorus following a sequential extraction scheme.³² These fractions are defined by the extraction method, but ideally each fraction corresponds

Downloaded From: https://complete.bioone.org/journals/Air,-Soil-and-Water-Research on 07 Jun 2025 Terms of Use: https://complete.bioone.org/terms-of-use

Air, Soil and Water Research 2012:5



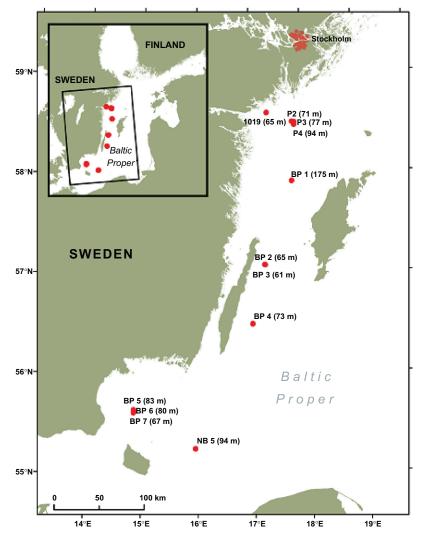


Figure 2. Positions of sediment sampling stations.

to a specific phosphorus-containing substance in the sediment. Generally, NH₄Cl-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 calciumbound phosphorus compounds. Residual phosphorus is given by subtracting extracted and identified phosphorus from total phosphorus. 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.

Chemical analyses of iron and manganese were performed by ALS Scandinavia AB. The sediments to be analysed for metal content were dissolved in nitric acid (7 M) and water (volume ratio 1:1) in a microwave oven. The water samples to be analysed for metal concentrations were acidified using nitric acid (14 M) and water (volume ratio 1:100). Analyses were performed according to modified EPA-standards 200.7 (ICP-AES) and 200.8 (ICP-SFMS).

Quantifying the pool of mobile phosphorus

To compute the amount of mobile phosphorus per area unit from sediment core data, the phosphorus concentration in deep sediment where sediment diagenesis has ceased, ie, the burial concentration, was subtracted from the higher concentrations in more shallow layers. As an alternative, 1000 μ g/g dry weight was used as a standardized burial concentration, since this is the typical burial concentration in sediments from other parts of the Baltic Sea.^{17,18,23,24}



Concentrations were multiplied with dry matter content (adjusting for sediment water content) to get the amount of mobile phosphorus in each layer. The surpluses in each sediment layer were taken as mobile phosphorus and integrated over the depth profile to obtain the amount of mobile phosphorus per square meter accumulation bottom area. This procedure was followed for total phosphorus as well as for the different phosphorus fractions. Three different estimates of the pool of mobile phosphorus in each core were made, ie, the amount of mobile total phosphorus using the burial concentration in each core as a measure of immobile phosphorus subtracted from the total amount ("Mobile TP"), the amount of mobile total phosphorus using 1000 µg/g dry weight as a measure of immobile phosphorus ("Mobile TP_{1000} ") and the sum of iron bound phosphorus, organic phosphorus, and residual phosphorus ("Sum of mobile P-fractions").

Results

Results from water sampling are shown in Table 1. CTD profiles are shown in Appendix 1. Anoxic conditions prevailed below approximately 70 m in the stations northwest from Gotland (1019, P2, P3, P4, and BP1), below 65 m east of Öland (BP2, BP3, and BP4) and again below 70 m in the southwestern stations (BP5, BP6, BP7, and NB5). The highest total phosphorus and dissolved inorganic phosphorus concentrations generally occurred in water samples close to the sediment surface.

Table 1. Results from water sampling.

Depth profiles of total phosphorus and the two mobile fractions (iron bound and organic phosphorus) in the 12 sediment cores are shown in Figure 3. Chemical data characterizing surface sediments are given in Table 2. Based on water and organic content and visual inspection of, eg, occurrence of laminations in the surface sediment³³ it appears that sediments collected below 70 m water depth were generally accumulation or long-term transportation areas. In addition, station 1019 at 65 m water depth was apparently located in an accumulation area which could be explained by topographic sheltering. The deep sediment sample in BP6 was lost before analysis, so one data point is missing. Oxygen measurements combined with visual inspection of sediment cores indicated that all sediments except 1019, BP2, and BP3 were anoxic.

Mobile amounts of total phosphorus calculated with three different methods are shown in Table 3. Tentative estimates of the total amount of mobile phosphorus in the entire Baltic Proper (excluding Gulfs of Riga and Finland and the Danish Straits) based on extrapolations of numbers in Table 3 are given in Table 4. For these calculations, hypsographic information from SMHI (Sweden's Meteorological and Hydrological Institute)³⁴ was used and the area at each 1 meter depth interval was multiplied with measured mobile phosphorus concentration. Mobile phosphorus was represented by measurements at different depths and linear interpolation between sampling depths. Below 175 m

Station	Water depth (m)	Sampling depth (m)	Salinity (psu)	Oxygen (g/m³)	TP (mg/m³)	DIP (mg/m³)	Fe (mg/m³)	Mn (mg/m³)
1019 (WG)	65	5	5.7	10.4	19	5	6.4	2.4
		60	7.8	4.5	109	98	13	31
P4 (WG)	94	5	5.8	10.2	25	7	2.5	1.1
		90	7.5	0.01	52	47	16	147
BP1 (WG)	175	5	6	10.2	18	5	15	1.1
		100	9.8	0.01	60	60	22	90
BP4 (WG)	73	5	6.3	10.4	20	5	1	0.9
		65	9	0.02	170	158	22	171
BP5 (HB)	83	5	6.5	10.1	20	5	1	0.8
		80	15.5	0.01	257	245	300	1330
NB5 (BOB)	94	5	6.5	10.4	23	6	1	1.1
		90	15.9	0.02	78	70	48	449
BP2 (WG)	65	5	6.2	10.4	18	6	1	0.9
		60	4.9	3.5	174	161	39	168

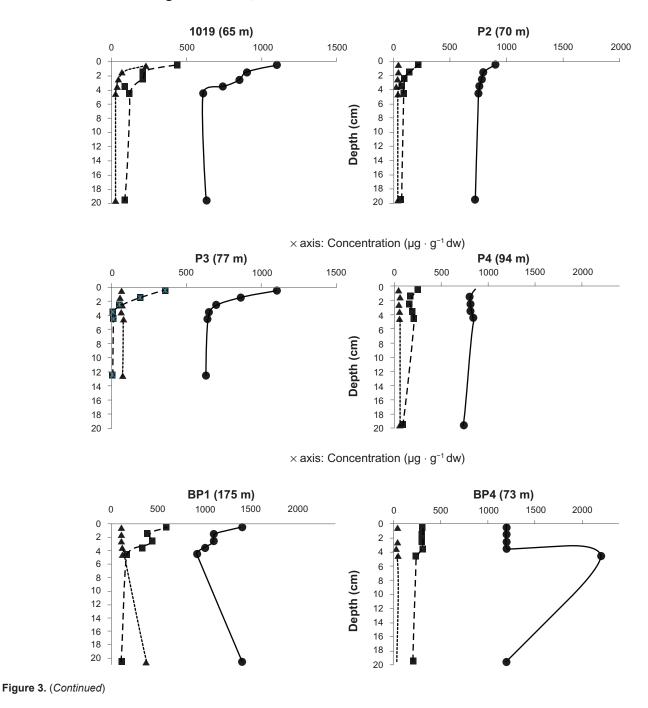
Abbreviations: WG, Western Gotland Basin; HB, Hanö Bay; BOB, Bornholm Basin; TP, total phosphorus; DIP, dissolved inorganic phosphorus.

Air, Soil and Water Research 2012:5



depth the concentration measured at BP1 was used. Estimated total amounts of mobile phosphorus ranged between 55,000 and 156,000 tonnes.

Combining hypsographic data with data on dissolved inorganic phosphorus and total phosphorus in the water column from the Shark database available via the Swedish Meteorological and Hydrological Institute July 2010 (20 depth levels, eight stations) allowed a very rough estimate of the phosphorus amount present in the water column. Using this method, we estimated the amount of dissolved inorganic phosphorus to 491,000 tonnes and the amount of total phosphorus to 659,000 tonnes in the entire water column of the Baltic Proper at the time of our sediment sampling. The dissolved inorganic phosphorus amount calculated for the water column is in the upper range of values estimated by Conley et al⁸ between 1970 and 2000. Savchuk⁷ estimated the total phosphorus amount in the Baltic Proper to 418,000 tonnes in a budget for the period 1991–1999.



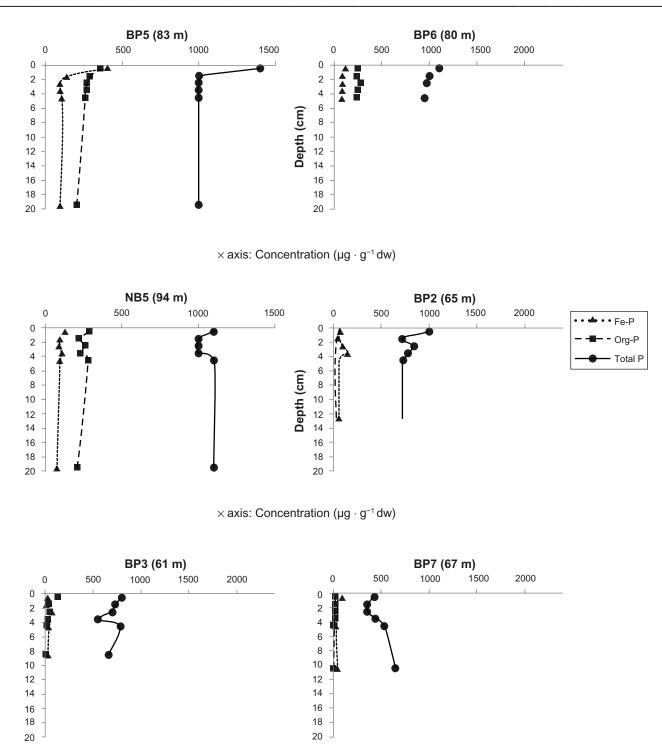


Figure 3. Depth profiles (cm) of iron bound phosphorus (Fe-P), organic phosphorus (Org-P) and Total phosphorus measured in µg/g dry weight. All profiles represent accumulation areas except BP2, BP3 and BP7 which represent transport areas.

Discussion

Apart from the redox potential, the ability of the sediments to absorb phosphorus from the water column also depends on the availability of iron and manganese in the sediment and bottom waters. A low iron:phosphorus ratio may limit the potential phosphate co-precipitation with iron oxyhydroxide.³⁵ There were no correlation between iron and phosphorus or between manganese and phosphorus in the surface sediments in this study ($r^2 < 0.2$), both if total

Air, Soil and Water Research 2012:5

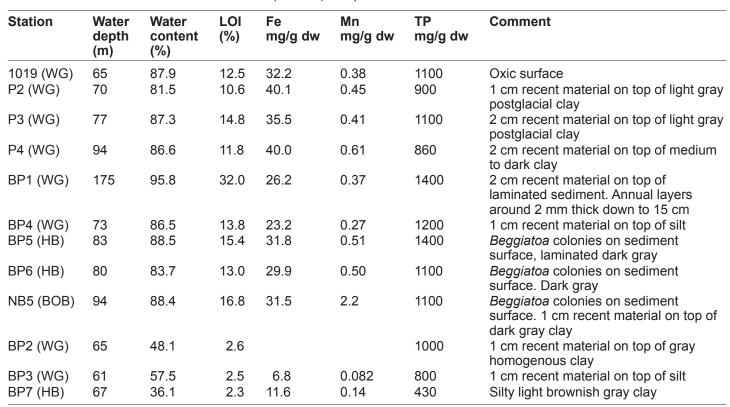


 Table 2. Characteristics of surface sediment (0–1 cm) samples.

Abbreviations: WG, Western Gotland Basin; HB, Hanö Bay; BOB, Bornholm Basin; LOI, loss on ignition; dw, dry weight.

phosphorus or iron bound phosphorus were used in the statistic. Karlsson et al³⁶ indicates that iron levels above 48 mg/g dry weight would be needed to allow iron bound phosphorus formation in sediments. Such high iron levels were not found in any surface sediment in this study. Iron concentrations in the water samples were generally lower than dissolved inorganic phosphorus concentrations, similar to results from a study in the north-western Baltic Proper,³⁵ while some water samples contained relatively high values of manganese concentrations. Correlations between dissolved inorganic phosphorus, iron, and manganese in the water column were significant $(n = 14; r^2 > 0.77)$. Similar statistics were obtained for the deep water samples (n = 7) but correlations were insignificant if only surface water samples were included, indicating that the correlation depends on common interactions with the sediments.

This study was based on a limited number of data from sediments in a restricted part of the Baltic Sea. This allows us only to make tentative extrapolations regarding the total amount of mobile phosphorus in the system. Still such order of magnitude estimates contain valuable information about the functioning of the system and the relative importance of the sediments in the phosphorus budget. This information complements earlier estimates of phosphorus pools and fluxes based on other methods. The limited amount of data is especially evident in transportation sediments which were only represented by three cores (BP2, BP3, and BP7). Accumulation or possibly long-term transportation sediments were represented by nine cores distributed at depths between 65 m and 175 m in the Western Gotland Basin, Hanö Bay, and Bornholm Basin. In total, the area below 65 m amounts to 89,400 km² or 43% of the bottom area of the Baltic Proper.

The applied method for calculating the amount of potentially mobile phosphorus in the sediment has previously been used in more shallow depths in coastal areas.^{18,24} The method may overestimate the mobile amount since it assumes that all the material in the sediment cores emanates from a prevailing (constant) sedimentological regime. In this study, many cores only contained 1 or 2 cm of recent material on top of silt or glacial/postglacial clays. Based on burial

Table 3. Mobile phosphorus present in collected sediments calculated as mobile TP (using TP concentration at stabilization depth to determine immobile phosphorus concentration), mobile TP₁₀₀₀ (assuming 1000 μ g/g dry weight as immobile phosphorus concentration) and as the sum of the mobile P-fractions.

	Water depth m	Mobile TP g/m²	Mobile TP ₁₀₀₀ g/m ²	Sum of mobile P-fractions g/m ²
BP3 (WG) ^{ox} 1019 (WG) ^{ox} BP2 (WG) ^{ox} BP7 (HB) P2 (WG) BP4 (WG) P3 (WG) BP6 (HB) BP5 (HB) P4 (WG) NB5 (BOB) BP1 (WG) Minimum Mean Maximum Standard	61 65 67 70 73 77 80 83 94 94 175	2.70 2.15 2.25 0 0.47 2.94 1.27 0.48 0.49 0.49 0.49 0.89 0.16 0.10 0 1.16 2.94 1.07	0 0.13 0 0 4.96 0.14 0.18 0.49 0 0.32 0.35 0 0.55 4.96 1.40	5.28 2.57 4.41 1.51 0.88 3.71 1.61 0.51 1.22 1.53 0.31 1.33 0.31 2.07 5.28 1.59
deviation				

Note: ^{ox}Visual inspection combined with water column oxygen profiles indicated that these cores were oxic.

Abbreviation: TP, total phosphorus.

concentrations of total phosphorus, layers below 5 cm or so do not appear to consist of recent material in several cores even if this was not revealed by the visual inspection. It should be kept in mind though that the sediment growth in offshore Baltic sediments is low, typically ranging from 1 to 2 mm/year,⁹ compared with coastal sediments typically growing 1–2 cm/year.³⁷

A reasonable guess is that total phosphorus concentrations below 1000 μ g/g dry weight represent material

 Table 4. Estimated amounts of mobile phosphorus in the
 Baltic Proper sediments using different methods to compute mobile phosphorus (compare with Table 3).

Depth interval	Area km²	Mobile TP tonnes	Mobile TP ₁₀₀₀ tonnes	Sum of mobile P-fractions tonnes
60–69 m	14,600	28,900	359	53,700
70–95 m	38,800	35,400	33,500	54,600
96–175 m	39,900	14,800	19,800	42,700
176–411 m	4050	412	1400	5390
Total	97,300	79,500	55,100	156,300

Abbreviation: TP, total phosphorus.

Air, Soil and Water Research 2012:5

not recently deposited (silt or glacial/postglacial clays) containing insignificant amounts of mobile phosphorus. Supporting this presumption is the minor concentrations of iron bound and organic phosphorus found in these layers. Following this presupposition the amount of potentially mobile phosphorus in the sediments is best represented by the lower estimates in Table 4. This estimate is particularly affected by the anomalous phosphorus concentration measured at 4-5 cm sediment depth in BP4 (Fig. 3). If the outlier values in BP4 were replaced with interpolated values between P2 and P3, the mobile phosphorus amount calculated with this method is reduced to 30,400 tonnes in the Baltic Proper. The other methods used for calculating the total amount of mobile phosphorus in the sediments are less sensitive to the BP4 anomaly. The numbers representing the total amount of mobile phosphorus in the offshore Baltic Sea may be compared with sediments along the Swedish east coast between Öregrund and Oxelösund estimated to between 1000 and 4000 tonnes,²⁴ representing considerably higher concentrations of phosphorus in surface sediments.

Based on our highest estimate, mobile phosphorus in the sediments below 60 m in the Baltic Proper (156,300 tonnes) account for around 25% of the dissolved inorganic phosphorus and around 20% of the total phosphorus in the system (water column plus sediments). Jonsson et al⁹ measured total phosphorus concentrations in eight surface sediments (0–5 cm) below 88 m depth in different parts of the Baltic Proper in 1986–1989 and found total phosphorus concentrations between 700 μ g/g and 1200 μ g/g dry weight indicating similarly small amounts of mobile phosphorus during a period of large dissolved inorganic phosphorus amounts in the water column.⁸

Assuming a typical potential of the sediments to retain mobile phosphorus to be 2 tonnes per km² (consistent with the regression by Conley et al,⁸ and consistent with our data and coastal data presented by Malmaeus et al,²⁴ the sediments below 65 m depth that presently contain little phosphorus could theoretically absorb 180,000 tonnes of phosphorus from the water column in the Baltic Proper if oxygenated. The corresponding number for the sediments between 65 m and 100 m water depth would be around 100,000 tonnes, and the area equivalent to the expansion of laminated sediments between 1960 and 1990 according



to Jonsson et al.⁹ Reducing the amount of phosphorus in the bottom waters by 100,000 tonnes corresponds to a decrease in phosphorus concentration around 30 mg/m³ in the deep water (below 65 m), and the effect would possibly be felt also in the surface water although less dramatic. It is worth reflecting on the fact that the adjacent Bothnian Sea, where almost all sediment surfaces are oxic,³⁸ typically has total phosphorus concentrations in surface water around 10 mg/m³ lower than the Baltic Proper,⁶ keeping in mind that also the external P loading is lower to this basin.³

It appears that nearly all mobile phosphorus is present in the top 3-4 cm of the sediments indicating a turnover time around 15-40 years given a sediment growth of 1-2 mm/year.9 This in turn implies an average annual release from the estimated sediment pool of mobile phosphorus to the water column around 0.1 g/m², which is the same order of magnitude as reported by Hille et al,¹⁵ but lower than the calculations presented by Emeis et al,¹⁴ Ahlgren et al,¹⁷ and Mort el al.¹⁶ One reason for the discrepancy could be that the studies by us and Hille et al¹⁵ integrate a number of sampling stations from soft bottoms of various depths, whereas the other studies were concentrated to deep holes (>100 m water depth). Presumably larger release rates can also be associated with shortterm redox conditions that may be present during some pore water studies but not representative for long-term conditions studied in sediment cores representing time integration over decades.

Given the recognition of the eutrophication problems in the Baltic Sea and the ambitious action plans to address them, such as the Baltic Sea Action Plan aiming to reduce annual external phosphorus inputs by some 15,000 tonnes, it remains of paramount importance to improve the knowledge about the pools and dynamics of mobile phosphorus in sediments. We suggest that further efforts to measure amounts of mobile phosphorus in sediments in different areas of the Baltic Sea should be made promptly and in concert with the development of future action plans.

Conclusion

Sediments below the redox cline in the Baltic Proper contained small amounts of mobile phosphorus. However, there were some anomalies in the data indicating that there may be some variation. Assuming that the low levels measured in most of the sediments below the redox cline were representative for the sediments in the study area the total amount of mobile phosphorus in the entire Baltic Proper sediments below 65 m water depth was estimated to 55,000 tonnes or less than 10% of the dissolved inorganic phosphorus in the system (water plus sediments). Using a different approach, the highest estimate of total amount of mobile phosphorus in the sediments below 65 m water depth in the area was 156,000 tonnes, or around 25% of the total amount of dissolved inorganic phosphorus in the system. We argue that the lower number is the most reasonable estimate of the pool of mobile phosphorus in the sediments. The amounts of mobile phosphorus in sediment cores with oxidized surface layers were higher compared with sediment cores with reduced surfaces, indicating that there is a potential P-binding capacity in sediments below the redox cline if they were oxygenated. Oxygenation of the Baltic Proper bottom water between 65 m and 100 m could probably remove around 100,000 tonnes of phosphorus from the water column and reduce phosphorus concentrations in the deep water by on average 30 mg/m³, which would possibly be felt also in the surface water.

Acknowledgments

We thank Professor Per Jonsson for sharing old sampling protocols and the crew of R/V Sunbeam for excellent field work. This study was funded by the European Commission and the foundation for the Swedish Environmental Research Institute through grant LIFE08 ENV/S/000271 WEBAP.

Disclosures

Author(s) have provided signed confirmations to the publisher of their compliance with all applicable legal and ethical obligations in respect to declaration of conflicts of interest, funding, authorship and contributorship, and compliance with ethical requirements in respect to treatment of human and animal test subjects. If this article contains identifiable human subject(s) author(s) were required to supply signed patient consent prior to publication. Author(s) have confirmed that the published article is unique and not under consideration nor published by any other publication and that they have consent to reproduce any copyrighted material. The peer reviewers declared no conflicts of interest.



References

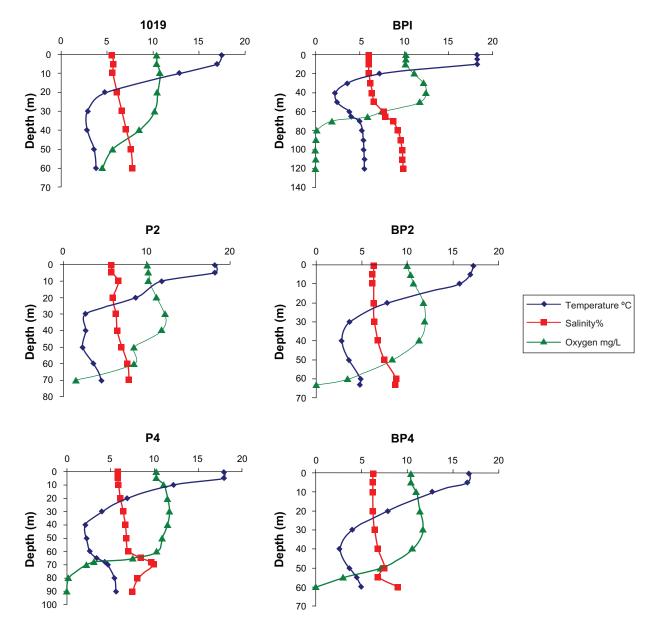
- O'Melia C, Boesch D, Hecky R, Schindler D, Seitzinger S. Eutrophication of Swedish seas. Swedish Environmental Protection Agency Report 5509. 2006. Available from: http://www.naturvardsverket.se. Accessed November 23, 2011.
- Helsinki Commission. Eutrophication in the Baltic Sea—an integrated thematic assessment of the effects of nutrient enrichment and eutrophication in the Baltic Sea region: executive summary. Balt Sea Environ Proc. No. 115A, 2009. Available from: http://meeting.helcom.fi/c/document_library/get_file?p_1_id=79889&folderId=377779&name=DLFE-36818.pdf. Accessed November 23, 2011.
- Helsinki Commission. The Fourth Baltic Sea Pollution Load Compilation (PLC-4). Balt Sea Environ Proc No. 93, 2004. Available from: http://www. helcom.fi/stc/files/Publications/Proceedings/bsep93.pdf.
- Helsinki Commission. Towards a Baltic Sea unaffected by eutrophication. Helsinki Commission Ministerial Meeting, Krakow, Poland, November 15, 2007. Available from: http://www.helcom.fi/stc/files/BSAP/Eutrophication_ draft%20overview%202007.pdf. Accessed November 23, 2011.
- Savchuk O, Wulff F. A model of the biogeochemical cycles of nitrogen and phosphorus in the Baltic. In: Wulff FV, Rahm LA, Larsson P, editors. *A Systems Analysis of the Baltic Sea. Ecological Studies 148.* Heidelberg, Germany: Springer; 2001.
- Håkanson L, Bryhn AC. Eutrophication in the Baltic Sea—Present Situation, Nutrient Transport Processes, Remedial Strategies. Berlin, Germany: Springer-Verlag; 2008.
- Savchuk OP. Resolving the Baltic Sea into seven subbasins: N and P budgets for 1991–1999. J Marine Syst. 2005;56:1–15.
- Conley DJ, Humborg C, Rahm L, Savchuk OP, Wulff F. Hypoxia in the Baltic sea and basin—scale changes in phosphorus biogeochemistry. *Environ Sci Technol.* 2002;36:5315–20.
- 9. Jonsson P, Carman R, Wulff F. Laminated sediments in the Baltic—a tool for evaluating nutrient mass balances. *Ambio.* 1990;19:152–8.
- Stigebrandt A, Gustafsson BG. Improvement of Baltic proper water quality using large-scale ecological engineering. *Ambio*. 2007;36:280–6.
- Pitkänen H, Lehtoranta J, Räike A. Internal nutrient fluxes counteract decreases in external load: The case of the estuarial Gulf of Finland. *Ambio*. 2001;30:195–201.
- Selig U, Baudler H, Krech M, Nausch G. Nutrient accumulation and nutrient retention in coastal waters—30 years investigation in Darss-Zingst Bodden chain. *Acta Hydrochim Hydrobiol*. 2006;34:9–19.
- Matthiesen H, Emeis K-C, Jensen BT. Evidence for phosphate release from sediment in the Gotland Deep during oxic bottom water conditions. *Meyniana*. 1998;50:175–90. German.
- Emeis K-C, Struck U, Leipe T, Pollehne F, Kunzendorf H, Christiansen C. 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. *Mar Geol.* 2000;167:43–59.
- Hille S, Nausch G, Leipe T. Sedimentary deposition and reflux of phosphorus (P) in the eastern Gotland Basin and their coupling with P concentrations in the water column. *Oceanologica*. 2005;47:663–79.
- Mort HP, Slomp CP, Gustafsson BG, Andersen TJ. Phosphorus recycling and burial in the Baltic Sea sediments with contrasting redox concentrations. *Geochim Cosmochim Acta*. 2010;74:1350–62.
- Ahlgren J, Reitzel K, Tranvik L, Gogoll A, Rydin E. Degradation of organic phosphorus compounds in anoxic Baltic Sea sediments: A 31P-NMR study. *Limnol Oceanogr.* 2006;51:2341–8.
- Rydin E, Malmaeus JM, Karlsson OM, Jonsson P. Phosphorus release from coastal Baltic Sea sediments as estimated from sediment profiles. *Estuarine*, *Coastal and Shelf Science*. 2011;92:111–7.

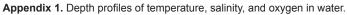
- Carman R, Jonsson P. Distribution patterns of different forms of phosphorus in some surficial sediments of the Baltic Sea. *Chem Geol.* 1991;90: 91–106.
- Carman R, Cederwall H. Sediments and acrofauna in the Baltic Seacharacteristics, nutrient contents and distribution. In: Wulff FV, Rahm LA, Larsson P, editors. A Systems Analysis of the Baltic Sea. Ecological Studies 148. Heidelberg, Germany: Springer; 2001.
- 21. Emelyanov EM. Biogenic components and elements in sediments of the Central Baltic and their redistribution. *Mar Geol*. 2001;172:23–41.
- Boström B. Potential mobility of phosphorus in different types of lake sediment. *Int Revue Ges Hydrobiol.* 1984;60:457–74. German.
- Lukkari K. Chemical characteristics and behaviour of sediment phosphorus in the Northeastern Baltic Sea. PhD thesis. Finnish Institute of Marine Research, Contribution No. 17, 2008.
- Malmaeus JM, Rydin E, Jonsson P, Lindgren D, Karlsson OM. Estimating the amount of mobile phosphorus in Baltic coastal soft sediments of central Sweden. *Boreal Environmental Research*. Accepted.
- 25. Ignatius H, Axberg S, Niemistö L, Winterhalter B. Quaternary geology of the Baltic Sea. In: Voipio A, editor. *The Baltic Sea*. Amsterdam, The Netherlands: Elsevier Oceanographic Series, Elsevier Scientific; 1981.
- Jonsson P. Large-scale changes of contaminants in Baltic Sea sediments during the twentieth century. PhD thesis, Uppsala University, Sweden, 1992.
- Håkanson L. A new functional view of the Baltic Sea. *Ambio* Special report number 7:19, 1990.
- Repecka M, Cato I, editors. Bottom sediment map of the central Baltic Sea. LGT series of marine geological maps/SGU Series BA no. 54, Vilnius-Uppsala, 1998. ISBN 9986-615-11-9.
- Håkanson L, Lindgren D. Water transport and water retention in five connected subbasins in the Baltic Sea—simulations using a general massbalance modeling approach for salt and substances. *Journal of Coastal Research.* 2010;26:241–64.
- Niemistö L. A gravity corer for studies of soft sediments. *Merentutkimuslait Julk/Havsforskningsinst Skr.* 1974;238:33–8.
- Koroleff F. Determination of nutrients. In: Grasshof K, Ehrhardt M, Kremling K, editors. *Methods of Seawater Analysis*. Berlin, Germany: Verlag Chemie; 1983.
- Psenner R, Boström B, Dinka M, Pettersson K, Puckso R. Fractionation of suspended matter and sediment. *Arch Hydrobiol Beih Ergebn Limnol*. 1988;30:98–103.
- Håkanson L, Rosenberg R. Practical Coastal Ecology. Solna, Sweden: Swedish Environmental Protection Agency Report; 1987. Swedish.
- 34. Swedish Meteorological and Hydrological Institute. Depth data for sea areas 2003. Swedish Meteorological and Hydrological Institute Oceanography Report 73. Norrköping, Sweden, 2004. Complementary material. Available from: http://www.smhi.se/sgn0102/n0205/havsomr/rapport_havsomr.htm. Accessed November 23, 2011.
- Blomqvist S, Gunnars A, Elmgren R. Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: A matter of salt. *Limnol Oceanogr.* 2004;49:2236–41.
- Karlsson M, Jonsson P, Malmaeus M, Rydin E. Sediment studies in the Stockholm archipelago 2008. IVL Report B1994, 2009. Available from: http://www.ivl.se. Accessed November 23, 2011.
- Jonsson P, editor; Persson J, Holmberg P. The seafloor of the archipelagoes. Swedish Environmental Protection Agency, Technical Report No. 5212; 2003.
- Algesten G, Brydsten L, Jonsson P, et al. Organic carbon budget for the Gulf of Bothnia. J Marine Syst. 2006;63:155–61.

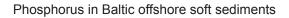
Air, Soil and Water Research 2012:5



Appendix









Publish with Libertas Academica and every scientist working in your field can read your article

"I would like to say that this is the most author-friendly editing process I have experienced in over 150 publications. Thank you most sincerely."

"The communication between your staff and me has been terrific. Whenever progress is made with the manuscript, I receive notice. Quite honestly, I've never had such complete communication with a journal."

"LA is different, and hopefully represents a kind of scientific publication machinery that removes the hurdles from free flow of scientific thought."

Your paper will be:

- Available to your entire community free of charge
- Fairly and quickly peer reviewed
- Yours! You retain copyright

http://www.la-press.com